

STATISTICAL ASSESSMENT OF PAST WATER CHEMISTRY TO PREDICT FUTURE CHEMISTRY AT NORANDA MINERALS' BELL MINE¹

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Abstract: Mining companies collect and analyze numerous water samples every year to protect the surrounding environment and to meet permit requirements. Through the years, the collective number of analyses can be in the thousands. Such water-chemistry databases eventually become valuable scientific tools for the estimation of water chemistry between monitoring events and into the future.

A statistical approach can be used to summarize and interpret a database and to create a site-specific "empirical water-chemistry model" for predictions. The predictions can then, for example, be used for: (1) estimating future water-treatment costs, (2) refining water-retention times in ponds to obtain a particular range of concentrations, (3) determining the acceptable degree of failure in water-quality control technologies such as clay covers, (4) negotiating closure bonds with government agencies, and (5) reducing the frequency of intense monitoring programs. The empirical model also shows that probability-duration times can be applied to various concentrations, similar to hydrologic storm events, such as the peak annual concentration of one-hour duration. The empirical water-chemistry model for Noranda Minerals' Bell Mine in British Columbia illustrates the approach and applications.

Key Words: mining, water chemistry, metal leaching, acidic drainage, statistical prediction, empirical modelling

1. Introduction

Metals can be transported around and from a minesite in pathways involving air, water, and solids. Each minesite has a site-specific combination of pathways that warrants monitoring, but surface and ground waters typically receive particular attention.

The monitoring of water chemistry around a minesite reflects the concerns of the mining company for protecting the local environment and the permit/license requirements of regulatory agencies. After a few years, a significant database of water-chemistry analyses accumulates and continues to grow, but often little is done with this database after its initial interpretation and reporting.

This paper shows how a pre-existing water-chemistry database can be valuable for estimating chemistry between monitoring events and into the future, through the compilation of an "empirical water-chemistry model". The reliability of the model increases with the number of samples and the number of years monitored. These points are illustrated through a case study involving thousands of analyses at

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It is not the intent of this paper to design, or critically comment on, monitoring programs at minesites, but to simply show the use of available databases for predictions. The value of these predictions can be found, for example, in their use for (1) estimating future water-treatment costs, (2) refining water-retention times in ponds to obtain a particular range of metal concentration, (3) determining the acceptable degree of failure in water-quality control technologies such as clay covers, (4) negotiating closure bonds with government agencies, and (5) reducing the frequency of monitoring.

2. Modelling and Statistical Distributions

The best way for predicting future water chemistry is to define each variable that exerts some control on chemistry and then to delineate how each variable will behave through time. These variables fall into three general categories. The first is *physical*, such as flow of water and air, temperature, and construction methods of a dump, tailings impoundment, pit, or underground working (Morin et al., 1991). The second is *chemical*, including pH and aqueous complexation. The last is *biological*, such as bacterial activity and changes to physical and chemical mechanisms caused by wildlife, vegetation, and humans. There are probably dozens of variables that can affect water chemistry, and the relative importance of each is likely site specific.

If each variable could be described and predicted, the resulting water chemistry could then also be predicted. This is commonly called *deterministic modelling*. An often-stated panacea to deterministic modelling is *stochastic modelling*, which uses statistical distributions of the variables in order to obtain a statistical prediction of the water chemistry. This type of modelling avoids the use of one value or a set of values, but instead requires the knowledge of the statistical distributions of the variables. For example, the delineation of groundwater flow may require hundreds of hydraulic-conductivity measurements in order to obtain a reasonably valid statistical distribution. As a result, data requirements for reliable stochastic modelling are often greater than for deterministic modelling.

Another type of modelling is labelled *empirical modelling*. This approach does not attempt mechanistic explanations through variables, but identifies patterns and cycles in measured data. Potential patterns include statistically normal distributions of values, or of logarithms of the values ("lognormal distribution", Aitchison and Brown, 1976). Geochemical data are often lognormally distributed (Davis, 1986).

