

## MDAG.com Case Study 40

# Fractal Characteristics, Short-Term Maximum Concentrations, and Appropriate Time Discretization of Minesite-Drainage Chemistry

by K.A. Morin

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### Abstract

Aqueous concentrations of individual elements in minesite drainage are not measured on a time-continuous basis, but are measured after discrete time intervals, like monthly and quarterly sampling. This results in “near-instantaneous” values with much larger intervening periods of time, and leads to questions like:

- What time-discretization interval should we use to understand and predict minesite-drainage chemistry reliably, by minimizing sufficiently the discretization error?
- How do we detect or predict short-term maximum concentrations of environmental significance?

These are the primary questions examined in this MDAG case study. The answers are important and timely, because there is a strong need to improve predictions of short-term concentrations for proposed minesites. There is also a strong need for existing and closed minesites to understand and anticipate their short-term maximum concentrations that may not be detected often, or at all, by their monitoring programs.

The preceding questions are addressed here using large drainage-chemistry databases spanning many years to decades, with some including high-frequency sampling as often as every four hours. The databases show that temporal trends in drainage chemistry can be orderly, generally following a trigonometric sine function over an annual period, with prominent and repeating short-term peaks and valleys. Other databases not included here show chaotic (non-orderly) trends. There are insufficient studies to understand when orderly or chaotic chemistry can be expected at a minesite, and such understanding is often lacking for other, non-mining systems.

To examine the effects of time discretization on maximum concentrations in orderly minesite drainage, two mathematical approaches are applied here: fractals and lognormal statistics.

A fractal is a repeating pattern that appears similar or the same as scale changes. Visual comparisons are made of (1) the temporal trends in aqueous concentrations, emphasizing copper, zinc, and cadmium, from the databases with near-neutral and acidic monitoring stations to (2) variable, but finite, numbers of terms in the infinite fractal sine wave. These comparisons show the temporal trends in copper, zinc, and cadmium display fractal characteristics over time periods of approximately days to a year. However, the data are not sufficient to determine whether this holds at the minesites for longer times like decades or for short times like hours and minutes. These observations are similar to those made elsewhere for non-mining-related watersheds. To resolve these uncertainties, more frequent sampling for long periods of time will be needed at minesites.

Lognormal statistics apply the Gaussian distribution and probabilities to values transformed mathematically to log<sub>10</sub> values. The large databases examined here lead to several observations including:

- Average-annual aqueous concentrations of elements like copper, zinc, and cadmium display trends that were dependent on “master parameters” like pH and sulphate.
- Within specific ranges of the master parameters, aqueous concentrations vary above and below the average mean in generally lognormal distributions. The annual lognormal variability could be described by a standard deviation expressed in log<sub>10</sub> cycles, and roughly the same values of the log<sub>10</sub> std dev often arise year after year.
- The log<sub>10</sub> standard deviation can be used with probability levels to calculate short-term maximum

- concentrations, like daily and hourly maximums, even when longer-frequency sampling may not detect these values (illustrated by the allegory of the “Lucky Mine” and the “Unlucky Mine”).
- The number of water analyses from the high-frequency sampling (four hourly to daily) was randomly reduced to simulate less-frequent sampling, like weekly and quarterly. This shows that the frequency of sampling would have to be at least weekly, but sometimes monthly, to calculate a log10 standard deviation within common analytical inaccuracy. This reasonably accurate value can then be used to calculate shorter-term maximum concentrations that may go undetected.
  - Although shorter-term maximum concentrations can be statistically calculated, this does not mean they actually exist and occur. For example, a maximum “ceiling”, such as solubility, may limit maximum concentrations only to the calculated monthly or weekly maximum, with no actual occurrence of the statistical one-day or one-hour maximum. This is seen in the databases examined here.
  - In the high-frequency database, the maximum concentrations (defined as 80-100% of measured maximum to allow for analytical inaccuracy) of copper, zinc, and cadmium are detected both (1) in contiguous samples representing less than a day or up to one week and (2) in non-contiguous samples separated by days to weeks of non-maximum concentrations. Thus, the simplistic concept that maximum values occur only as one continuous interval is ruled out for this database, which would be more consistent with fractals.
  - The number of days that maximum concentrations should be detected, based on lognormal probabilities, exceeds the number of actual measured days. As a result, the usage of lognormal probabilities over-predict the cumulative duration of maximum concentrations. However, there is one exception: cadmium at the monitoring station sampled every four hours. The discrepancies between the lognormal-probability-based durations of maximum concentrations and the actual durations generally follow power-law trends, which are characteristic of fractals.

Overall, the fractal and lognormal approaches both have some value in predicting and understanding short-term maximum concentrations, but neither approach is highly successful with the current databases. However, on the question of time discretization and sampling frequency, the lognormal approach indicated weekly, and sometimes monthly, sampling would provide sufficiently reliable statistics to calculate shorter-term maximums. Additional, larger long-term and higher-frequency databases of minesite-drainage chemistry are needed to address these questions more reliably, and to understand the conditions when orderly or chaotic drainage chemistry may arise.

Interestingly, this MDAG case study addresses short-term maximum concentrations without including underlying mechanisms, such as sulphide oxidation and metal leaching rates. This is attributable to the emergence of dominant processes at the full scale of minesite components that are minor at smaller scales.

## 1. INTRODUCTION

Although philosophers and physicists still ponder the meaning of time, we can view the dimension of time as a continuous function moving in one direction: from past to future. We can, and do, discretize time into discrete intervals, like milliseconds, minutes, months, and years, just as we do with spatial dimensions (millimeters, kilometers, etc.). However, time is not static within our arbitrary intervals, unlike a video shown at one frame per second where each second displays static conditions. Thus, discretization of time (and spatial dimensions) inevitably results in some degree of error (“discretization error”).

At minesites, surface waters flow through ditches, and into and from reservoirs and holding ponds. Subsurface groundwaters flow around and through open spaces in rock walls, rock piles, tailings, sediments, and bedrock. “Flow” is spatial dimension(s) divided by time, and is also a continuous function. However, flow is often measured at discrete times, such as hourly or monthly. Even “continuous” flow recorders typically require some discrete time interval for measuring and recording flow. There are implications to this discretization of time on our understanding of minesite drainage.

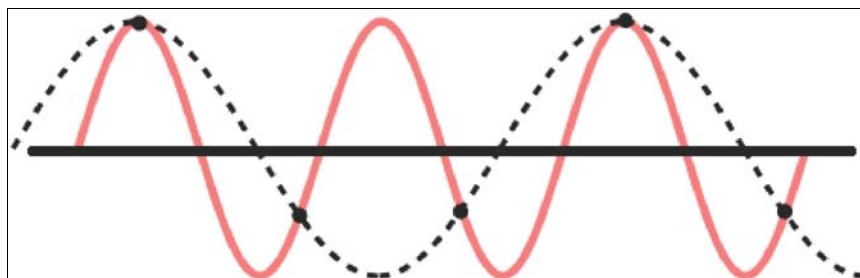
Superimposed on minesite flow is the chemistry of the drainage: the chemical elements and compounds dissolved or suspended in the water. (Dissolved vs. suspended is also a discretization of a continuous condition.) Even if a particular flowrate remains constant, the aqueous chemistry within that flow can vary significantly as a continuous function.

All this leads to an interesting question: What discretization interval should we use to understand and predict minesite-drainage chemistry reliably, by minimizing sufficiently the discretization error? An ancillary question is: How do we detect or predict short-term maximum concentrations of environmental significance? These questions are far from trivial, and the answers can have major impacts on the reliability of environmental assessments and predictions.

A simple illustration of these impacts is a trigonometric sine wave with a certain wavelength and amplitude (solid wavy line in Figure 1). This wavy line can represent temporal variations, including minimum and maximum values, in aqueous concentrations (mg/L) or flow (m<sup>3</sup>/s) at a minesite. Discrete sampling of this variability (dashed wavy line in Figure 1) produces “near-instantaneous” (relative to the time between sampling events) datapoints. These datapoints (solid points on the dashed line in Figure 1), can falsely suggest an incorrect variability, or an incorrect higher minimum and lower maximum, depending on how they are connected by interpretation.

Furthermore, how informative would a long-term average be in this case (thick horizontal line in Figure 1)?

These issues are examined in this MDAG case study. We will see that the current state-of-the-art at minesites is not sufficient to ensure the protection and maintenance of the surrounding environment and aquatic ecosystems.



**Figure 1.** A hypothetical example of minesite-drainage chemistry (or flow) varying through time (solid wavy line). Depending on the length and frequency of the sampling events (solid dots on dashed wavy line), incorrect interpretations on variability and minimum-maximum can result. A long-term average (solid horizontal line) provides no information on variability or minimum-maximum.

## 2. REALITY

Over decades of monitoring, minesite-drainage chemistry can be relatively orderly through time (e.g., Figures 2 and 3) or chaotic (not shown), due to “nonlinear science” (Morin, in prep).

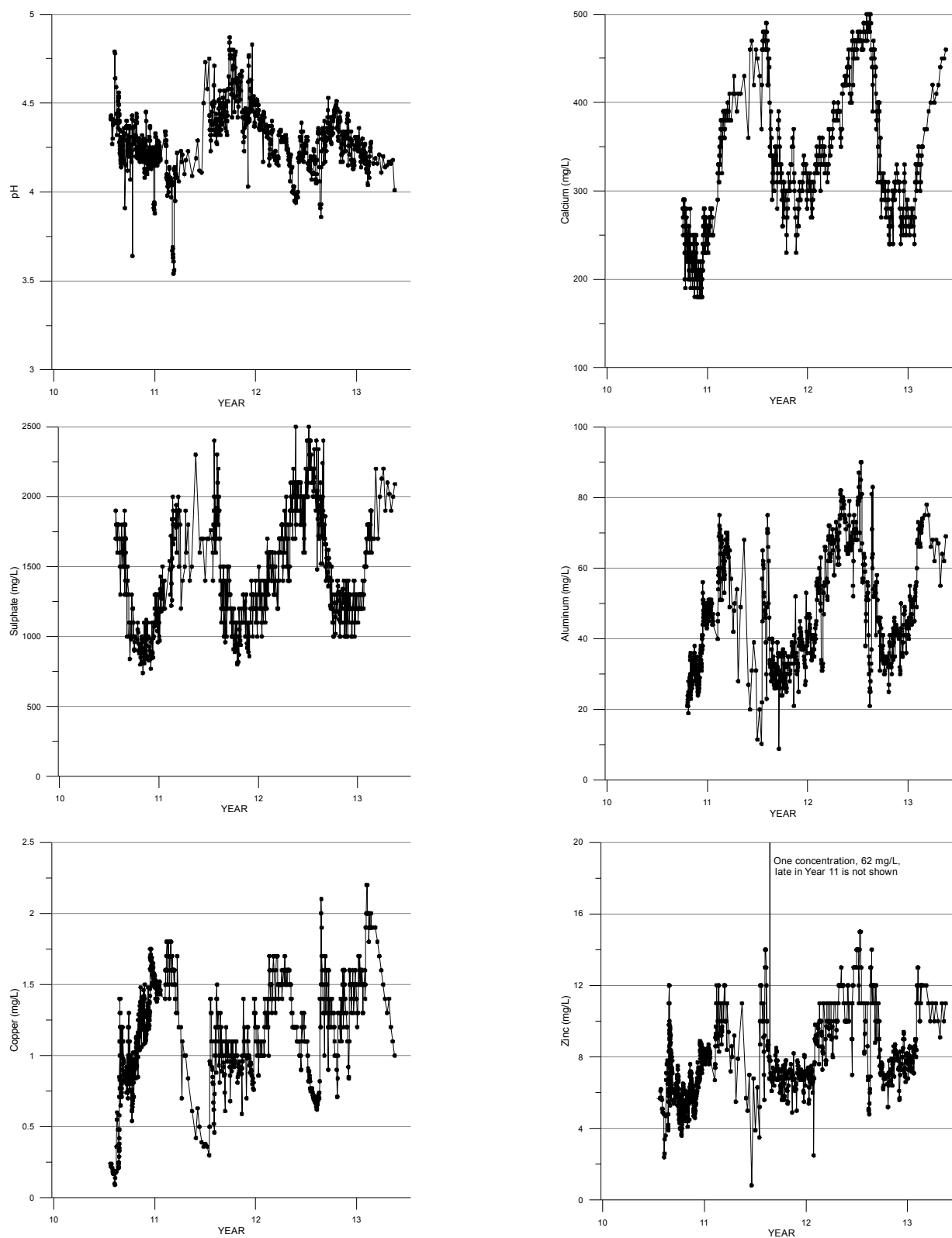
“We currently have no general techniques (and very few special ones) for telling whether a particular nonlinear system will exhibit the complexity of chaos, or the simplicity of order.” (Meiss, 2003)

Thus, we cannot currently predict whether trends in drainage chemistry at a proposed minesite will be orderly or chaotic. This is partly due to the general lack of large, detailed monitoring databases to show us how to reliably distinguish order from chaos at existing minesites. Even simplistic Figure 1 shows that infrequent sampling of a sine wave could suggest a chaotic trend where order really exists.

