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MDAG-com Case Study 53 - Propagation-of-Uncertainty in Net Potential Ratios for Predictions of Acid-Rock Drainage

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Abstract

The prediction of whether geologic materials like rock, soil, or tailings will release acid-rock drainage (ARD) at some point often focusses on values of the Net Potential Ratio (NPR). In concept and calculation, NPR is remarkably simple:

NPR (dimensionless) = ENP / EAP

where ENP = Effective Neutralization Potential, such as in kg $CaCO_3$ equivalent/tonne

EAP = Effective Acid Potential, in the same units as ENP

ENP is often estimated starting with an acid titration of a solid sample. EAP is often calculated from the portion of solid-phase sulphur considered acid generating:

EAP = %S acid-generating sulphur * 31.25

In reality, ENP and EAP are very difficult to estimate reliably. This MDAG case study assumes that ENP and EAP of samples are reliably estimated, although this is rarely the case, yet still include some uncertainty as a range above and below the reported values.

There are two types of ranges of uncertainty examined here for ENP, EAP, and NPR. First, the uncertainty is viewed as normal statistical distributions centered on the reported values of ENP and EAP. The uncertainty is thus expressed as ±one or more standard deviations. For numerical reasons, this case study mostly focusses on relative standard deviations (RSD), also known as the Coefficient of Variation, which is the standard deviation divided by ENP or EAP.

The second range of uncertainty examined here is ±a percentage (PER) of the reported values of ENP and EAP, as a step-like boxcar distribution. In this distribution, all probabilities outside the ±PER range are zero, and all probabilities inside the ±PER range are equal so that there is no peak probability like a normal distribution.

Propagation-of-uncertainty (POU), also know as propagation-of-error (POE), is used here with these two types of uncertainty for ENP and EAP. POU is used to learn the resulting uncertainty in NPR when the uncertainty in ENP is divided by the uncertainty in EAP. For normal distributions, this is relatively straightforward, using relatively simple equations. For boxcar distributions, Monte Carlo simulations are needed, and 5000 random calculations were used for each boxcar example in this case study.

For normal distributions of ENP and EAP uncertainty, POU shows the resulting NPR uncertainty is a normal or lognormal distribution, but with a standard deviation greater than that of both ENP and EAP. For boxcar distributions of ENP and EAP uncertainty, the resulting NPR uncertainty can resemble normal, lognormal, or less regular distributions, depending on the ratio of the PER values for ENP and EAP and the NPR value. A multiplicative variant of the Central Limit Theorem may explain some of these results.

Based on a criterion of 2.0 separating net-acid-generating from net-acid-neutralizing samples, all hypothetical samples with a reported NPR of exactly 2.0 have a 50% probability of being less than 2.0. This applies to all samples in this case study with both normal and boxcar distributions.

For normal input distributions of ENP and EAP, hypothetical samples with a reported NPR of even 2.2 have at least a notable 48% probability of actually being less than 2.0, when the relative standard deviations (RSD) of ENP and EAP are at least 1.0. These RSD values are typical of ENP and EAP close to their lower detection limits. Also at the reported NPR of 2.2, the probability of a sample's NPR being less than 2.0 decreases from 48% to 10% as the RSD decreases to 0.05, typical of very high-accuracy values far above the lower detection limit.

In comparison, at a reported NPR of 3.0, the probability of being less than 2.0 is above 40% at RSD values above 1.0, compared with above >48% at NPR 2.2. The probability of NPR actually being less than 2.0 when reported as 3.0 becomes negligible as RSD decreases to 0.05.

For boxcar input distributions of ENP and EAP, hypothetical samples with a reported NPR of even 2.2 have significant probabilities of being less than 2.0 (≥14% probability). The exception is for very high-accuracy values of both ENP and EAP at PER levels of ±5%.

In comparison, at a reported NPR of 3.0, the probability of NPR being less than 2.0 increases to about 33% when the PER of ENP approaches ±100%. This is similar to the normal-distribution probability rising above 40% as RSD increases above 1.0. The probability of NPR actually being less than 2.0 when reported as 3.0 is negligible for most lower boxcar ranges of PER examined here.