A normal or lognormal distribution is convenient because it can be summarized through statistical moments, such as means and standard deviations, and can be associated easily with probability levels. The mean defines the average value and the standard deviation reflects the variability about the mean. Most computer spreadsheets include options for calculating means and standard deviations.

From a deterministic perspective, the variability about the mean in a normal distribution reflects the sum of the effect of each variable on water chemistry, adjusted by an individual weighting value:

$$\text{Normal variability} = (\text{Variable}_1 * \text{Weight}_1) + (\text{Variable}_2 * \text{Weight}_2) + \dots \quad (1)$$

On the other hand, the variability in a lognormal distribution reflects the multiplicative product of each variable, adjusted by its weighting value:

$$\text{Lognormal variability} = (\text{Variable}_1 * \text{Weight}_1) * (\text{Variable}_2 * \text{Weight}_2) * \dots \quad (2)$$

These equations link empirical modelling by its statistical distributions, which implicitly recognize all variables (Equation 1 or 2), to deterministic and stochastic modelling as discussed above. However, the site-specific delineation of all relevant variables and their weighting values is at least decades away and may not even be possible in an open-environment system.

As a result, the current state of deterministic and stochastic modelling of water chemistry lies in predictions from a subset of variables and weighting values that a particular modeller considers most important. The subset varies from modeller to modeller (Perkins et al., 1994; Morin et al., 1991). Empirical modelling generally lags behind due to the perception that modelling should be based on underlying mechanisms and variables. The optimum situation is for these extremes of modelling to move towards each other and meet, and this paper takes a step in that direction from the side of empirical modelling.

This paper focusses on empirical modelling of water chemistry using a relatively large database. However, some deterministic modelling is included here, but only where data are sufficient to identify a variable's relative importance.

3. Methodology for Empirical Modelling of Minesite Water Chemistry

3.1 Search for a Regular Distribution for Simplicity

The first major task in this approach to empirical modelling is to reduce a water-chemistry database with thousands of numbers to a more manageable level, preferably through statistical concepts. The simplest of these concepts includes means and standard deviations (Section 2). Other distributions can be determined from more rigorous software such as BestFit (Palisade Software, 1994).

At Bell Mine, which closed in 1993, water-chemistry data were collected for more than 10 years from surface ditches surrounding waste-rock dumps, the tailings impoundment and its rock dams, the pit, and the plantsite (Morin and Hutt, 1993a and 1993b). The entire dissolved-copper database displays a general lognormal distribution (Figure 1) and thus a mean and standard deviation can be calculated from logarithms of the data. For the entire minesite, the \log_{10} (mean copper concentration) is -0.457 (0.35 mg/L) and 68% of all values statistically lie within one standard deviation (1.25 log cycles or a factor of 17.8) about the mean. However, the entire database spans almost six orders of magnitude and the standard deviation is relatively large. This can be reduced through the next step in the methodology.

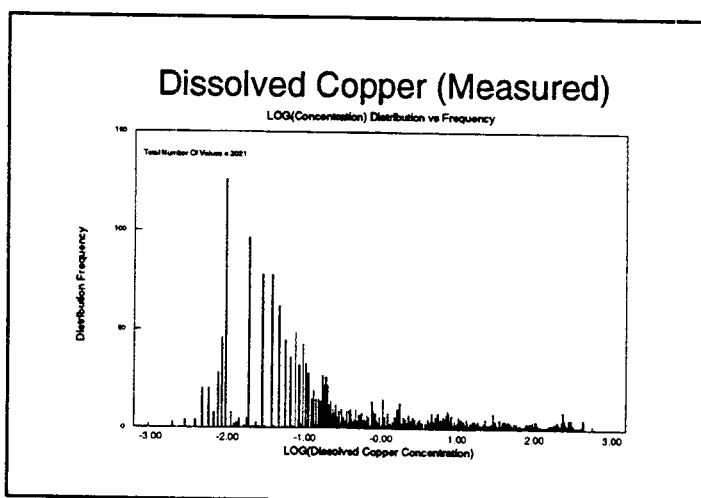


FIGURE 1. Analyses of Dissolved Copper at Bell Mine to 1991.