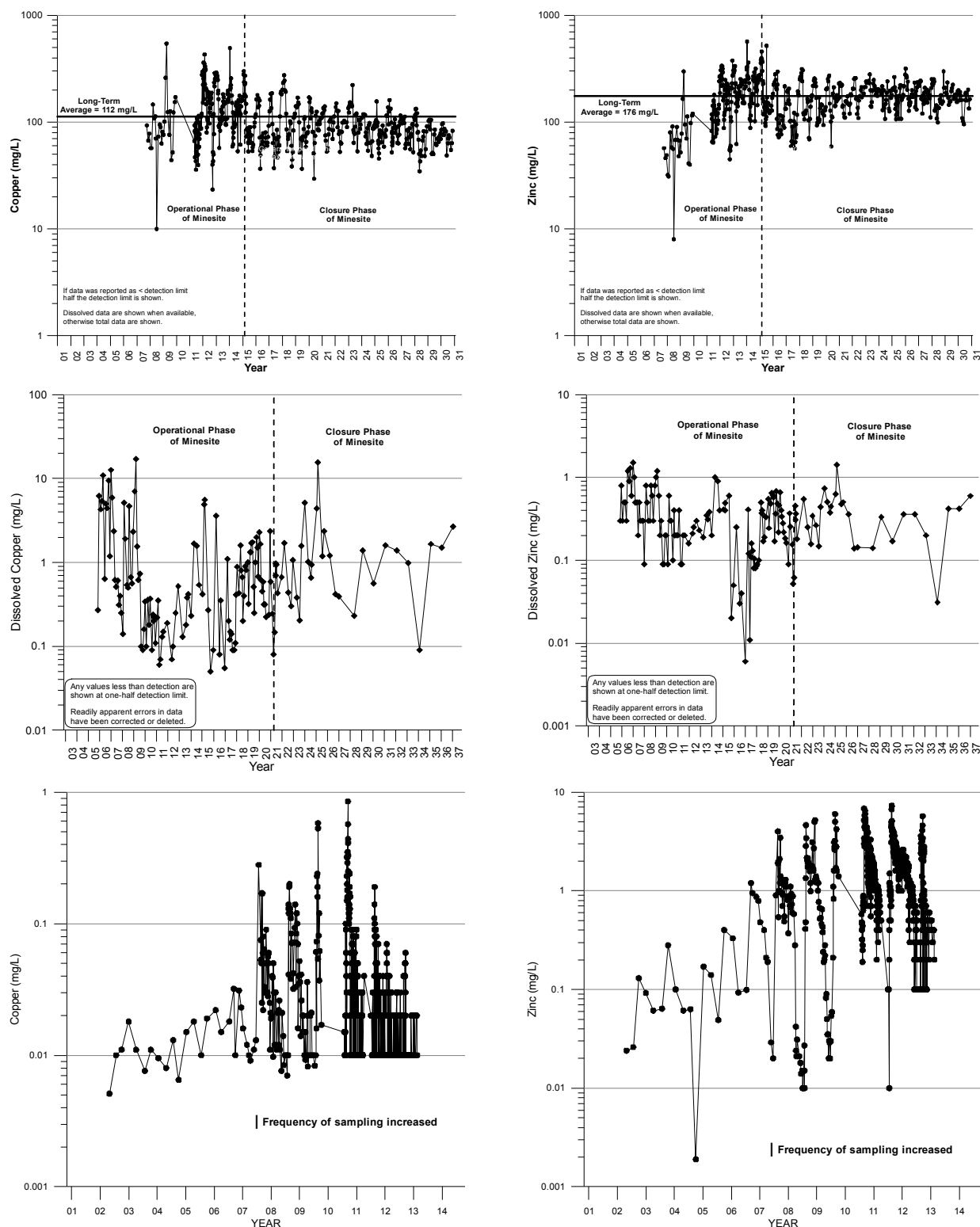
Because the current understanding of drainage chemistry at minesites is relatively poor due to the lack of large, detailed monitoring databases, how does the standard approach of predicting the chemical trends shown in Figures 2 and 3 fare? Surprisingly, the standard approach, accepted by provincial and federal governments in my country of Canada, is simply the prediction of the annual average (see the horizontal line in Figure 1). There is often little consideration to short-term variations and maximum concentrations.

The common approach to estimate aqueous annual-average concentrations for full-scale minesite components is seriously unreliable (Morin, 2014). It frequently under-predicts the severity of concentrations and thus frequently underestimates the environmental effects of minesite drainage (Morin, 2010).

Moreover, water-quality guidelines and criteria in Canada (and many other jurisdictions) are based on “near-instantaneous” samples (e.g., collected over one minute) or on 30-day averages of a certain number of near-instantaneous samples. Therefore, no matter how reliably predicted the aqueous annual-average concentration may be, it is of little value in determining whether downstream ecosystems might be harmed by shorter-term (e.g., one-month or one-week) higher concentrations. This is reinforced by the observation that shorter-term variability in the few large, detailed databases can approach and exceed a factor of ten to one hundred above the annual average (shown later).



**Figure 2.** Examples of temporal trends in full-scale acidic minesite-drainage chemistry at one minesite, spanning a few years, based on near-instantaneous samples (e.g., one-minute collection time) from one monitoring location, collected as frequently as every four hours. Note: y-axis is arithmetic, not logarithmic like Figure 3.



**Figure 3. Examples of temporal trends in full-scale minesite-drainage chemistry, spanning at least one decade, based on near-instantaneous samples (e.g., one-minute collection time) from three minesites, collected as frequently as every four hours. Upper row (Minesite 1): acidic drainage; middle (Minesite 2) and lower (Minesite 3) rows: near-neutral drainage. Left column (note: y-axis is log<sub>10</sub> (concentration)): copper; right column: zinc. Data from Morin and Hutt (2010a and 2010b) and Morin et al. (1993, 1994, 2010).**

In simplistic terms using Figure 1:

- the solid wavy line represents reality at minesites, reflecting the variability that can span up to orders of magnitude and representing the associated potential toxicity exposure of downstream ecosystems by minesite drainage;
- the dashed wavy line is indicative of current sampling at existing minesites that may or may not reliably characterize the variability and the short-term minimum-maximum; and
- the solid horizontal line is the current standard predictive practice for proposed minesites.

There is a strong need for improvement here, both to protect the surrounding environment and to improve public confidence in mining companies. There are ways to predict or explain short-term concentrations even when they are not detected. This was the intent of Morin and Hutt (1998) when they discussed the hypothetical “Lucky Mine” and “Unlucky Mine”:

“The Lucky Mine collects grab samples of drainage once a month, but by coincidence has never collected one during the [short-term maximum, such as the hourly maximum]. The Unlucky Mine happened to collect one monthly sample during [a short-term maximum] and there is panic. The analytical laboratory is asked to repeat the analysis, and the laboratory confirms a high concentration. The mining company suspects contamination during collection or analysis, and collects another sample days or weeks after the [short-term maximum]. Of course, the concentration in this new sample is much lower, and the former analysis is dismissed as anomalous and erroneous.”

A better understanding and estimation of short-term maximum concentrations would have shown the Lucky and Unlucky Mines have about the same drainage chemistry. Therefore, short-term maximum concentrations should receive greater attention at proposed, operating, and closed minesites.

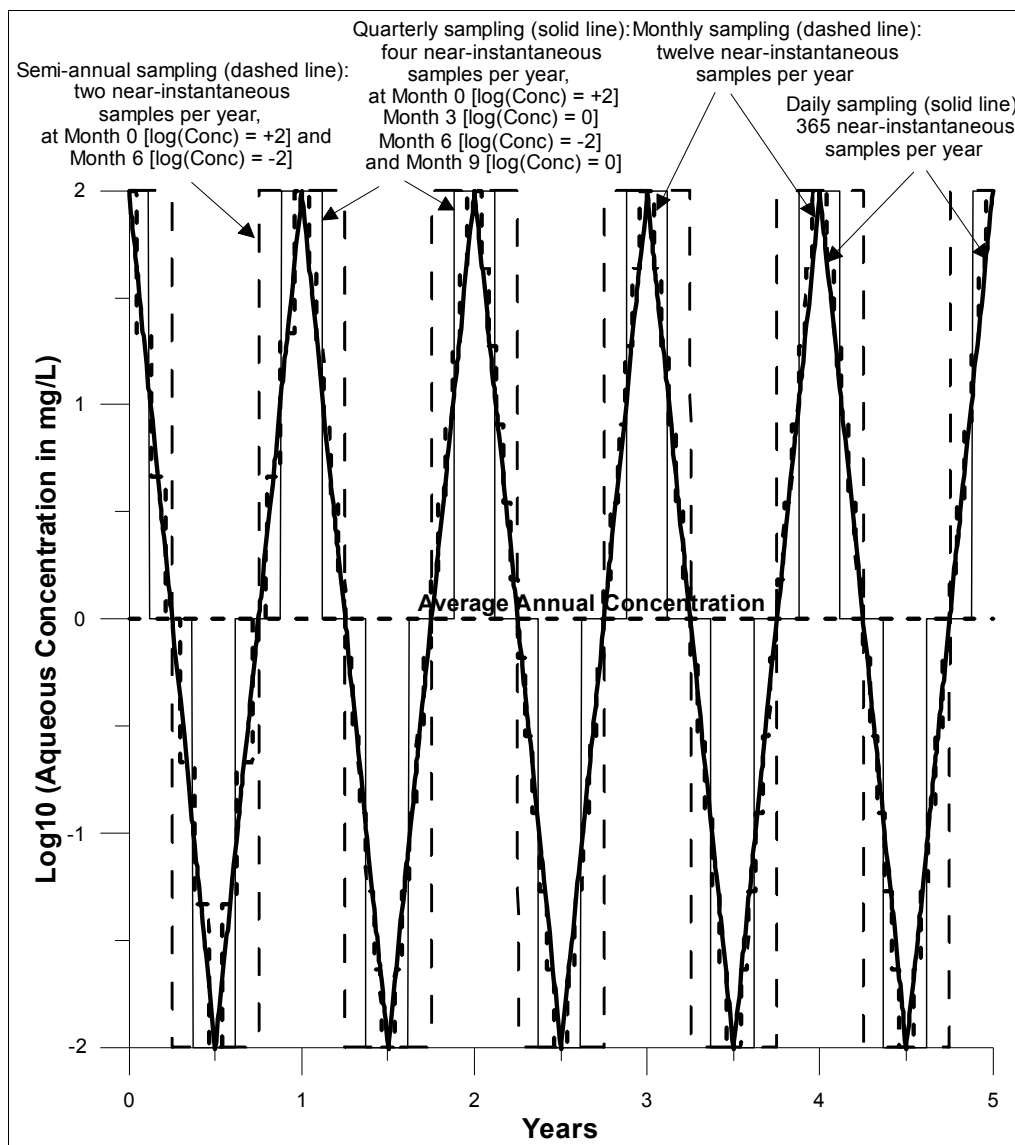
### 3. TEMPORAL VARIABILITY AND DISCRETIZATION OF TIME

When we look at Figures 2 and 3, we see significant temporal variability in aqueous concentrations that generally range from high to low each year, year after year. This cannot usually be seen from samples collected twice a year, for example.

Site-specific toxicity studies show aquatic organisms can be adversely affected, acutely or chronically, after a day or week of exposure. Therefore, how often should water samples be collected at a monitoring station to determine if toxic minewater is being released during one day? Does this require intensive and constant daily sampling?

The first step in answering this question is to look more closely at the discretization of time. In the simplistic step-wise example of Figure 4, the maximum concentration at a minesite station (100 mg/L, or  $\log_{10} = 2$ ) occurs only on the first day of each year, and the minimum (0.01 mg/L or  $\log_{10} = -2$ ) occurs only on Day 182. There is a logarithmic distribution between these extremes, repeating yearly, with a geometric annual-average concentration of 1 mg/L ( $\log_{10} = 0$ ).





**Figure 4.** A simplistic step-wise example of concentrations at a hypothetical minesite monitoring station. Concentrations vary orderly from a high of 100 mg/L ( $\log_{10} = +2$ ) only on the first day of each year, to a low of 0.01 mg/L ( $\log_{10} = -2$ ) only on Day 182 of each year, with a geometric average-annual concentration of 1 mg/L ( $\log_{10} = 0$ ). One sample a year would not likely coincide with the real annual average. Fortuitous semi-annual sampling exactly at Month 0.0 ( $\log_{10} = +2$ ) and Month 6.0 ( $\log_{10} = -2$ ) would yield the real maximum and minimum concentrations, and the geometric annual average. However, this is unlikely, and thus the two samples would yield an unreliable annual average and likely erroneously low statistics on maximum short-term concentrations. As sampling frequency increases to daily, the real shape of the daily distribution becomes apparent, with a suggestion that monthly or weekly sampling may be sufficient to estimate the statistics for daily or hourly sampling. This is discussed in detail in the following Section 5.

What is the probability that one sample a year would yield the real average annual in Figure 4? There are two days each year when this is possible with a combined probability of 0.5% (2/365). So it is unlikely. Even if successful, it would say nothing about the substantial, potentially toxic concentrations that occur each year on shorter intervals.

As explained in Section 2 above, a single prediction of average-annual concentration is standard practice today for proposed minesites, accepted by regulatory agencies. Figure 4 illustrates how uninformative and potentially environmental degrading this is.

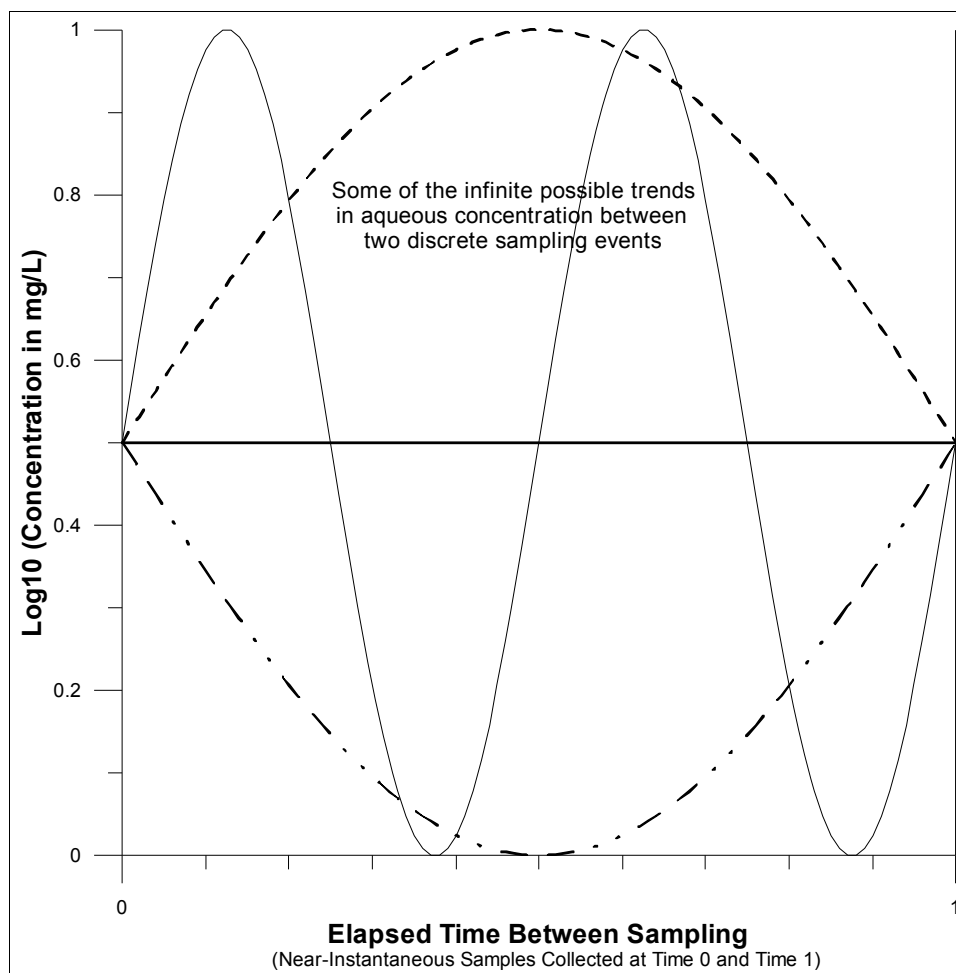
Semi-annual sampling would not likely take place on the two days with the highest and lowest concentrations in Figure 4. Thus, statistical values like daily maximum would very likely be inaccurately low.