Based on these examples, this MDAG case study shows that a "safe" NPR criterion of 2.0 to distinguish net-acid-generating from net-acid-neutralizing geologic materials is not consistently "safe" even for samples with NPR levels of 3.0. The probabilities exceed 30% that a sample with a reported NPR of 3.0 is actually less than 2.0 when ENP and EAP are close to detection limits and/or have relatively high uncertainties. A sample with a reported NPR of 2.2 has a probability above 10% that its NPR is actually less than 2.0 at common levels of normal and boxcar uncertainty. However, the probability of NPR misclassification drops to negligible levels when excellent and minimal uncertainty is reached.

Therefore, in light of uncertainties that exist within constituent values of Effective Neutralization Potential and Effective Acid Potential, a Net Potential Ratio criterion of any value is not assuredly "safe" for avoiding net-acid-generating samples within about one NPR unit.

1. Introduction

The prediction of whether geologic materials like rock, soil, or tailings will release acid-rock drainage (ARD) at some point often focusses on values of the Net Potential Ratio (NPR). In concept and calculation (e.g., Morin and Hutt, 1997a and 2001a; Price, 2009), NPR is remarkably simple:

NPR (dimensionless) = ENP / EAP (Eq. 1-1)

where ENP = Effective Neutralization Potential, such as in kg $CaCO_3$ equivalent/tonne

EAP = Effective Acid Potential, in the same units as ENP

ENP is often estimated starting with an acid titration of a solid sample. EAP is often calculated from the portion of solid-phase sulphur considered acid generating:

EAP = %S acid-generating sulphur * 31.25 (Eq. 1-2)

The numerator, ENP, is discussed in Section 1.1, and the denominator, EAP, in Section 1.2. The discussion of NPR then continues in Section 2.

1.1 Effective Neutralization Potential (ENP)

Books could be written on ENP, particularly the way it is often overestimated and thus ARD is underestimated. A valuable reference on ARD prediction (Price, 2009) explains,

> *"One of the most important concepts to be understood in NP prediction is the 'effective neutralization potential' (ENP) (e.g. Morin and Hutt, 1994, 1997, 2008b and 2008c). Effective neutralization potential is the acid neutralization that can neutralize internal and external acidity inputs sufficiently to maintain a near-neutral drainage pH."*

This definition points out that ENP includes consideration of "external acidity inputs", which means that ENP reflects conditions outside as well as inside the sample being considered. This is the first hint that ENP is not a simple matter.

Some or most measurable NP in a sample can initially be occluded inside coarser particle sizes. As they weather and slake, this NP is exposed through time and thus becomes "effective" at various times. Also, the opposite can happen, where initial ENP is coated by secondary-mineral precipitants and is thus rendered ineffective through time (e.g., Morin and Hutt, 2008a). As a result, the second hint at complexity is that ENP of a sample can change substantially with time.

The complexity of ENP cascades from here. For example, unlike intrinsic elements in the Periodic Table, NP is an extrinsic property of a sample (Morin and Hutt, 2009). NP is dependent on, and defined by, its methodology, as shown by the many NP methods currently available. Sadly, there are arguments over which NP method is superior to the others, which makes sense for chemical elements but is nonsense for NP (Morin, 2009a and 2009b).

Scale is another example where ENP becomes complex. How much ENP per kilogram would be needed to prevent ARD flowing from a full-scale 10^8-tonne minesite component? Would it be similar to the ENP needed for a single 1-kg sample? There are no easy answers, because they depend on many factors. For example, only a small amount of ARD-releasing rock might be needed for ARD to drain (Morin, 2017a), where that ARD-releasing rock is concentrated in certain spatial locations (Morin et al., 1997; Morin and Hutt, 1997b, 2000, and 2001b; Morin, 2017b). Also, a case study of larger-scale in-field testwork on layering, based on 20 tonnes, has shown that unavailable NP for some rock can be an impressive 100 kg/t, leaving only 3% of measured NP as ENP (Morin and Hutt, 2008a).

1.2 Effective Acid Potential (EAP)

Similar to ENP, Price (2009) defined EAP as,

> *"Effective Acid Potential - The fraction of the AP that is physically available and sufficiently acid generating. Depends on the drainage chemistry, especially the pH, minerals contributing to the measured acid potential (AP) and their elemental composition, physical occlusion and reaction rate."*

Thus, EAP is subject to many of the same complexities as ENP, such as varying EAP values through time, encapsulation by secondary-mineral precipitants, and substantial effects of changing scale.