3.2 Remove the Numerical Effects of Major Variables to Reduce the Standard Deviation

This second step in the methodology leads to a lower standard deviation for a water-chemistry distribution through the examination of some major independent variables contributing to the deviation. This blending of deterministic and empirical modelling is explained in Section 2 and Equations 1 and 2.

Major variables influencing water chemistry can include pH, time, sulfate, flow rate, temperature, and rock type. However, the number of variables targeted for independent prediction (additional work) should be balanced against the remaining variability in the model-predicted results (less variability). A

simplified example helps to illustrate this point. If pH, flow rate, and rock type were the major independent variables for a particular database, then the filtering of pH effects from the database alone would decrease the variability in the predictions to that caused only by changes in flow and the various rock types. In general, a variable should be filtered from a database if (1) the decrease in variability of the remaining database is significant (that is, if the weighting value in Equation 1 or 2 is high) and (2) sufficient data for the variable are available to reliably delineate its influence (discussed in Section 4.1).

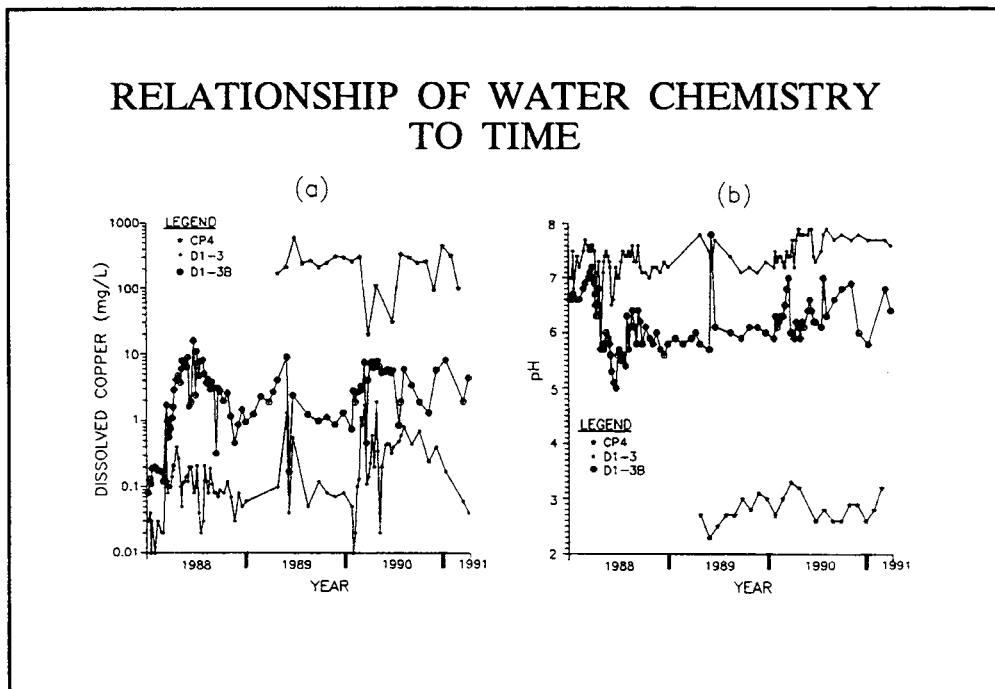


FIGURE 2. Relationship of (a) Dissolved Copper and (b) pH to Time at Selected Locations around Bell Mine.

For the Bell Mine database on dissolved copper, the rate of ditch flow and the passage of time (several years) were found not to have major effects on concentrations at most locations (e.g., Figure 2), which was also noted at another minesite in British Columbia (Morin et al., 1994; Morin et al., submitted). However, pH was found to have a major influence on concentrations (Figure 3). A clarification of pH as a major variable is made in Section 4.3.