Figure 4 shows that, as sampling frequency increases to daily, the real daily distribution becomes apparent. Two important questions arising at this point are:

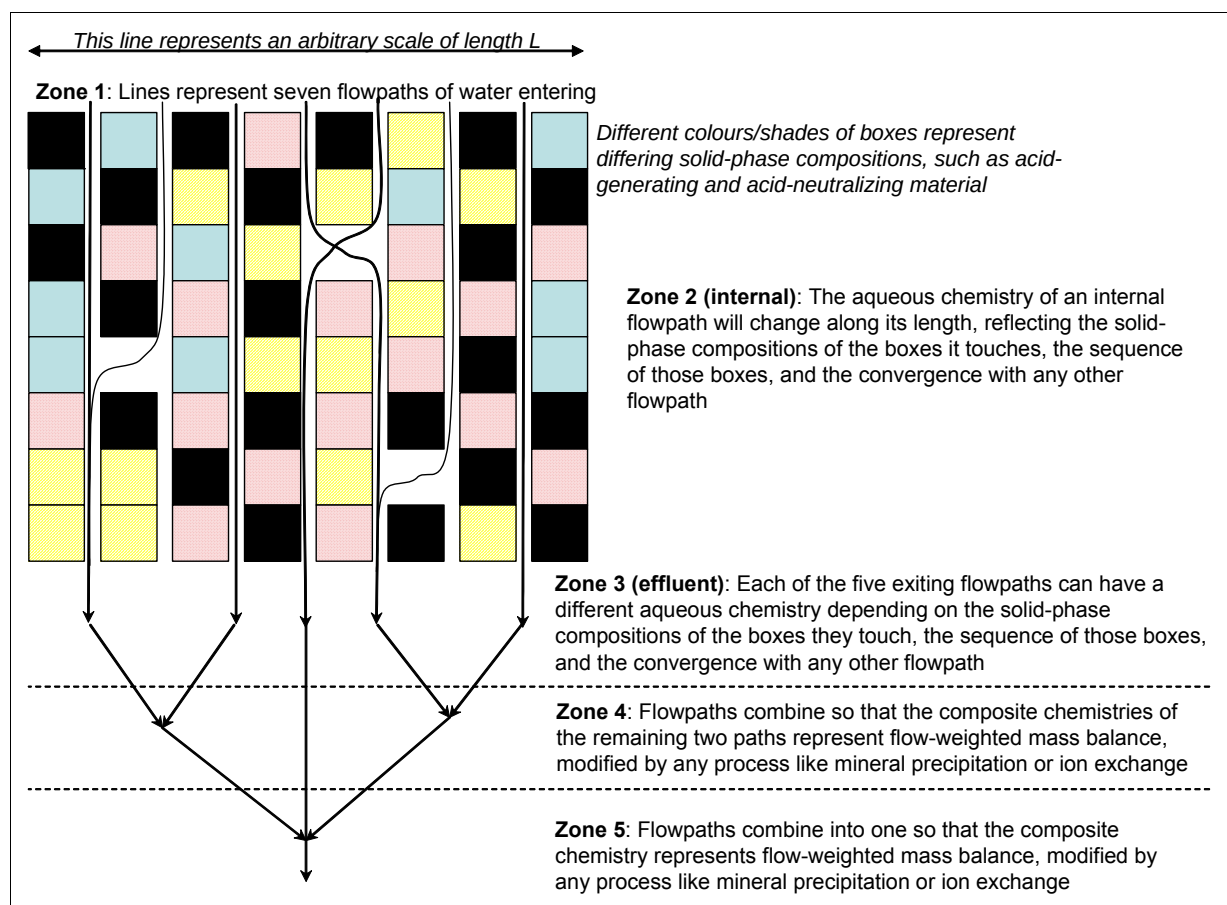
- Can the real daily distribution be detected by a frequency less than daily, perhaps by monthly sampling, to within an acceptable discretization error as suggested visually by Figure 4?
- What if there is variability on a shorter time discretization than daily (e.g., Figure 5)? This is actually documented at minesites (see Figures 2 and 3, and Section 5) and in streams below minesites (e.g., Nimick et al., 2010; Shope et al., 2006; Nimick et al., 2003). What can we do then?

These questions are answered in the following sections.

As a final note in this section, it is important to understand that this MDAG case study focusses on temporal discretization. Spatial discretization (Zone 2 of Figure 6; also, e.g., Li, 1999), and the effects of homogenizing flowpaths with differing aqueous chemistries (Zones 4 and 5), can also affect temporal trends of aqueous concentrations but are not discussed here. In this MDAG case study, all data (e.g., Figures 2 and 3) are from Zones 4 and 5 (Figure 6), external to the component and subjected to some spatial homogenization. For more details on spatial discretization, see Morin (2014 and in prep) and Morin and Hutt (2007).



**Figure 5. Possible variations in minesite-drainage concentrations between two near-instantaneous sampling events relative to the time between sampling. To resolve this, the sampling frequency can be increased, but unless it becomes continuous the possible variations between the more frequent samples remains. This is discussed further in Sections 4 and 5, with potential mathematical resolutions.**



**Figure 6. Schematic diagram of adjoining blocks of differing chemical composition, with flowpaths for water and air, showing Zones 4 and 5 as becoming spatially homogenized and thus not spatially discrete (from Morin and Hutt, 2007).**

#### 4. FRACTALS AND SELF-SIMILARITY

As a noun:

“A fractal is a natural phenomenon or a mathematical set that exhibits a repeating pattern that displays at every scale. It is also known as expanding symmetry or evolving symmetry. If the replication is exactly the same at every scale, it is called a self-similar pattern. . . . Fractals can also be nearly the same at different levels. . . . Fractals also include the idea of a detailed pattern that repeats itself.” (Wikipedia, 2015a).

Also,

“A fractal is a never-ending pattern. Fractals are infinitely complex patterns that are self-similar across different scales. They are created by repeating a simple process over and over in an ongoing feedback loop . . . Fractal patterns are extremely familiar, since nature is full of fractals. For instance: trees, rivers, coastlines, mountains, clouds, seashells, hurricanes, etc. Abstract fractals – such as the Mandelbrot Set – can be generated by a computer calculating a simple equation over and over.” (Fractal Foundation, 2015).

One can wonder if “repeating patterns at every scale” and “infinitely complex patterns” can apply to temporal trends in minesite-drainage chemistry. The answer is yes, and the easiest way to show this with an early fractal equation known as “the Weierstrass function” (Wikipedia.org, 2015b).

The general form of the fractal Weierstrass function is:

$$f(x) = \sum_{n=0}^{\infty} a^n \cos(b^n \pi x) \quad (\text{Equation 1})$$

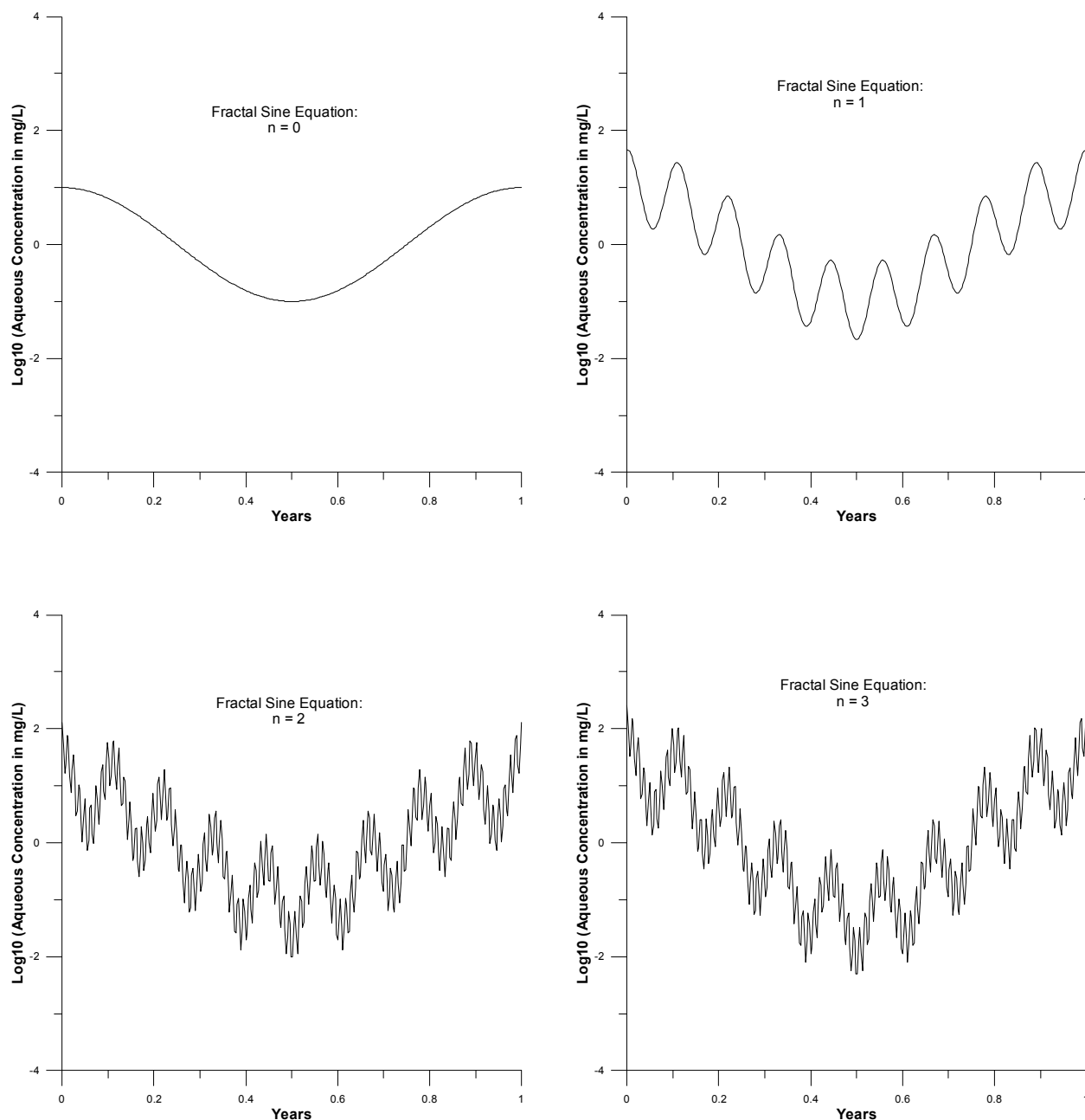
Based on Figures 1 to 4 above, coefficients a and b can be specified to represent a fractal sine wave (Daulton, 2015), with x (time in years) multiplied by 2 to represent a one-year cycle:

$$f(x) = \sum_{n=0}^{\infty} (2/3)^n \cos(9^n \pi 2x) \quad (\text{Equation 2})$$