EAP also has additional complexities, like mineralogy-dependent factors for converting sulphur to EAP, such as 31.25 in Equation 1-2. Values between zero and at least 125 are possible, but 31.25 remains widely applicable (Price, 2009, Morin, 1990).

Overall, the effects of the complexities on EAP are much less well documented than for ENP.

2. Net Potential Ratio (NPR), and the Main Objective of this MDAG Case Study

2.1 Initial Assumptions

In light of all the complexity and uncertainty with ENP (Section 1.1) and EAP (Section 1.2), one should be skeptical of the reliability of any NPR value calculated from Equation 1-1. However, for this MDAG case study, *and for this case study only*, ENP and EAP are considered reliably characterized, which is a long stretch indeed and often wrong.

This unreliable assumption is necessary here to discuss additional, less apparent uncertainties in the usage of NPR to predict eventual ARD. In other words, reasonably accurate estimates of ENP and EAP, when combined as NPR, reveal additional uncertainties not usually discussed.

2.2 NPR Criteria

Like ENP (Section 1.1) and EAP (Section 1.2), NPR is not as simple as it may seem. For example, only when ENP reaches zero, and thus NPR also becomes zero, can acidic conditions arise. Yet, there are many reported and published cases where that is wrong (Morin, 2014, and Morin and Hutt, 2008b), mostly because initial ENP was significantly overestimated.

In any case, NPR is used with a numerical criterion (Equation 2-1).

$NPR < criterion$: (Eq. 2-1a)

means the sample is predicted to become acidic eventually, perhaps after a long lag time

$NPR \geq criterion$: (Eq. 2-1b)

means the sample is predicted to remain near-neutral pH indefinitely.

The most common NPR criterion is 2.0. In this case, all samples with NPR < 2.0 are predicted to become acidic eventually, and all samples with NPR ≥ 2.0 are predicted to remain near neutral indefinitely.

Problematically, a range in the NPR criterion, such as 1.0-2.0, is often called “uncertain”. This is an initial, preliminary category that must be eliminated with further site-specific testwork (Morin and Hutt, 1997a; Price, 2009). Where it cannot be eliminated, then the upper value of the “uncertain” range becomes the site-specific NPR criterion.

It is fascinating to read NPR-based literature showing the NPR criterion, often 2.0, was treated as some type of biblical edict. This is a very rigid approach that is not justified. For example, site-specific and rock-unit-specific NPR criteria can be as low as 1.0, and probably lower, and as high as 6.0, and probably higher (Morin and Hutt, 1997; Morin, 2003; Price, 2009). This is due to many site-specific factors like mineralogy, scale, and waste-management strategies.

For example, an NPR criterion like 2.0 for hand-sized samples fails to predict ARD reliably from a full-scale minesite component in spite of many corresponding hand-sized samples having NPR > 2.0 (e.g., Morin and Hutt, 1997b, 2000, and 2008a; Morin, 2017a and 2017b).

Obviously, the reliable identification of a site-specific NPR criterion can be critical to ARD predictions. For example, a sample with an NPR of 3.4 would be predicted to remain near neutral under a criterion of 2.0, but eventually acidic under a criterion of 4.0. However, testwork needed to reliably determine a site-specific NPR criterion, like closedown procedures at the end of humidity-cell testing (Morin, 2003), is rarely completed.

Overall, an NPR criterion between 1.0 and 2.0 is common. This is because it reflects the ratio of ENP consumption to EAP consumption in closed systems and open systems of sulphide oxidation followed by carbonate-mineral dissolution. So, while a criterion between 1.0-2.0 is common, it is not automatically applicable to all geologic materials.

2.3 Main Objective of this MDAG Case Study

This MDAG case study is not about selecting NPR criteria, just like it is not about problems with ENP (Section 1.1) and EAP (Section 1.2). Instead, this MDAG study considers any value of NPR criterion to be reliably justified, with the common criterion of 2.0 used here, and with ENP and EAP of samples being reliably estimated also.