The filtering of pH effects from the Bell Mine database was accomplished by defining a "best-fit line" relating mean copper concentrations to pH (Figure 3). The datapoints above and below the best-fit line, parallel to the y-axis, were then found to be lognormally distributed (Figure 4). In Figure 4, the log(prediction

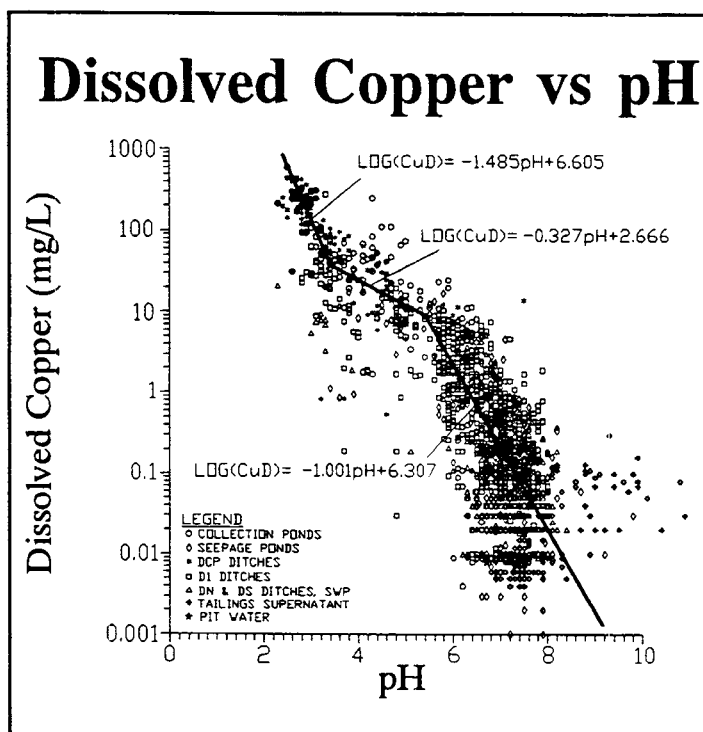


FIGURE 3. Dissolved Copper vs. pH at Bell Mine Through 1991.

error) is equal to: $\log_{10}(\text{predicted value from best-fit line at measured pH}) - \log_{10}(\text{measured copper concentration})$ for 2017 values. If pH is predicted to be 2.5, then the corresponding mean copper concentration is 780 mg/L (log value = 2.89 from the best-fit equation) and the standard deviation at that pH (and at all pH values) is 0.69 log cycles.

At this point, several important observations should be made. First, the interpretation of a logarithmic standard deviation is different from an arithmetic standard deviation. The antilog of the log standard deviation is not easily used for interpretations (discussed further in the Section 4.2 and in Aitchison and Brown, 1976).

Second, most of the copper datapoints on Figure 3 lie in the near-neutral pH range and initially appear to be generally independent of pH (note the large vertical scatter between pH 6 and 8). The vertical scatter at acidic pH is less. However, Figure 4 shows that all datapoints in fact form a general lognormal distribution about the best-fit line. The larger vertical scatter at neutral pH should actually be expected, because there are more datapoints in this range and thus a greater portion of the lognormal distribution is filled in by measured data. Upon dividing the datapoints into 332 values below pH 5.0 and 1685 datapoints above, similar values of standard deviation are obtained (0.50 and 0.72, respectively) and are not markedly different from the overall value of 0.69. As a result, the effect of pH on the standard deviation is considered relatively unimportant and is treated as a constant. Only the mean value then changes with pH.

Third, since pH effects were filtered from the database, the remaining variability and standard deviation are caused by other natural and artificial variables. This was explained in Section 2 and is examined further in Section 4.1.

Fourth, the position of the best-fit line (Figure 3) can be optimized by adjusting it vertically upwards or downwards until the mean value of $\log(\text{prediction error})$ of Figure 4 becomes exactly zero. The reported log value of 0.133 indicates the current predicted mean values are roughly within 0.133 log cycles of the optimized values and are thus acceptable.