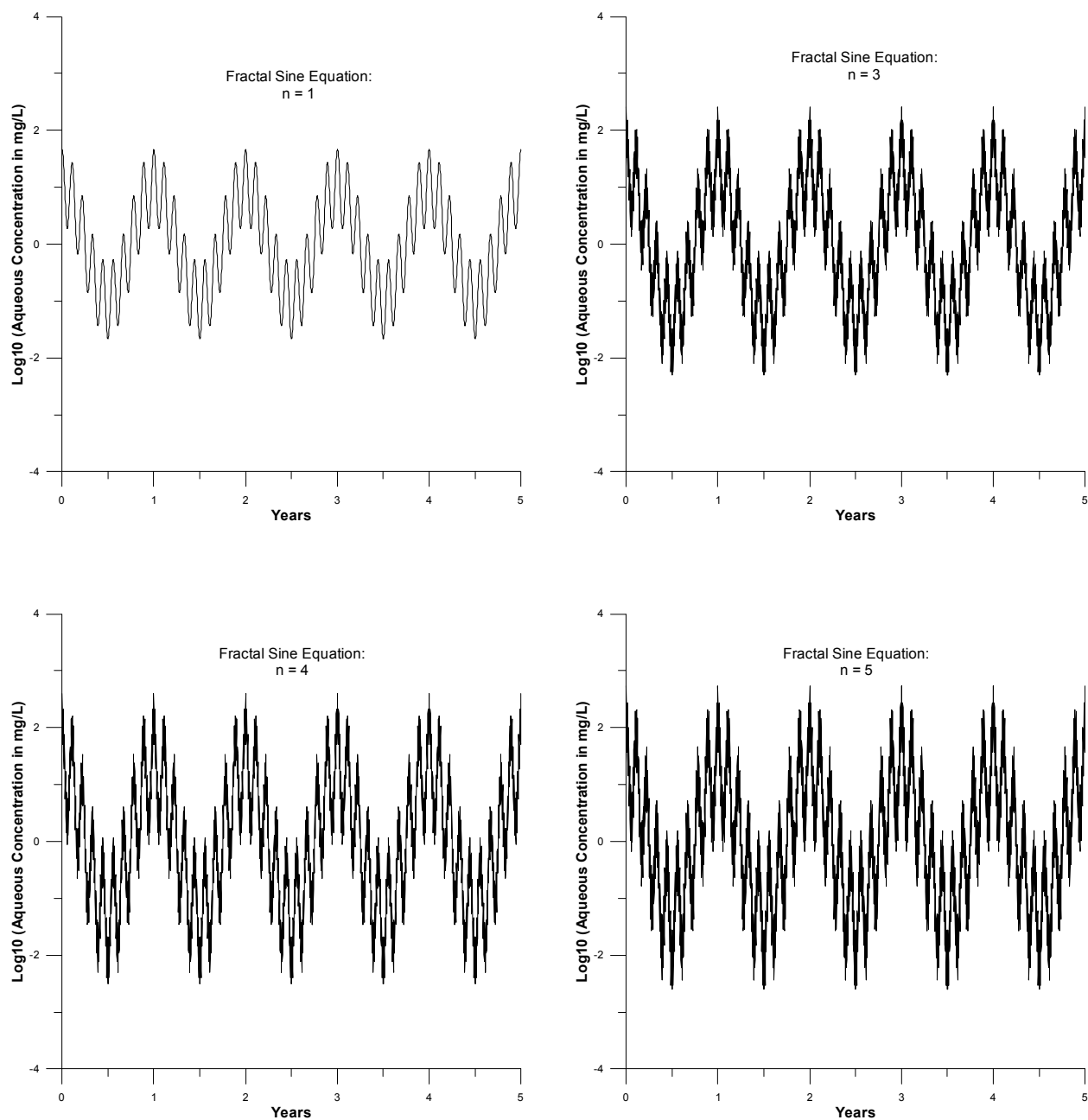
In theory, the summation of n in Equation 2 should continue to infinity. However, starting simply with n=0, we obtain a simple sine curve (upper left diagram of Figure 7). With n=1, in effect each part of the sine curve is divided up into a series of sine curves (upper right diagram of Figure 7). With increasing n, we can see the complexity of the curve growing, but representing a sine curve on all temporal scales.

Figure 7 is based on one year of time. As the time increases to five years (Figure 8), the fractal characteristics are not as apparent, but are still there.

Visual comparisons of Figure 2 with Figure 7, and Figure 3 with Figure 8, show that temporal trends in orderly minesite-drainage chemistry display fractal characteristics.



**Figure 7.** The fractal sine wave applied the logarithmic aqueous concentration through a single year. As an additional term ( $n$ ) is added to the abbreviated infinite sum ( $\Sigma$ ) of Equation 2, each wavelength is partitioned into several wavelengths, leading to the self-similarity with scale, or fractal characteristic. Note the minimum and maximum values increase with increasing  $n$ . Compare this diagram to Figure 2 for the potential of minesite-drainage chemistry to have fractal characteristics in the temporal dimension.



**Figure 8.** The fractal sine wave applied the logarithmic aqueous concentration across several years. The self-similarity is more obscured on this scale than in Figure 7. Compare this diagram to Figure 3 for the potential of minesite-drainage chemistry to have fractal characteristics in the temporal dimension.

However, because Figures 2 and 3 are based on near-instantaneous measurements as frequently as every four hours, fractal characteristics below roughly one day cannot be reliably assessed with the current databases (the “Nyquist frequency”). Also, there may be cycles on a scale larger than several years, such as over several decades (e.g., Minesite 3 in Figure 3), but the monitoring record is not yet long enough to assess this. Additional, longer-term and more frequent data are needed.

Therefore, orderly minesite-drainage chemistry can display fractal characteristics over time scales of at least days to years. However, the calculation of the short-term maximum concentration depends on how far the self-similarity extends into decreasing time intervals. Without long-term continuous monitoring, this cannot be addressed. Perhaps a simplistic approach would be to extend the infinite series of Equation 2 out to some value of  $n$  that approximates the time duration of interest, or the minimum time duration over which chronic or acute toxicity would arise. This issue, as well as a non-fractal alternative, are discussed in Section 5.

Fractals have been applied in geochemistry, almost invariably to solid-phase samples. These samples are taken from sources such as from ore zones, soil anomalies, and mineral intergrowths. One of many examples is Birdi (2013).

In contrast, the application of fractals to minesite-drainage chemistry is virtually non-existent. However, the application of fractals to the aqueous geochemistry of natural elements, draining from relatively undisturbed and non-mining-disturbed watersheds, has been discussed by a few researchers, such as Aubert et al., (2013), Kirchener and Neal (2013), and Kirchener et al. (2000). These researchers reached conclusions such as:

- In one studied watershed, combined high- and low-frequency sampling “revealed  $1/f$  spectral [fractal] scaling of streamwater concentrations clear across the periodic table” (dozens of elements were analyzed). Also, “The dominant spectral slopes appear to vary surprisingly little among diverse solutes characterized by different export processes, widely varying chemical reactivity and widely differing natural and anthropogenic sources.”
- Despite the limited number of intensively studied watersheds, the occurrence of fractals in drainage-water time series was considered “universal”.
- “Time series that exhibit  $1/f$  [fractal] scaling . . . are ‘nonself-averaging’; that is, measurements averaged over longer and longer periods of time do not converge to stable averages. . . . An important implication is that averages and trends in such time series are not nearly as reliable as conventional statistics would suggest.” This has implications for Section 5 of this study.
- However, nonself-averaging did not apply to all aqueous elements at all time scales in a monitored watershed: “. . . these three solutes (sulphate, nitrate, and dissolved organic carbon) should exhibit conventional self-averaging behavior, with more stable means and reliable trends, over time scales much longer than 1 year. For the fourth solute, Cl [chloride],  $1/f$  scaling extends to the lowest measured frequencies [and thus the longest measured time scales], suggesting that there is no end in sight to its nonself-averaging behavior, even on decadal time scales.”
- “[A]lthough our results argue for the generality of fractal  $1/f$  scaling of stream chemistry at time scales of years to days, they also point to deviations from  $1/f$  scaling for some solutes at both long and short wavelengths.”
- “This occurrence of universal fractal scaling demands a mechanistic explanation. The mechanisms involved must be general across watersheds . . . as well as the range of sites. . . . It has been previously shown . . . that random chemical fluctuations occurring across a landscape can be transformed by downslope advection and dispersion acting across a range of transport



length scales to yield  $1/f$  time series in streamwater. Downslope advection and dispersion are clearly dominant transport processes in a wide range of watersheds . . . and also for a wide range of solutes except, perhaps, for those that are very strongly retained by adsorption onto soil particles, or those that are dominantly controlled by in-stream processes. Thus, this mechanism is a plausible candidate for the origin of widespread fractal scaling in stream chemistry time series.”

- However, explanations other than advection-dispersion are also plausible. “Laboratory investigations and field studies have called into question the advection-dispersion equation as a description of chemical transport in fracture networks and other highly heterogeneous environments. . . . [A] random series of perturbations, when filtered by the catchment, should have a  $1/f$  power spectrum above a low-frequency limit [and] there should be a high-frequency limit as well, determined by the duration of the original perturbations themselves, or by dispersion occurring within the channel network.”

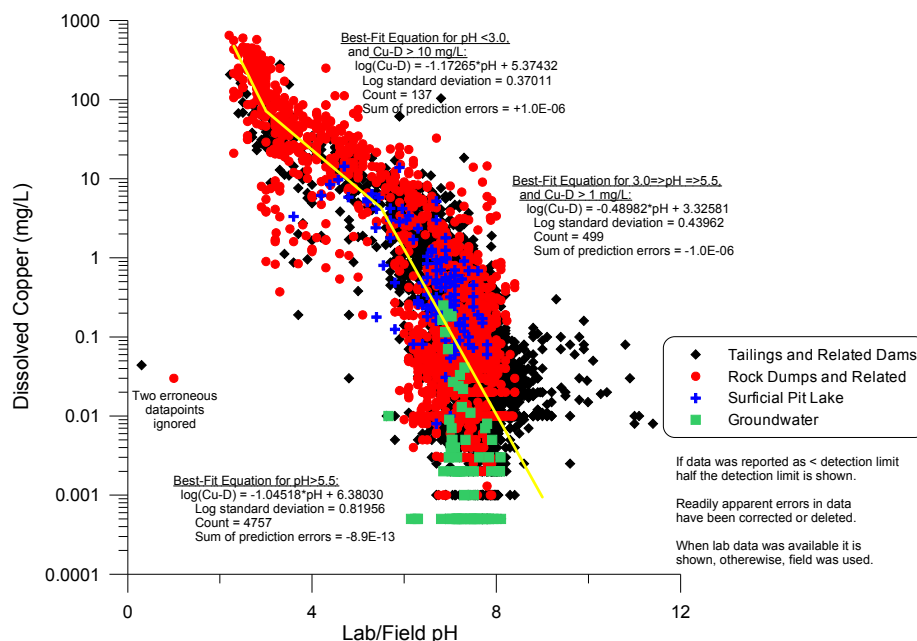
It will be interesting to see if such conclusions also apply to minesite-drainage chemistry as higher-frequency databases spanning longer times become available. This would lead to a new understanding of minesite drainage and to new approaches for predicting short-term, potentially toxic peaks in aqueous concentrations. This would be welcome, particularly because the current standard approach of scaling factors is unreliable and often wrong (Morin, 2014).

## 5. STATISTICS AND LOGNORMAL DISTRIBUTIONS

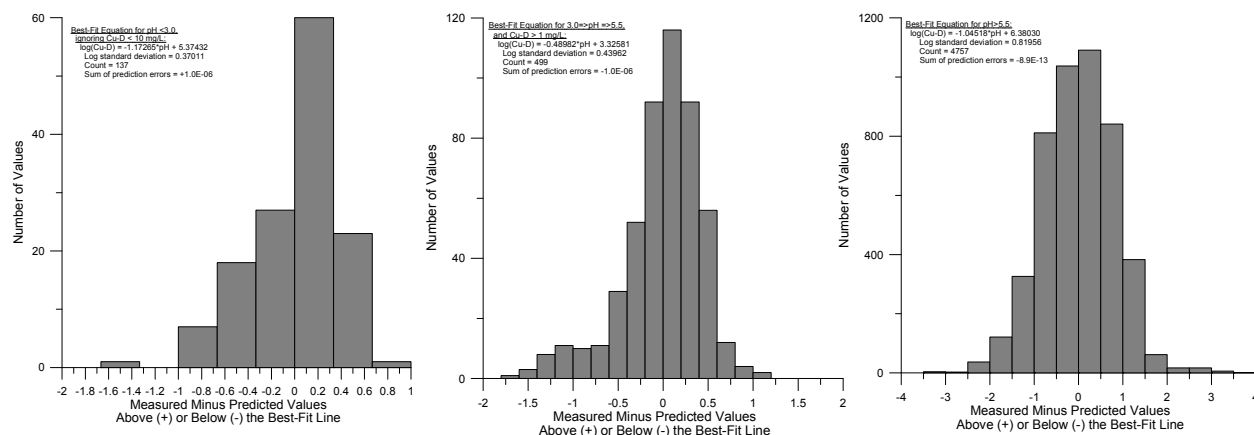
As explained in Section 4 above, orderly minesite-drainage chemistry can generally resemble a sine wave over a one-year period, with fractal characteristics showing self-similarity in decreasing time intervals (e.g., compare Figure 7 with Figure 2). There is another way to mathematically examine this annual cycling.

Based on large databases containing decades of drainage analyses from individual minesites, statistical patterns appeared relative to “master parameters” like pH and sulphate (e.g., Figures 9 and 10). These patterns generally appeared as lognormal distributions of individual chemical elements within particular ranges of a master parameter, with the lognormal distribution approximately repeating year after year (Morin and Hutt, 1997, 2001, 2010a, and 2010b; Morin et al., 1993, 1994, 1995, and 2010).

Most or all monitoring stations at each minesite could be combined into one scatterplot, signifying large-scale spatial statistical consistency. An average-annual “best-fit” equation could be fitted through the data, providing a mean annual concentration at a particular value of the master parameter. More important to this MDAG case study is the logarithmic standard deviation that was also calculated, statistically representing the shorter-term variability of aqueous concentrations (bottom of Figures 9 and 10). The compilation of average-annual equations and log standard deviations was called an “Empirical Drainage Chemistry Model” (EDCM) for that minesite (e.g., Table 1).