So what is this MDAG study about if ENP, EAP, and the NPR criterion are assumed, commonly but often incorrectly, to be reasonably estimated? This case study will show that, even under these limiting assumptions, there are additional uncertainties that can cause ARD to flow from geologic materials with NPR values greater than the NPR criterion.

This uncertainty arises from the recognition that any analytical value has some uncertainty associated with it, such as from analytical-machine inaccuracy, method ambiguity, and random error (e.g., Wikipedia, 2018b, 2018c, and 2018d). The analytical value may be “reasonably” measured or estimated, but it is not 100% exact, accurate, and precise. It is often the “best guess” from a range of possible values.

Therefore, the main objective of this MDAG case study is to examine uncertainties in hypothetical sample NPR values relative to a specified NPR criterion (2.0 is used here). It does this using propagation-of-uncertainty (POU), also called propagation-of-error (POE). POU carries (propagates) common analytical inaccuracies, such as ± one standard deviation or a percentage, in ENP and EAP forward into the resulting NPR value obtained through mathematical division (Equation 1-1).

From this perspective, it starts to appear that, to be relatively certain a sample will not become acidic, its sample NPR must be significantly above the NPR criterion! This is not consistent with Equation 2-1 above. This is also not consistent with much of the published work on NPR values. After all, what is the utility of an NPR criterion if it is not a reliable criterion?

By extension, the effect of scale is also briefly considered here. For example, if a 1-kg sample is removed from a 1-tonne mass for ABA analysis, then only 0.1% of that tonne is reliably characterized. Each kg of the remaining 99.9% of the tonne can contain very different ENP and EAP levels. How much higher should the 1-kg NPR be above the site NPR criterion to minimize the probability of that entire tonne becoming acidic?

Of importance, ENP and EAP represent "compositional" values, whose total in a sample, combined with all other elements and components, must equal 100%. Thus, compositional data requires mathematical adjustments for accurate statistical investigation (e.g., Aitcheson, 1982; Wikipedia, 2018e). However, in this case study, ENP and EAP are relatively low compared with 100%, and thus are not adjusted for compositional summation. Also, ENP and EAP are often statistically independent at minesites (discussed further in Section 3.1), which is only possible for relatively minor sample components.

3. Propagation-of-Uncertainty with Mathematical Division to Calculate Net Potential Ratio

Solid-phase analyses, like Neutralization Potential (NP) and sulphur (Section 1), contain various uncertainties and errors. Thus, the "reported concentration" can be considered a "best guess" within a range of possibilities. Because ENP (Section 1.1) and EAP (Section 1.2) are derived from solid-phase analyses, they inherit these uncertainties. These uncertainties are then carried into the NPR (Section 2) through propagation-of-uncertainty (POU).

The range of uncertainty in solid-phase measurements can be expressed in many ways. Two ranges examined here are based on standard deviation (σ), as discussed in Section 3.1 below, and on percentage (%) relative to the mean (μ), discussed in Section 3.2.

3.1 Relative Standard Deviation of a Solid-Phase Concentration

Relative standard deviation (RSD), also known as Coefficient of Variation, is defined as:

$$RSD = \sigma / \mu = \sigma / RC \qquad \text{(Eq. 3-1)}$$

where σ = arithmetic standard deviation, in units such as kg/t
μ = arithmetic mean, which in this case is the reported concentration (RC), in units such as kg/t

An example of relative standard deviation (RSD) is 15 kg/t ± 0.2, where 0.2 represents a standard deviation of 3 kg/t (15 * 0.2). A few important observations about RSD follow.