This same approach was used for many metals, nonmetals, and titration-based parameters such as acidity (Figures 5 and 6) at Bell Mine. All best-fit equations and corresponding standard deviations were then compiled into a "empirical water-chemistry model" that applied to the entire minesite (Table 1). The implications and applications of this model are discussed further in Section 4.

3.3 Identify Temporal Cycles

One final step in the methodology is to search for cyclical appearances of the variability and standard deviation. As explained in Section 3.2, the copper concentrations at locations around Bell Mine

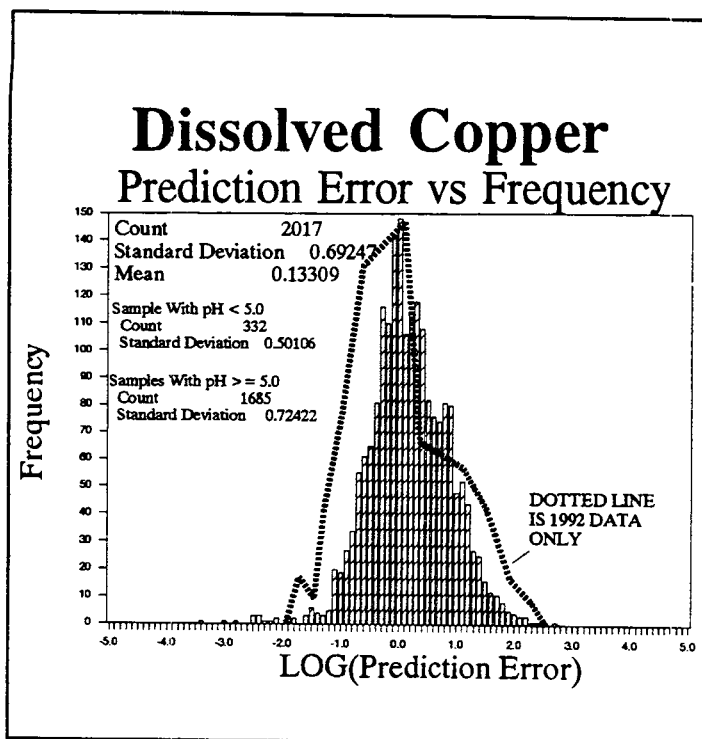


FIGURE 4. Prediction Error for Dissolved Copper Through 1991 (dotted line is 1992 data).

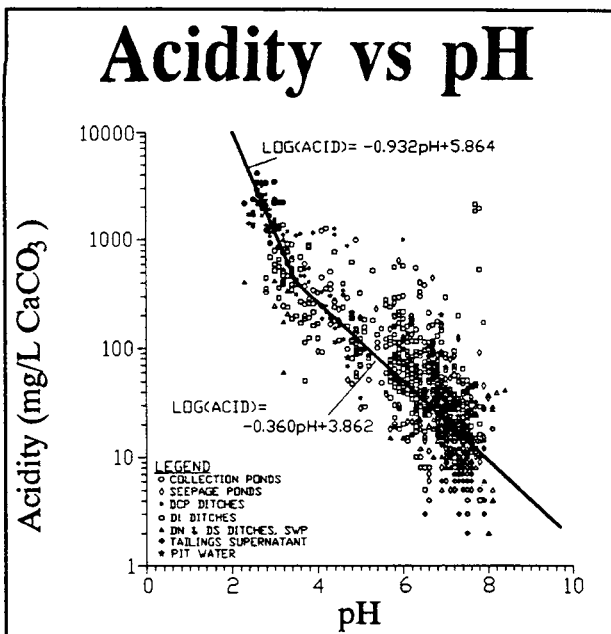


FIGURE 5. Acidity vs. pH at Bell Mine Through 1991.