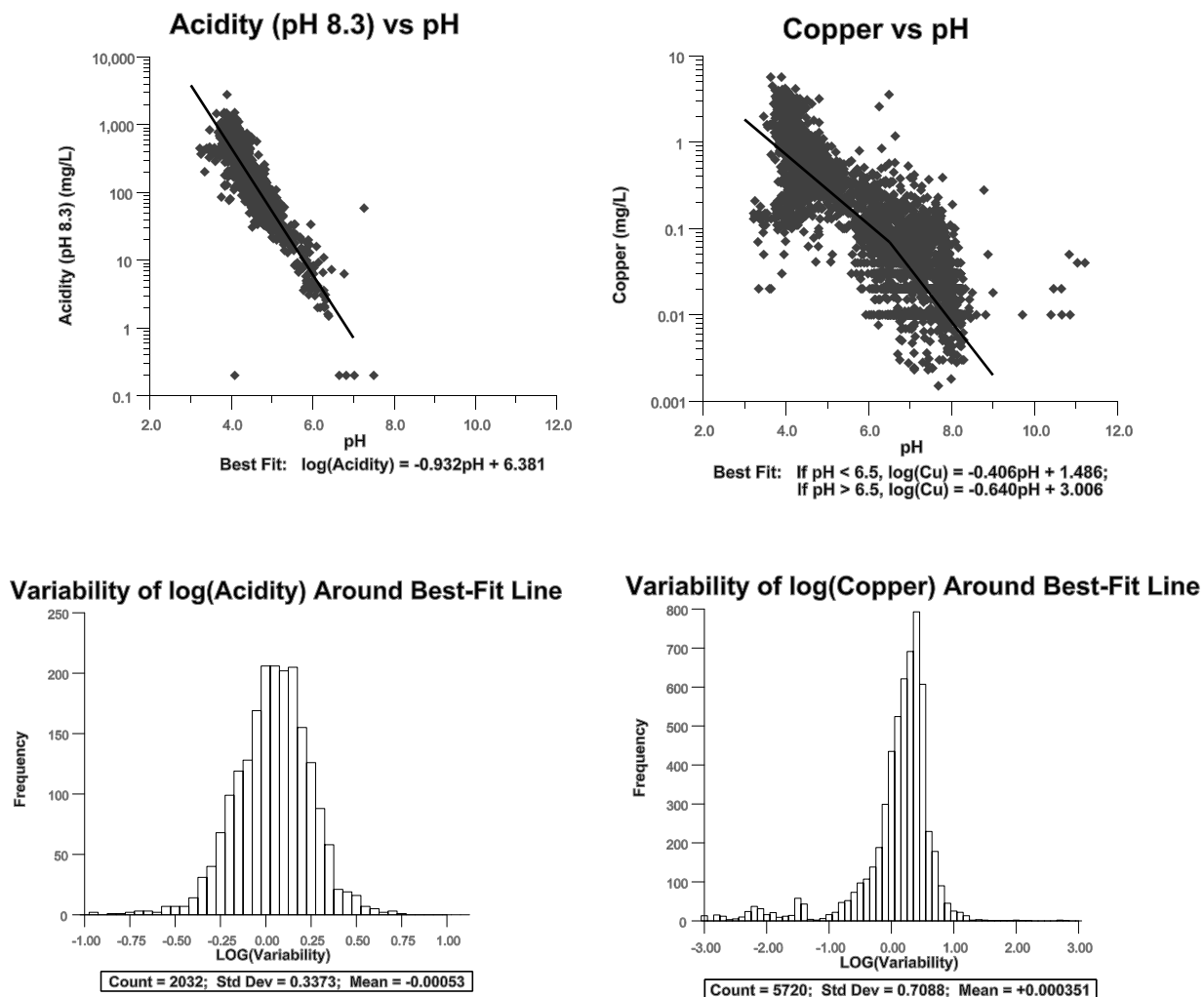


a) Best-fit equation for dissolved copper vs. pH,  
representing the pH-dependent average-annual concentration



b) Lognormal distributions around the average-annual concentration (zero on the x-axis),  
for pH less than 3.0 (left diagram), between 3.0 and 5.5 (middle), and above 5.5 (right diagram)

**Figure 9. An example of (a) pH-dependent annual-average values for dissolved copper, with  
(b) shorter-term (sub-annual) lognormal distributions around the annual average  
(from Morin and Hutt, 2010b).**



**Figure 10.** An example of pH-dependent annual-average values for acidity (upper left) with shorter-term (sub-annual) lognormal distribution around the annual average (lower left), and for copper (right side) (from Morin et al., 1995).

| <b>TABLE 1</b><br><b>Example of an Empirical Drainage-Chemistry Model (EDCM),</b><br><b>including an open pit, several waste-rock dumps, and a tailings impoundment</b><br><b>(from Morin and Hutt, 1997 and 2001)</b> |                 |                                                     |                     |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------|-----------------------------------------------------|---------------------|
| <u>Parameter</u>                                                                                                                                                                                                       | <u>pH Range</u> | <u>Best-Fit Equation</u>                            | <u>Log(Std Dev)</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               |
| Dissolved Aluminum                                                                                                                                                                                                     | pH < 6.0        | $\log(\text{Al}) = -0.925\text{pH} + 4.851$         | 0.429               |
|                                                                                                                                                                                                                        | pH > 6.0        | Al = 0.2 mg/L                                       |                     |
| Dissolved Arsenic                                                                                                                                                                                                      |                 | < 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                                                                                                                                                                                                      |                 | $\log(\text{Ca}) = +0.619\log(\text{SO}_4) + 0.524$ | 0.375               |
| Dissolved 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                                                                                                                                                                                                           |                 | $\log(\text{CuT}) = +0.962\log(\text{CuD}) + 0.180$ | 0.23                |
| Dissolved 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                | 0                   |
| Dissolved Lead                                                                                                                                                                                                         |                 | Pb = 0.05 mg/L                                      | 0                   |
| Dissolved Nickel                                                                                                                                                                                                       |                 | $\log(\text{Ni}) = -0.317\text{pH} + 0.853$         | 0.607               |
| Total Nickel                                                                                                                                                                                                           |                 | total Ni = diss Ni                                  | 0.613               |
| Dissolved Selenium                                                                                                                                                                                                     |                 | Se = 0.2 mg/L                                       |                     |
| Dissolved Silver                                                                                                                                                                                                       |                 | Ag = 0.015 mg/L                                     |                     |
| Dissolved Zinc                                                                                                                                                                                                         |                 | $\log(\text{Zn}) = -0.441\text{pH} + 1.838$         | 0.667               |
| Total Zinc                                                                                                                                                                                                             |                 | total Zn = diss Zn                                  | 0.144               |

Morin et al. (1993 and 1994) and Morin and Hutt (1997 and 2001) narrowed this approach and looked at a single one-year cycle at one minesite. At this minesite, drainage ditches were mostly dry about half the year, from roughly April through September, and thus sampling during this dry semi-annual period was minimal. During the wet semi-annual period (the “hydrologic year”), samples were collected at least daily and as often as every four hours at some locations, except during mechanical failures and other problems.

Based on time discretization in Figure 4, evenly spaced semi-annual (twice-a-year) sampling would be sufficient if there were only two concentrations, with each persisting for six months each year. Monthly sampling would be needed if 7 different concentrations each persisted for an entire month during the downward trend and 5 repeated each for an entire month during the upward trend. The minimum and maximum concentrations each occur only for one month during an annual period. Note that the peak one-month concentration is of particular interest in this case study.

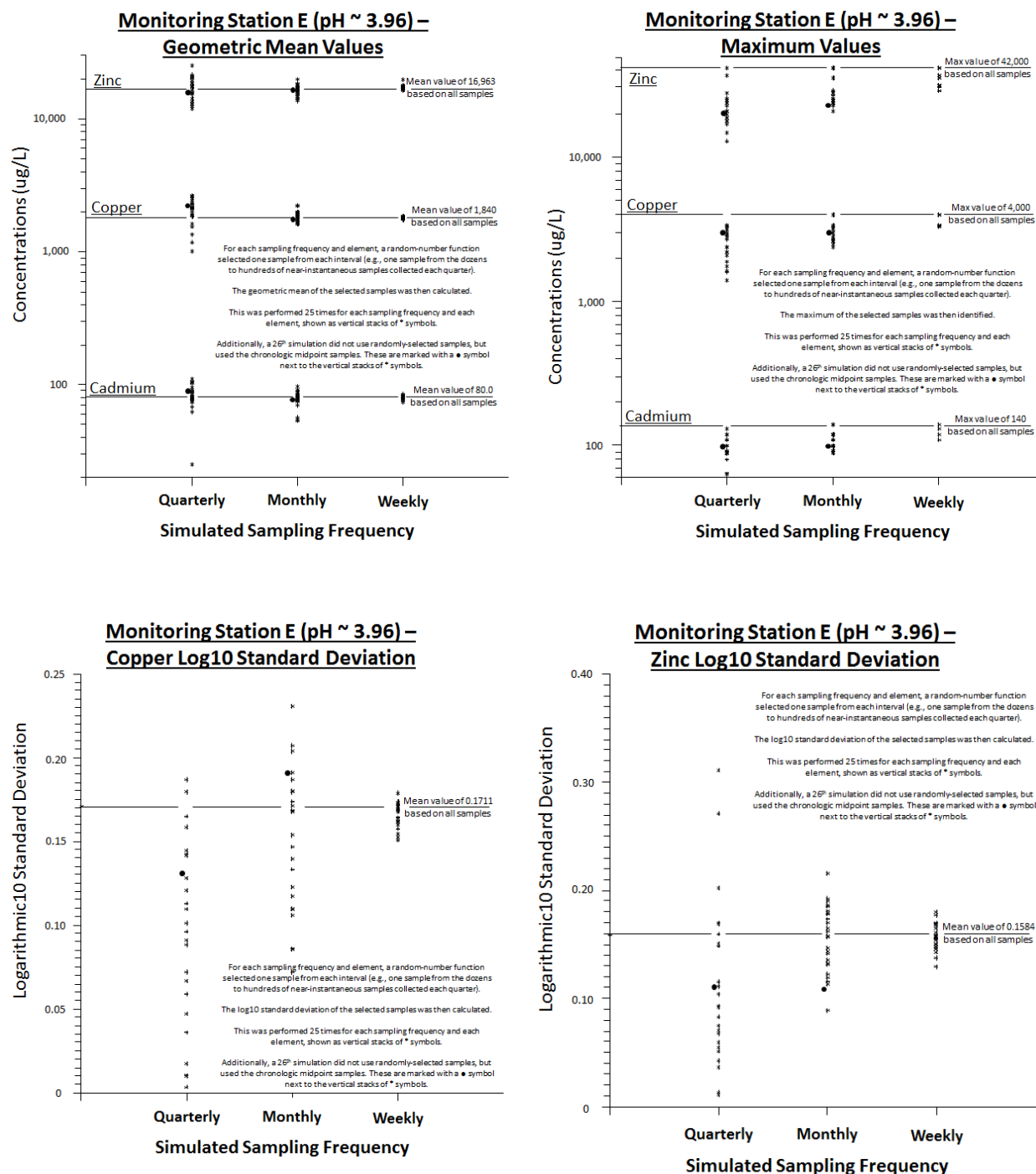
At sampling frequencies up to every four hours in this one-year period and hydrologic year, realistic annual “mean values” and log10 standard deviations were calculated using these high-frequency data, and the maximum measured concentration identified. However, what if these monitoring sites were not sampled daily or every four hours? What if they were sampled only quarterly or monthly or weekly? Would this less frequent sampling still yield means, log standard deviations, and maximum values similar to the most frequent sampling?

To answer these questions, Morin et al. (1993 and 1994) and Morin and Hutt (1997 and 2001) used a random-number function as follows.

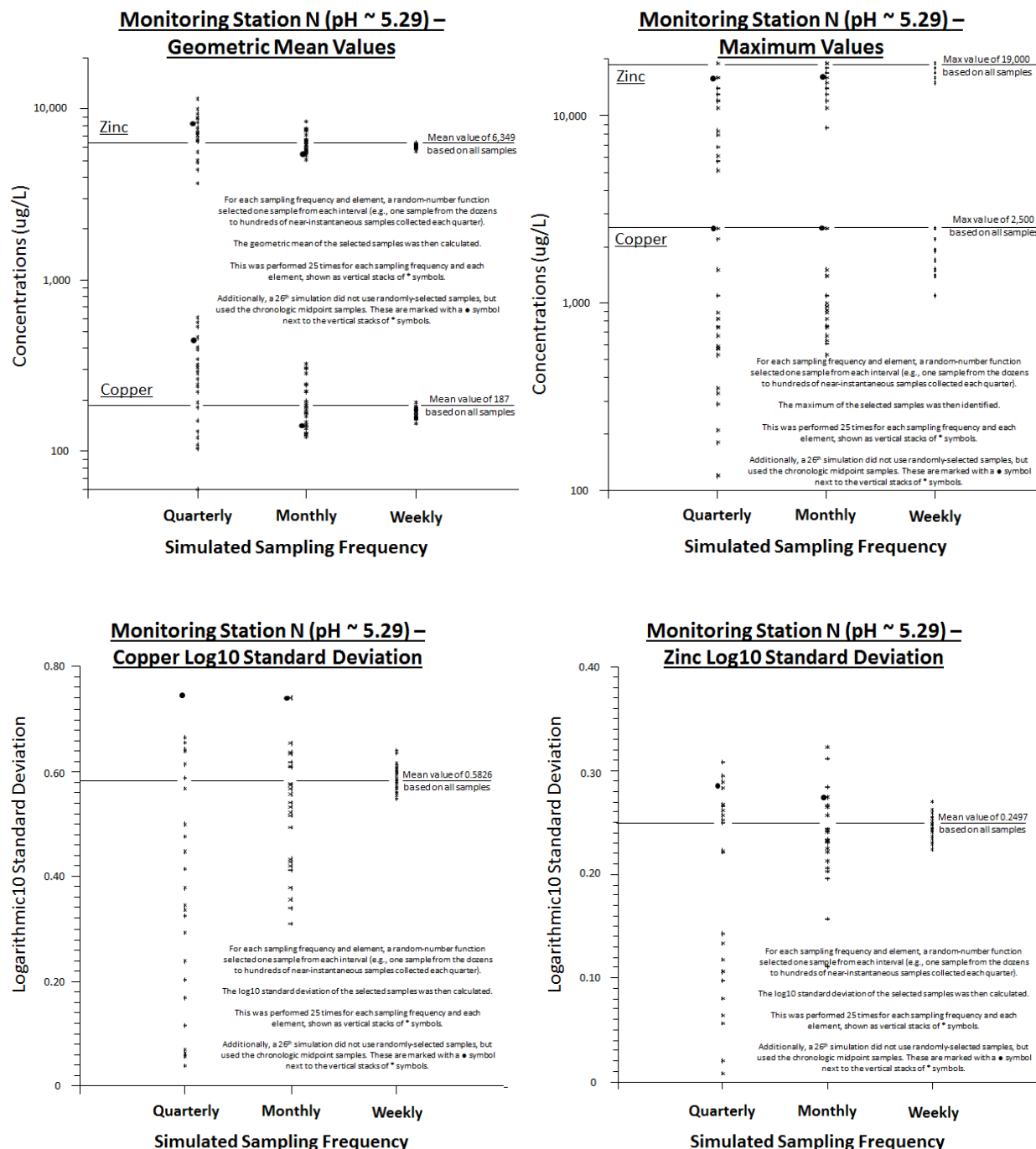
- To simulate quarterly sampling, one random sample was chosen from each of the two hydrologic quarters when there was active drainage, and the resulting mean, log standard deviation, and maximum were determined. This was done 25 times, plus a 26th set was based on calendar midpoints to simulate equally spaced sampling. These were then compared to the high-frequency (entire-database) values.
- To simulate monthly sampling, one random sample was chosen from each of the six hydrologic months when there was active drainage, and the resulting mean, log standard deviation, and maximum were determined. This was done 25 times, plus a 26th set was based on calendar midpoints to simulate equally spaced sampling. These were then compared to the high-frequency (entire-database) values.
- The same procedure was followed for weekly sampling, and for daily sampling when more than one sample was collected daily.