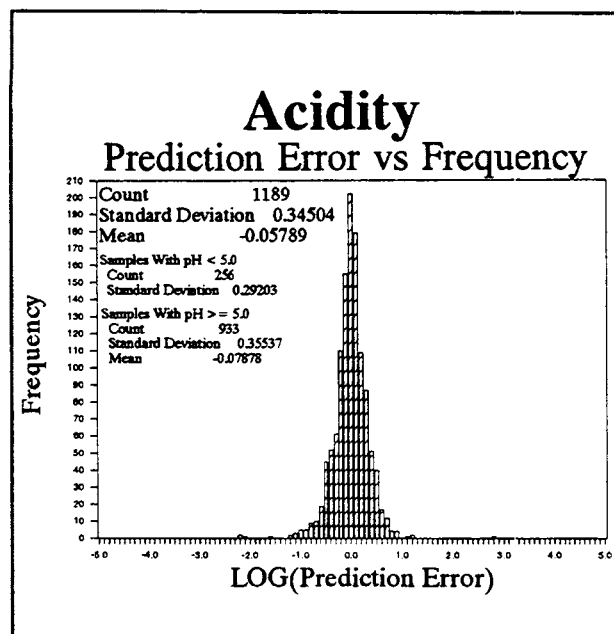


FIGURE 6. Prediction Error for Acidity Through 1991.

did not increase or decrease over several years. However, the concentrations remained generally within the same range from year to year (Figure 2). This can be seen more clearly in Figure 4 where the measured range in 1992 resembled that of pre-1992 data. Such repeating annual cycles in chemistry have also been noted elsewhere (Morin et al., 1994; Morin et al., submitted). This is discussed further in Section 4.2.

4. Implications and Applications of the Empirical Water-Chemistry Model

4.1 Natural, Artificial, and Unknown Variables

As explained in Section 2, lognormal distributions implicitly depict the multiplicative effect of several variables. Each variable contributes variability or scatter to the overall distribution of water chemistry through its unique variability and weighting value. However, the delineation of all major variables may not be possible from a practical perspective.

At Bell Mine, another important variable may have been wind direction, for example, but there are insufficient data to evaluate its effect. Also, because chemical analyses are human-based activities, there are artificial variables such as errors during sampling and analysis. Although the contributions from each natural, artificial, and any unidentified variable may not be possible, a key benefit to empirical modelling is that all variables are implicitly included and considered.

4.2 Short-term Peaks of Concentrations

One benefit of the empirical water-chemistry model is derived from its ability to estimate concentrations that probably occurred between monitoring events. This is based on the recognition of annual cycles (Section 3.3) and that the amplitude of these cycles are defined by standard deviations (Section 3.2). Calculations of unmeasured short-term concentrations can lead to more reasonable estimates of the items listed in Section 1.

TABLE 1

THE EMPIRICAL WATER-CHEMISTRY MODEL FOR BELL MINE

| <u>PARAMETER</u> | <u>pH RANGE</u> | <u>BEST-FIT EQUATION</u> | <u>LOG (STD DEVIATION)</u> |
|------------------|-----------------|---|----------------------------|
| Acidity | pH < 3.5 | $\log(\text{Acid}) = -0.932\text{pH} + 5.864$ | 0.345 |
| | pH > 3.5 | $\log(\text{Acid}) = -0.360\text{pH} + 3.862$ | |
| Alkalinity | pH > 4.5 | $\log(\text{Alk}) = +0.698\text{pH} - 3.141$ | 0.654 |
| Diss Aluminum | pH < 6.0 | $\log(\text{Al}) = -0.925\text{pH} + 4.851$ | 0.429 |
| | pH > 6.0 | Al = 0.2 mg/L | |
| Total Aluminum | | If diss Al > 0.3 mg/L, total Al = diss Al | |
| Diss Arsenic | | < 0.2 mg/L | |
| Diss Cadmium | pH < 3.0 | Cd = 0.07 mg/L | |
| | pH > 3.0 | Cd = 0.015 mg/L | |
| Diss Calcium | | $\log(\text{Ca}) = +0.619\log(\text{SO}_4) + 0.524$ | 0.375 |
| Diss Chromium | pH < 3.0 | Cr = 0.08 mg/L | |
| | pH > 3.0 | Cr = 0.015 mg/L | |
| Diss Copper | 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 | $\log(\text{Cu}) = -1.001\text{pH} + 6.307$ | |
| Total Copper | | $\log(\text{CuT}) = +0.962\log(\text{CuD}) + 0.180$ | 0.230 |
| Diss Iron | pH < 4.4 | $\log(\text{Fe}) = -1.429\text{pH} + 6.286$ | 0.807 |
| | pH > 4.4 | $\log(\text{Fe}) = -0.455\text{pH} + 2.000$ | |
| Total Iron | | If diss Fe > 1.0, total Fe = diss Fe | |
| Diss Lead | | Pb = 0.05 mg/L | |
| Diss Nickel | | $\log(\text{Ni}) = -0.317\text{pH} + 0.853$ | 0.607 |
| Total Nickel | | total Ni = diss Ni | 0.613 |
| Diss Selenium | | Se = 0.2 mg/L | |
| Diss Silver | | Ag = 0.015 mg/L | |
| Diss Zinc | | $\log(\text{Zn}) = -0.441\text{pH} + 1.838$ | 0.667 |
| Total Zinc | | total Zn = diss Zn | 0.144 |

At Bell Mine, the annual repetition of the lognormal distribution and standard deviation indicates that the entire range of concentrations probably also repeats annually. Since lognormal and normal distributions have theoretically infinite extents, there is a negligible finite probability that an unusually high concentration appears at the minesite at some moment each year. These short-term peaks can be estimated by applying the probability-distribution relationship to one year of time (Table 2). For example, the highest annual concentration of one-hour duration at Bell Mine is +3.85 log standard deviations above the mean. For dissolved copper at pH 7.0 and 2.5, the one-hour peak concentrations would be 92 mg/L (antilog of $-0.70 + 3.85 \cdot 0.692$) and 360,000 mg/L, respectively.

| TABLE 2 | | | | | |
|---|--------|---------|--------|-------|--------|
| PROBABILITY LEVELS AND CORRESPONDING TIME INTERVALS | | | | | |
| Time interval | 1 Year | 1 Month | 1 Week | 1 Day | 1 Hour |
| Probability | 100% | 8.3% | 1.9% | 0.27% | 0.011% |
| No. of std deviations above mean ¹ | +0.00 | +1.73 | +2.34 | +3.00 | +3.85 |

¹ obtained from normal-distribution tables (e.g., Pollard, 1977) after dividing by 2

Whereas a concentration of 92 mg/L may be marginally possible at neutral pH, a value is 360,000 mg/L is probably not possible at pH 2.5. This is a consequence of secondary-mineral precipitation which naturally truncates the lognormal distribution at higher values, as the detection limit artificially truncates the lower values. The implications of this are discussed further in Section 4.3.

4.3 Effects of Secondary Minerals

The correlation of copper concentrations with pH at Bell Mine (Figure 3) identified pH as a major independent variable, but did not establish a cause-and-effect relationship and the underlying mechanism. Calculations by the equilibrium-speciation model, MINTEQ (Allison et al., 1990), indicated copper concentrations were probably controlled to some extent by the solubility of the secondary mineral, CuSO_4 , at acidic pH and by CuCO_3 around neutral pH. In both pH ranges, copper concentrations increase as pH decreases due to the increased solubilities of the minerals. However, as pH falls from neutral values towards 5.0, CuSO_4 apparently becomes less soluble than CuCO_3 and thus begins regulating copper concentrations below pH 5.4.