This multi-frequency, random-number-generated sampling was conducted for copper, zinc, and cadmium, at an acidic monitoring station (Station E, high-frequency mean pH = 3.96, Figure 11) and at two near-neutral stations (Station N, high-frequency mean pH = 5.29, Figure 12; Station W, high-frequency mean pH = 6.75, Figure 13). Of note, the Central Limit Theorem and the Law of Large Numbers likely play a role in the results.

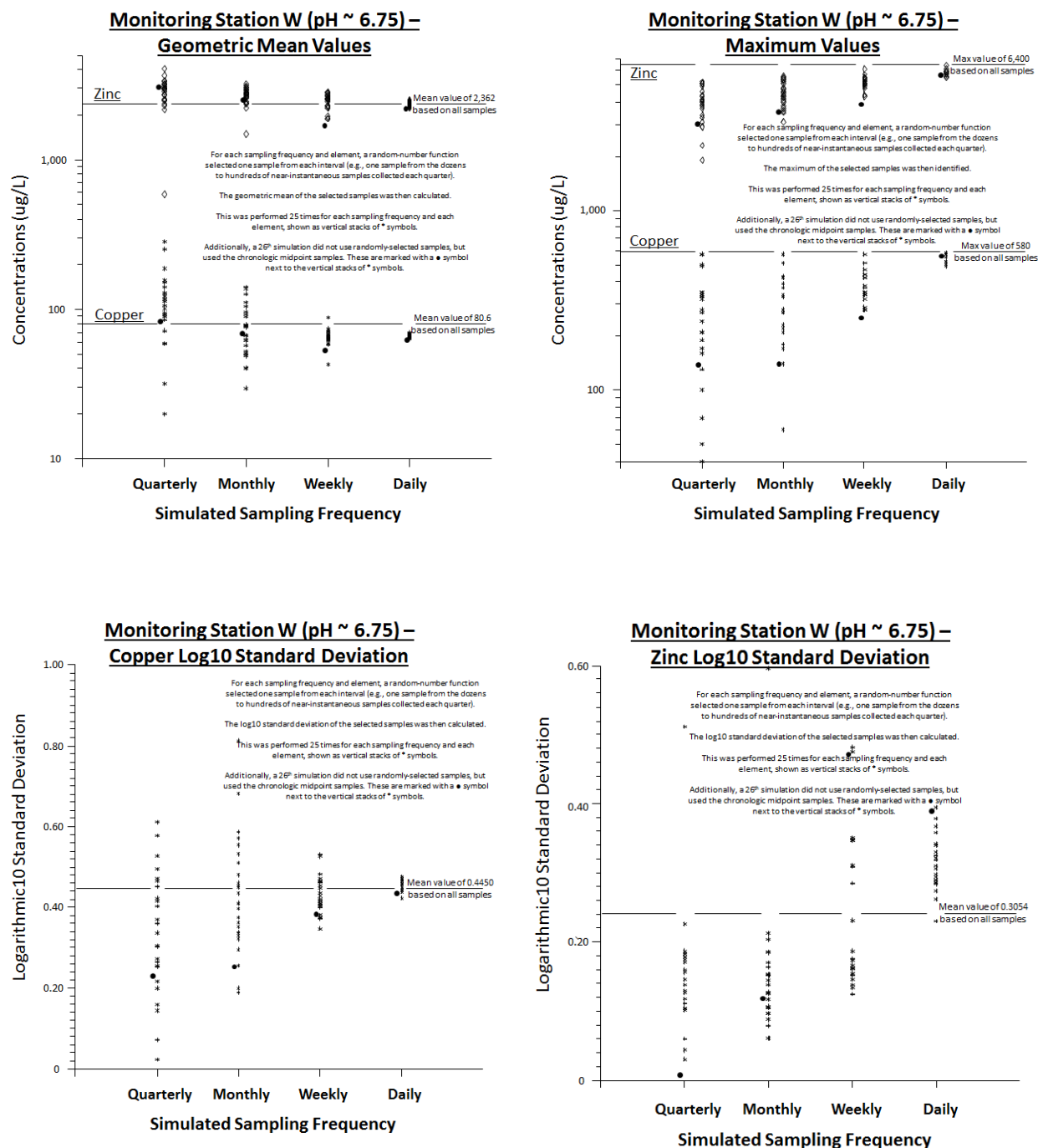
The results show that quarterly sampling may or may not yield realistic statistics compared to the high-frequency sampling, and the reliability could not be known in advance without the high-frequency sampling. Calendar mid-point sampling is similarly of uncertain reliability. However, as simulated sampling frequency increases, the range (vertical spread) of the 26 values decreases and in most cases converges on the high-frequency values (Figures 11 to 13). For example, the high-frequency maximum concentration (upper-right plots) is rarely or not detected with lower-frequency sampling, but is more closely approached as frequency increases.



**Figure 11. One hydrologic year of near-instantaneous sampling, on a daily basis, at acidic Monitoring Station E, with simulated quarterly, monthly, and weekly sampling (explained in text). Upper left: geometric mean values; upper right: maximum measured values; lower left: log10 standard deviation of copper; lower right: log10 standard deviation of zinc.**



**Figure 12.** One hydrologic year of near-instantaneous sampling, on a daily basis, at near-neutral Monitoring Station N, with simulated quarterly, monthly, and weekly sampling (explained in text). Upper left: geometric mean values; upper right: maximum measured values; lower left: log10 standard deviation of copper; lower right: log10 standard deviation of zinc.



**Figure 13. One hydrologic year of near-instantaneous sampling, on an every-four-hour basis, at near-neutral Monitoring Station N, with simulated quarterly, monthly, weekly, and daily sampling (explained in text). Upper left: geometric mean values; upper right: maximum measured values; lower left: log10 standard deviation of copper; lower right: log10 standard deviation of zinc.**



Based on general analytical inaccuracies of 10-20%, the authors concluded that weekly, and in some cases monthly sampling, may be sufficient to obtain statistics allowing the realistic calculation of shorter-term maximum concentrations. This can be seen visually in Figure 4, where monthly sampling resembles daily sampling, and this is examined mathematically below.

The next step is to use these statistics to estimate shorter-term peaks which may not have been measured at lower-frequency sampling. Based on a normal (Gaussian) distribution and annual sine waves discussed in Sections 3 and 4, the maximum one-month aqueous concentration each year would be +1.73 log<sub>10</sub> standard deviations above the annual mean (Table 2), and the maximum one-day concentration each year would be +3.00 log<sub>10</sub> standard deviations above the annual mean.

| <b>TABLE 2</b>                                                               |               |                |               |              |               |
|------------------------------------------------------------------------------|---------------|----------------|---------------|--------------|---------------|
| <b>Probability levels and corresponding time intervals within a year</b>     |               |                |               |              |               |
| <u>Time interval</u>                                                         | <u>1 Year</u> | <u>1 Month</u> | <u>1 Week</u> | <u>1 Day</u> | <u>1 Hour</u> |
| Probability                                                                  | 100%          | 8.3%           | 1.9%          | 0.27%        | 0.011%        |
| No. of std. deviations above/below mean <sup>1</sup>                         | 0.00          | 1.73           | 2.34          | 3.00         | 3.85          |
| <sup>1</sup> From normal-distribution tables after dividing probability by 2 |               |                |               |              |               |

The question is whether the statistical maximum one-day concentration actually exists and persists for an entire one-day period. If it persists, this would cast doubt on the fractal approach in Section 4.

It is already obvious that Figures 2 and 3 only approximate Figure 4, and do not show persistent maximum values over an entire period like a week or month. However, it is informative to look more closely at shorter periods of time. This involves two questions:

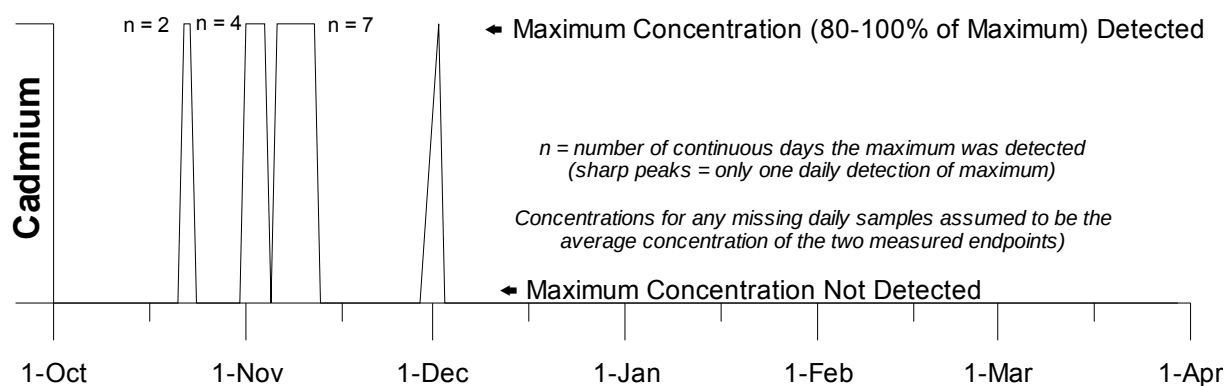
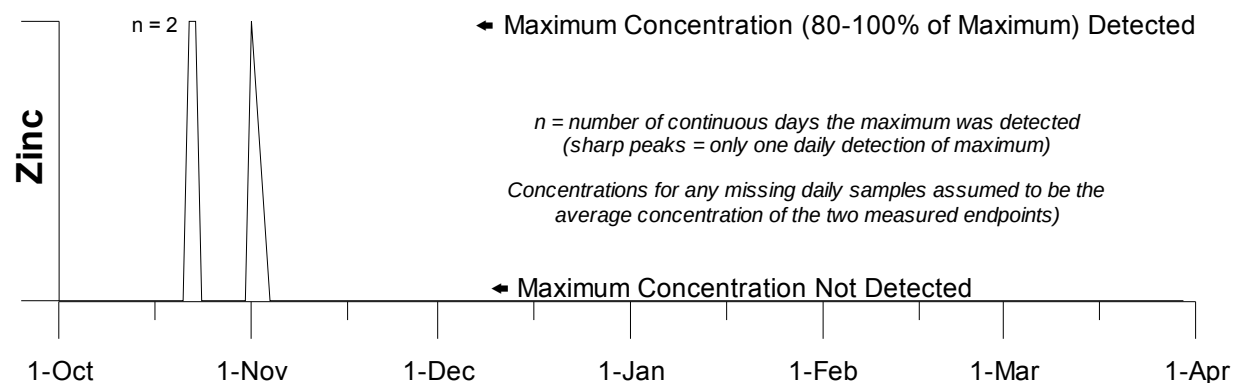
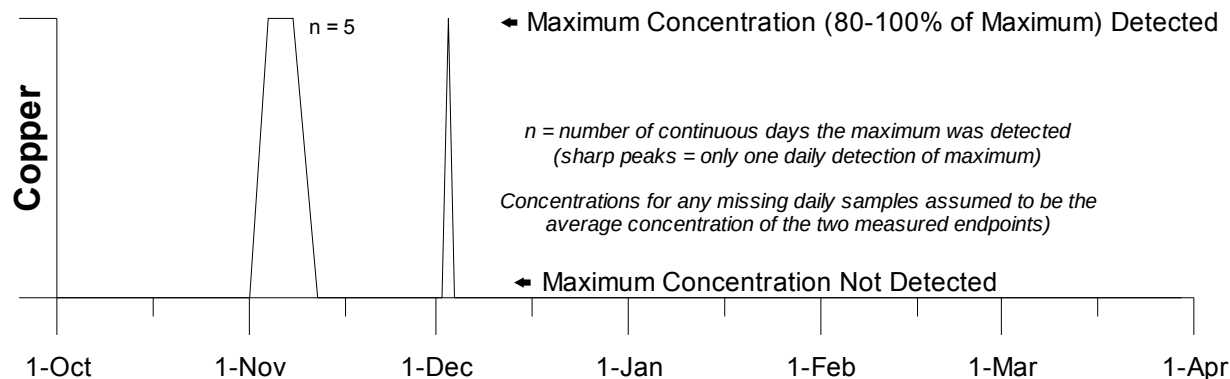
- 1) How often was the maximum value (defined here as 80-100% of the measured maximum to allow for analytical error) detected by daily or four-hourly sampling in the hydrologic year, and were those occurrences contiguous?
- 2) According to Table 2, how often should the maximum value (again, 80-100% of measured maximum) have been detected if Gaussian statistics applied?

For the first question, Figures 11, 12, and 13 show the dates when the maximum was detected at the three monitoring stations, by displaying a step function (yes or no) through time for each station.

For acidic Station E with daily sampling (upper plot in Figure 11), maximum copper was detected six times, the five in November being contiguous. Maximum zinc was detected only on three days, two being contiguous. In contrast, maximum cadmium was detected in 14 daily samples, with the longest contiguous interval of 7 days. All three elements produced maximums in early November, with cadmium also sharing one maximum with copper in early December and one maximum with zinc in later October.