The secondary copper minerals precipitate from waters affected by primary sulfide oxidation and metal leaching (Rate_1 , Figure 7), thereby lowering aqueous concentrations appearing in surrounding surface and ground waters ($\text{Rate}_2 > 0$ so $\text{Rate}_3 < \text{Rate}_1$; $\text{Rate}_4 \sim 0$). This process can continue until all primary copper-bearing and sulfide minerals are exhausted ($\text{Rate}_1 = 0$). At that point, the secondary minerals may start to dissolve until exhausted at a much later time ($\text{Rate}_4 > 0$). Primary reactions

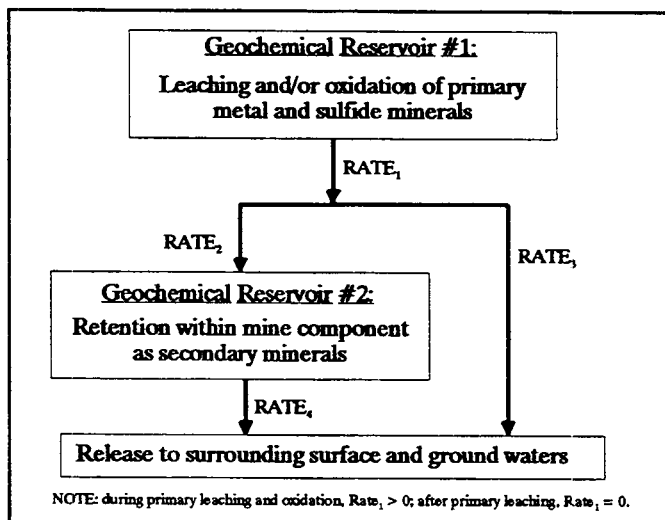


FIGURE 7. Primary and Secondary Geochemical Pathways Affecting Effluent Water Chemistry.

(Rate₁) are discussed by Morin et al. (1995, these proceedings).

The initial process of secondary mineral precipitation (Rate₂ > 0, Figure 7) results in the geochemical retention of metals within dumps, dams, tailings, and mine walls. For waste-rock dumps, Morin and Hutt (1994) interpreted the reported retention of 80-95% (Rate₂ = 0.80-0.95* Rate₁, Figure 7) from a predominantly physical perspective: rock surfaces remaining unflushed by infiltrating water. In reality, both physical and geochemical retention can play a role:

$$\text{Total Retention} = (1-x) \cdot (\text{Geochemical Retention}) + (x) \cdot (\text{Physical Retention}) \quad (3)$$

where $x = 0.0$ to 1.0

In any case, the total retention results in lower annual concentrations and loadings into surrounding waters, but these lower levels continue for a longer period of time.

4.4 Evolution of Water Chemistry Through Time and As the Independent Variables Change

At Bell Mine, static and kinetic tests for the prediction of water chemistry associated with acidic and pH-neutral drainage involved over 200 acid-base accounts, 7 humidity cells containing 1 kg of sample, and 24 long-term heap leach tests ranging in scale from 23 to 30,000 kg. Based on these tests, some mine-rock dumps and dams that are currently neutral are expected to become acidic after several years to decades, and then return to near neutrality. Timelines of pH evolution were generated for each mine component (Morin and Hutt, 1993b). Because the effects of pH variations were filtered from the database, the empirical model (Table 1) remains valid for predictions as pH evolves along the timelines. In this way, the empirical model becomes a predictor of water chemistry at Bell Mine over periods of centuries, based on the assumption that observed patterns will continue to repeat as they have for over the last decade.

5. Conclusion

This paper has presented an empirical approach for modelling water chemistry at minesites using only the existing monitoring database. The resulting model is based on statistical evaluations of the database using relatively simple means and standard deviations. With the assumption that past patterns will continue into the future, the empirical model becomes a predictive tool for future water chemistry.

The water-chemistry database from Noranda Minerals' Bell Mine was used to illustrate the methodology for examining the data and reducing its scatter through use of deterministic modelling. This culminated in a site-specific model that can be used to estimate yearly chemistry, even between monitoring events, and future chemistry as mine-rock dumps, tailings, and pit walls evolve from pH-neutral to acidic and back to neutral conditions.

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