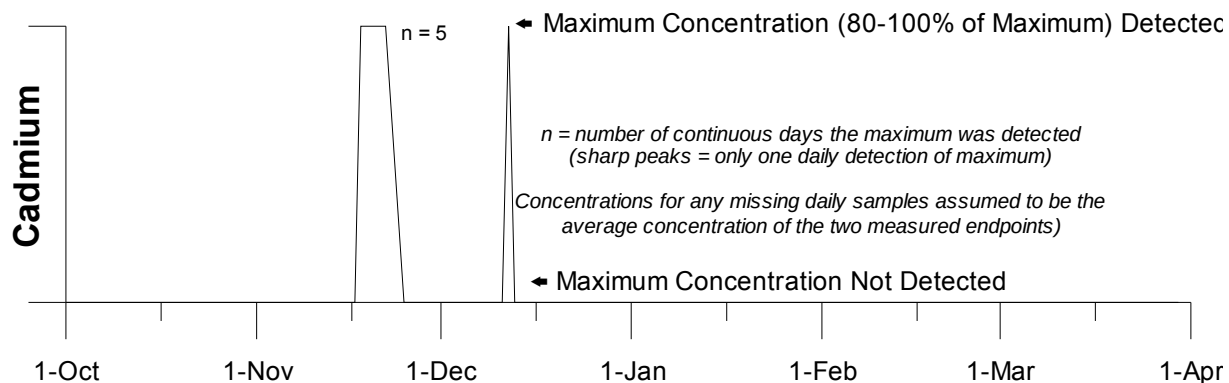
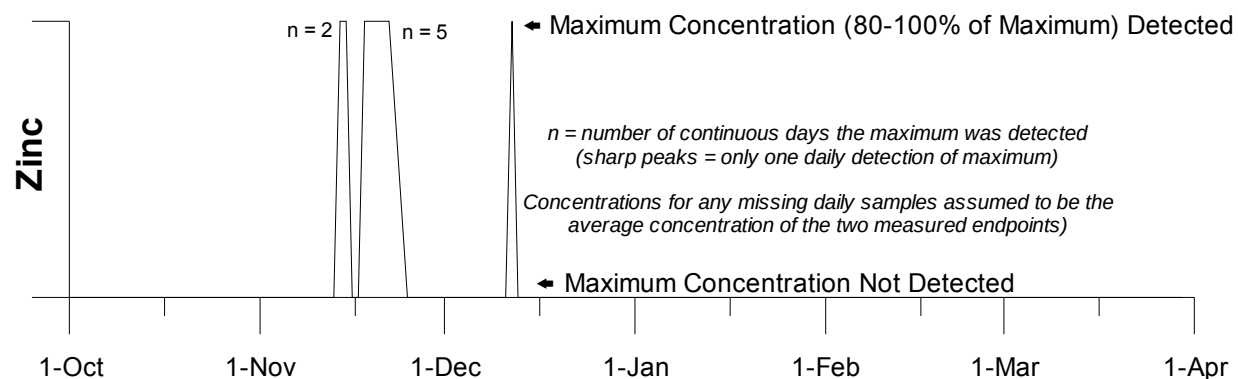
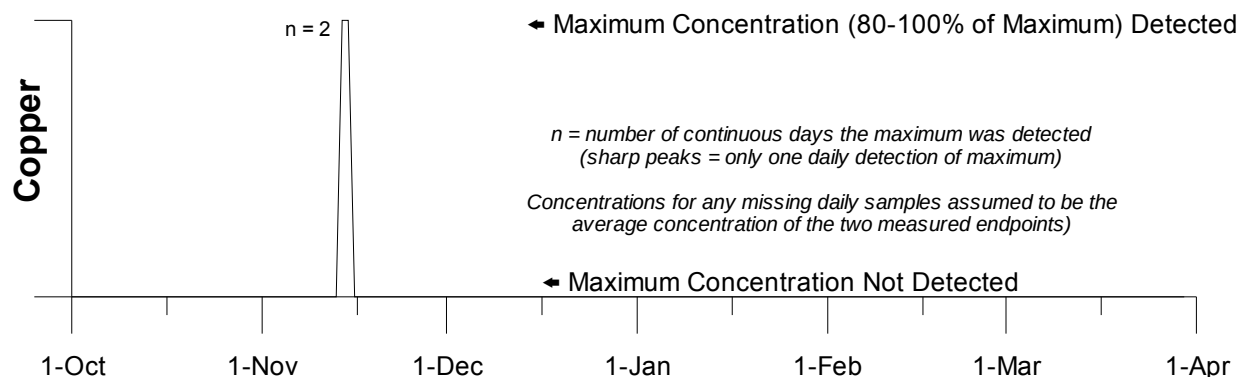
For near-neutral Station N (Figure 12), two-day maximums of copper and zinc occurred just before November 15, followed shortly thereafter by five-day maximums of zinc and cadmium. Single measurements of maximums were also made for zinc and cadmium near mid-December.

## Monitoring Station E (pH ~ 3.96) Daily Sampling

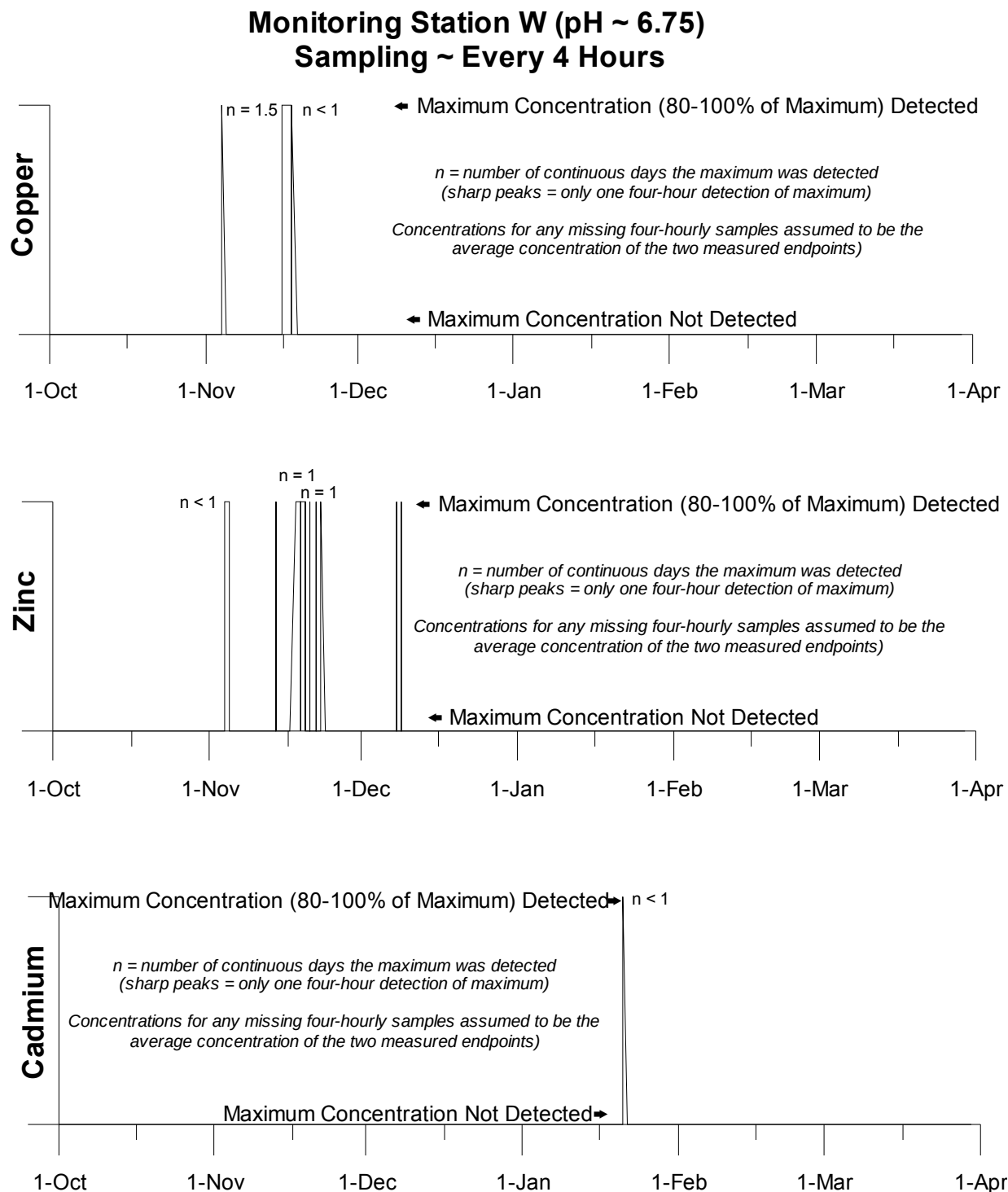


**Figure 11. Step-function yes-no plots showing the daily sampling dates when the maximum aqueous concentration was detected at acidic Monitoring Station E; top: copper, middle: zinc, lower: cadmium.**

## Monitoring Station N (pH ~ 5.29) Daily Sampling



**Figure 12. Step-function yes-no plots showing the daily sampling dates when the maximum aqueous concentration was detected at near-neutral Monitoring Station N; top: copper, middle: zinc, lower: cadmium.**



**Figure 13. Step-function yes-no plots showing the four-hourly sampling dates when the maximum aqueous concentration was detected at near-neutral Monitoring Station W; top: copper, middle: zinc, lower: cadmium.**

For near-neutral Station W with the highest mean pH (Figure 13), maximum values of copper, zinc, and cadmium based on four-hourly sampling were less continuous than the other two stations. If six four-hourly samples were at maximum contiguously,  $n$  was set at  $n=1$  day in Figure 13. The initial zinc maximums were detected about the dates as the fewer copper maximums. However, only one cadmium maximum was detected, in late January and not coinciding with maximums of copper and zinc. This one cadmium maximum is not considered an error, because preceding and subsequent concentrations were elevated but not at maximum.

Some occurrences of maximums at all three stations were contiguous or separated by only a few days. However, some were separated by weeks. Therefore, the simplistic step-wise temporal trend of Figure 4 does not apply to these stations.

The second question implicitly rules out fractal distributions (self-similar with scale) at high sampling frequencies, such as hourly or minute sampling, simply due to the presumption of a finite maximum between sampling events (raised in Figure 5). Also, the repeated detections of maximum values in Figures 11-13, some being non-contiguous, may be coincidental, but more probably (statistically speaking) reflect true maximum concentrations. Thus, it is more likely the measured maximum concentrations represent real quantitative “ceilings”, such as solubility constraints, that persist for periods longer than the sampling frequency but not necessarily over a single period. In other words, there are no higher one-hour and one-minute maximums due to the ceilings, which invalidates both the fractal and lognormal approaches at shorter times.

Based on Table 2 and Figures 11-13, the difference between the  $\log_{10}$  Measured Maximum and the  $\log_{10}$  Calculated Mean, expressed as the number of  $\log_{10}$  standard deviation cycles, determines the period of time that the Measured Maximum statistically should be detectable (x-axis of Figure 14, in days). This can be compared to the cumulative total number of days that the Measured Maximums were actually detected (y-axis of Figure 14). Except for a single detection of cadmium maximum at one station using four-hourly sampling, this comparison showed that most maximums were not detected as often as simple probability predicted. This indicates the lognormal approach substantially overestimates the real durations of maximum concentrations in this database, which weakens its reliability but remains environmentally protective under the precautionary principle.

Although the maximums were detected less often than statistically expected based on the number of  $\log_{10}$  std dev above the means, there is a relationship between these two parameters (Figure 15). The two power-law trends in the left plot of Figure 15 can be reconciled into one power-law trend (right side) by counting the number of times the maximum was detected instead of the number of contiguous or non-contiguous days. This makes a difference for four-hourly sampling, where six near-instantaneous samples comprised one day of monitoring instead of one near-instantaneous sample. In any case, power laws are known to play a role in Zipf's Law, structural self-similarity of fractals, and scaling laws in biological systems.

Whereas fractal behaviour was not apparent from Figures 11-13, Figures 14 and 15 showed lognormal behaviour was also not reliably portrayed, which in turn raises the possibility of fractal characteristics at shorter time intervals such as hours and minutes. In summary, the fractal and lognormal approaches both have some value in predicting and understanding short-term maximums, but neither approach is highly successful with the current databases. Additional, larger long-term and higher-frequency databases of minesite-drainage chemistry are needed to address this more reliability, and to understand the conditions when orderly or chaotic drainage chemistry may arise.

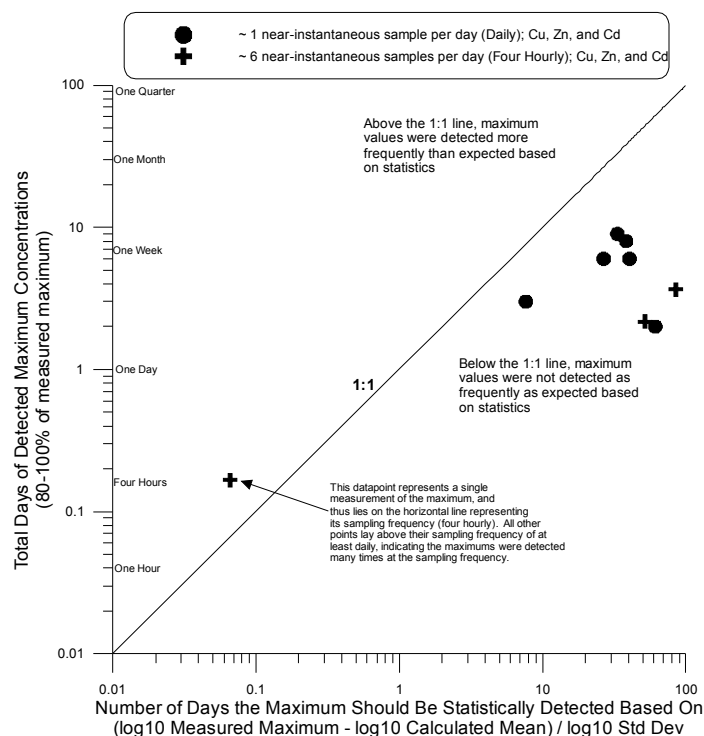


Figure 14. Total number of days that the maximum concentrations were detected vs. the number of days that maximums were expected based on the number of log10 standard deviations separating the maximums and their means (see Table 2).

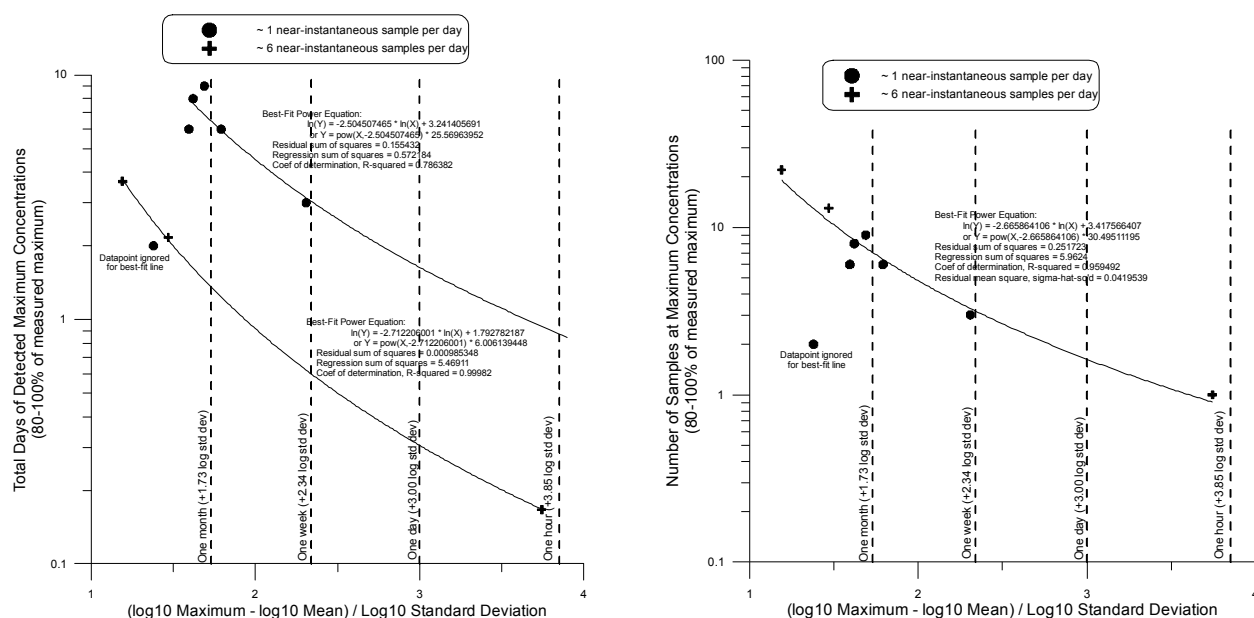


Figure 15. Total number of days (left side) or total number of sampling events (daily or four-hourly, right side) that the maximum concentrations were detected vs. the number of log10 standard deviations separating the maximums and their means. (When Table 2 is applied to the x-axis to the left plot, Figure 14 is obtained.)

## 6. CONCLUSION

This MDAG case study has focussed on two primary questions:

- What time-discretization interval should we use to understand and predict minesite-drainage chemistry reliably, by minimizing sufficiently the discretization error?
- How do we detect or predict short-term maximum concentrations of environmental significance?

The answers are important and timely, because there is a strong need to improve predictions of short-term concentrations for proposed minesites. There is also a strong need for existing and closed minesites to understand and anticipate their short-term maximum concentrations that may not be detected often, or at all, by their monitoring programs.

The questions on time discretization and short-term maximum concentrations were addressed here using large minesite-drainage-chemistry databases spanning many years to decades, and including high-frequency sampling as often as every four hours. These showed that temporal trends in drainage chemistry can be orderly, generally following a trigonometric sine function over an annual period, with prominent and repeating short-term peaks and valleys. Other databases showed chaotic (non-orderly) trends. There are insufficient studies to understand when orderly or chaotic chemistry can be expected at a minesite, and such understanding is often lacking for other, non-mining systems.

To examine the effects of time discretization on maximum concentrations in orderly minesite drainage, two mathematical approaches were applied here: fractals and lognormal statistics.

For fractals, visual comparisons were made of (1) the temporal trends in aqueous concentrations, emphasizing copper, zinc, and cadmium, from the databases with acidic and near-neutral monitoring stations to (2) variable, but finite, numbers of terms in the infinite fractal sine wave. The comparisons showed the temporal trends in chemistry display fractal characteristics over days to years for copper, zinc, and cadmium. However, the data were not sufficient to determine whether this holds for longer times like decades or for short times like hours and minutes. These observations were similar to those made elsewhere for non-mining-related watersheds. To resolve these uncertainties, more frequent sampling for long periods of time will be needed at minesites.

With lognormal statistics, large databases of minesite-drainage chemistry showed that average-annual aqueous concentrations of elements like copper, zinc, and cadmium displayed trends that were dependent on “master parameters” like pH and sulphate. Within specific ranges of the master parameters, aqueous concentrations varied above and below the average mean in generally lognormal distributions. The annual lognormal variability could be described by a standard deviation expressed in log10 cycles, and the log10 std dev often repeated year after year. This information was used with probability levels to calculate short-term maximum concentrations of specific durations.

With a random-number function, the number of water analyses from the high-frequency sampling was reduced to simulate less-frequent sampling, like weekly and quarterly. This showed that the frequency of sampling would have to be at least weekly, but sometimes monthly, to calculate a log10 standard deviation within common analytical inaccuracy. This reasonably accurate value could then be used to calculate shorter-term maximum concentrations that may go undetected.

Although shorter-term maximum concentrations can be statistically calculated, this does not mean they actually exist and occur. For example, a maximum “ceiling”, such as solubility, may limit maximum concentrations only to the calculated monthly or weekly maximum, with no actual occurrence of the statistical one-day or one-hour maximum. This was seen in the databases examined here.

The high-frequency database showed that the maximum concentrations (defined as 80-100% of measured maximum to allow for analytical inaccuracy) of copper, zinc, and cadmium were detected both (1) in contiguous samples representing less than a day or up to one week and (2) in non-contiguous samples separated by days to weeks of non-maximum concentrations. Thus, the simplistic concept that maximum values occurred only as one continuous interval was ruled out for this database, which would be more consistent with fractals.

Furthermore, the number of days that maximum concentrations should be detected, based on lognormal probabilities, exceeded the number of actual measured days. As a result, the usage of lognormal probabilities over-predicted the cumulative duration of maximum concentrations. However, there was one exception: cadmium at the monitoring station sampled every four hours.

Notably, the discrepancies between the lognormal-probability-based durations of maximum concentrations and the actual durations generally followed power-law trends. Power laws are characteristic of fractals.

In summary, the fractal and lognormal approaches both have some value in predicting and understanding short-term maximum concentrations, but neither approach is highly successful with the current databases. However, on the question of time discretization and sampling frequency, the lognormal approach indicated weekly, and sometimes monthly, sampling would provide sufficiently reliable statistics to calculate shorter-term maximums. Additional, larger long-term and higher-frequency databases of minesite-drainage chemistry are needed to address these questions more reliability, and to understand the conditions when orderly or chaotic drainage chemistry may arise.

Interestingly, this MDAG case study has addressed short-term maximum concentrations without including underlying mechanisms, such as sulphide oxidation and metal leaching rates. This is attributable to emergent processes that arise and dominate as scale increases up to full-scale minesite components (Morin and Hutt, 2007; Morin, 2014 and in prep).



## 7. REFERENCES

- Aubert, A.H., J.W. Kirchner, C. Gascuel-Oudou, M. Fauchoux, G. Gruau, and P. Mérot. 2013. Fractal Water Quality Fluctuations Spanning the Periodic Table in an Intensively Farmed Watershed. *Environmental Science and Technology*, 48, p. 930-937. Doi:10.1021/es403723r
- Birdi, K.S. 2013. *Fractals in Chemistry, Geochemistry, and Biophysics: An Introduction*. Springer. ISBN: 9781489911247.
- Daulton, R. 2015. What is the function for a ‘fractal sine wave’? Accessed October 2015 at [math.stackexchange.com/questions/1484403/what-is-the-function-for-a-fractal-sine-wave](http://math.stackexchange.com/questions/1484403/what-is-the-function-for-a-fractal-sine-wave).
- Fractal Foundation. 2015. What are Fractals? Accessed November 2015 at <http://fractalfoundation.org/resources/what-are-fractals/>
- Kirchner, J.W., and C. Neal. 2013. Universal fractal scaling in stream chemistry and its implications for solute transport and water quality trend detection. *Proceedings of the National Academy of Sciences*, 110, p. 12213-12218. Doi:10.1073/pnas.1304328110
- Kirchner, J.W., X. Feng, and C. Neal. 2000. Fractal stream chemistry and its implications for contaminant transport in catchments. *Nature*, 403, p. 524-527.
- Li, M. 1999. Hydrology and Solute Transport in Oxidised Waste Rock from Stratmat Site, N.B. Canadian MEND Report 2.36.2b
- Meiss, J.D. 2003. Frequently Asked Questions about Nonlinear Science. Version 2.0. Accessed October 2015 at: <http://amath.colorado.edu/faculty/jdm/faq.html>
- Morin, K.A. In preparation. Nonlinear Science of Minesite-Drainage Chemistry. 1 - Scaling and Buffering. MDAG Internet Case Study, [www.mdag.com](http://www.mdag.com)
- Morin, K.A. 2014. Applicability of scaling factors to humidity-cell kinetic rates for larger-scale predictions. IN: 21st Annual BC/MEND Metal Leaching/Acid Rock Drainage Workshop, Challenges and Best Practices in Metal Leaching and Acid Rock Drainage December 3-4, 2014, Simon Fraser University Harbour Centre, Vancouver, British Columbia, Canada.
- Morin, K.A. 2010. The Science and Non-Science of Minesite-Drainage Chemistry. MDAG Internet Case Study #37, [www.mdag.com/case\\_studies/cs37.html](http://www.mdag.com/case_studies/cs37.html)
- Morin, K.A., and N.M. Hutt. 2010a. Twenty-Nine Years of Monitoring Minesite-Drainage Chemistry, During Operation and After Closure: The Granisle Minesite, British Columbia, Canada. MDAG Internet Case Study #34, [www.mdag.com/case\\_studies/cs34.html](http://www.mdag.com/case_studies/cs34.html)
- Morin, K.A., and N.M. Hutt. 2010b. Thirty-One Years of Monitoring Minesite-Drainage Chemistry, During Operation and After Closure: The Bell Minesite, British Columbia, Canada. MDAG Internet Case Study #33, [www.mdag.com/case\\_studies/cs33.html](http://www.mdag.com/case_studies/cs33.html)
- Morin, K.A., and N.M. Hutt. 2007. Scaling and Equilibrium Concentrations in Minesite-Drainage

Chemistry. MDAG Internet Case Study #26, [www.mdag.com/case\\_studies/cs26.html](http://www.mdag.com/case_studies/cs26.html)

Morin, K.A., and N.M. Hutt. 2001. *Environmental Geochemistry of Minesite Drainage: Practical Theory and Case Studies, Digital Edition*. MDAG Publishing (www.mdag.com), Surrey, British Columbia. ISBN: 0-9682039-1-4.

Morin, K.A., and N.M. Hutt. 1998. Minesite drainage chemistry is like rain. MDAG Internet Case Study #3, [www.mdag.com/case\\_studies/cs1-98.html](http://www.mdag.com/case_studies/cs1-98.html)

Morin, K.A., and N.M. Hutt. 1997. *Environmental Geochemistry of Minesite Drainage: Practical Theory and Case Studies*. MDAG Publishing (www.mdag.com), Surrey, British Columbia. ISBN: 0-9682039-0-6.

Morin, K.A., N.M. Hutt, and M.L. Aziz. 2010. Twenty-Three Years of Monitoring Minesite-Drainage Chemistry, During Operation and After Closure: The Equity Silver Minesite, British Columbia, Canada. MDAG Internet Case Study #35, [www.mdag.com/case\\_studies/cs35.html](http://www.mdag.com/case_studies/cs35.html)

Morin K.A., N.M. Hutt, and I.A. Horne. 1995. Prediction of future water chemistry from Island Copper Mine's On-Land Dumps. IN: Proceedings of the 19th Annual British Columbia Mine Reclamation Symposium, Dawson Creek, British Columbia, Canada, June 19-23, p. 224-233.

Morin, K.A., I.A. Horne, and D. Riehm. 1994. High-frequency geochemical monitoring of toe seepage from mine-rock dumps, BHP Minerals' Island Copper Mine, British Columbia. IN: Proceedings of the Third International Conference on the Abatement of Acidic Drainage, Pittsburgh, Pennsylvania, USA, April 24-29, Volume 1, p.346-354

Morin, K.A., N.M. Hutt, and D. Flather. 1993. The appropriate geochemical monitoring of toe seepage from a mine-rock dump. IN: Proceedings of the 17th Annual Mine Reclamation Symposium, Port Hardy, British Columbia, May 4-7, p.119-129. Mining Association of British Columbia.

Nimick, D.A., C.H. Gammons, and S.R. Parker. 2010. Diel biogeochemical processes and their effect on the aqueous chemistry of streams: A review. *Chemical Geology*, 283, p. 3-17.

Nimick, D.A., C.H. Gammons, T.E. Cleasby, J.P. Madison, D. Skaar, and C.M. Brickand. 2003. Diel cycles in dissolved metal concentrations in streams: Occurrence and possible causes. *Water Resources Research*, 39, p. 1247

Shope, C.L., Y. Xie, and C.H. Gammons. 2006. The influence of hydrous Mn–Zn oxides on diel cycling of Zn in an alkaline stream draining abandoned mine lands. *Applied Geochemistry*, 21, p. 476-491.

Wikipedia.org. 2015a. Fractal. Accessed October 2015 at [en.wikipedia.org/wiki/Fractal](http://en.wikipedia.org/wiki/Fractal)

Wikipedia.org. 2015b. Fractal. Accessed October 2015 at [en.wikipedia.org/wiki/Weierstrass\\_function](http://en.wikipedia.org/wiki/Weierstrass_function).