- These arithmetic statistics imply the range of uncertainty around a mean value is a normal distribution, and that is exactly what is assumed here. A measured range that not is normal cannot use the POU equations later in this subsection, and thus requires POU using other techniques like Monte Carlo methods (Section 3.2).
- Because the uncertainty range is a normal distribution, the possible "real" concentration extends to infinity, at extremely low probability, as standard deviation increases. Statistically, the "real" concentration has a 68% probability of occurring between ±1 σ around the reported concentration (RC).
- Most geochemical literature does not use the RSD and instead usually reports the SD (σ), such as 15 kg/t ± 1.5 kg/t. However, for ENP and EAP, if a value rises from 15 kg/t to 150 kg/t, for example, the standard deviation does usually not stay at 1.5 kg/t. Instead, it typically increases too, such as to 15 kg/t. The RSD is used here to characterize the proportional increase in the standard deviation as the mean increases.
- The causes of uncertainty in a reported value are legion and too numerous to discuss here (e.g., Wikipedia, 2018b, 2018c, and 2018d). All causes are being simplified to one standard deviation for a reported value, typical of analytical results.
- While NP is measured by an analytical method, ENP is calculated, often by subtracting one or more values for various unavailable NPs (UNPs) from the measured NP. Based on the assumption that each UNP value is a constant without its own RSD, it is subtracted from the measured NP. The resulting ENP still has the same absolute value of standard deviation as the NP analysis, but the RSD has increased because the RC in Equation 3-1 (ENP < measured NP) has decreased.

Because NPR is ENP divided by EAP (Equation 1-1), the corresponding propagation-of-uncertainty equation (Wikipedia, 2018a) indicates the resulting standard deviation of NPR (σ_{NPR}) for a sample is equal to:

$$\sigma_{NPR} = (NPR) * [(\sigma_{ENP}/ENP)^2 + (\sigma_{EAP}/EAP)^2 - 2*\sigma_{ENP,EAP} /(ENP * EAP)]^{0.5} \quad \text{(Eq. 3-3)}$$

where σ_{NPR} = standard deviation of the calculated NPR of a sample, dimensionless
NPR = the calculated NPR (>0) of a sample = ENP/EAP, dimensionless
ENP = reported ENP of a sample, in units such as kg/t
σ_{ENP} = standard deviation of the reported ENP = RSD_{ENP} * ENP, in units such as kg/t
EAP = reported EAP of a sample, in units such as kg/t
σ_{EAP} = standard deviation of the reported EAP = RSD_{EAP} * EAP = 31.25 * $\sigma_{\%S}$ = $RSD_{\%S}$ * 31.25 * reported %S, in units such as kg/t
$\sigma_{ENP,EAP}$ = covariance of ENP and EAP = correlation coefficient * σ_{ENP} * σ_{EAP}, in units such as $(kg/t)^2$

In many studies of full-scale minesites and mineral deposits, the linear correlation of sulphur and NP is typically close to zero. As a result, Equations 3-1 and 3-3 reduce to Equation 3-4.

$$\sigma_{NPR} = (NPR) * [(\sigma_{ENP}/ENP)^2 + (\sigma_{EAP}/EAP)^2]^{0.5} = (NPR) * [RSD_{ENP}^2 + RSD_{EAP}^2]^{0.5} \quad \text{(Eq. 3-4)}$$

Based on the normal-distribution probability density functions of ENP and EAP (Figure 3-1), the POU values for σ_{NPR} (Equation 3-4) lead to probabilities that the "real" NPR lies within a certain range around the calculated NPR. For example, there is a 68% probability that the real NPR lies within ± 1 σ_{NPR} of the calculated NPR.

Interestingly, parts of Equations 3-3 and 3-4 represent the standard deviations of the lognormal distributions of ENP and EAP, namely their RSDs, or (σ_{ENP}/ENP) and (σ_{EAP}/EAP). Lognormal distributions are important, particularly for full-scale minesite components, but that will be a topic of a later MDAG case study.

3.2 Relative Percentage of a Solid-Phase Concentration

Relative percentage (PER) is defined as:

$$PER = (UNC / \mu) * 100\% = (UNC / RC) * 100\% \quad \text{(Eq. 3-5)}$$

where PER = boxcar (step-function) range of uncertainty as percentage of the reported concentration (RC)
μ = arithmetic mean, which in this case is the RC, in units such as kg/t
UNC = boxcar uncertainty in the RC, in units such as kg/t

An example of relative percentage (PER) is 15 kg/t ± 10%, which is equivalent to 15 kg/t ± 1.5 kg/t, where 1.5 is 10% of the mean (reported) value. A few important observations about PER follow.

- The range of uncertainty around the mean is a boxcar function (Figure 3-2). There is zero probability of a possible "real" concentration greater than (μ + PER) and less than (μ - PER). There is 100% probability of the real concentration being in the range of (μ ± PER).

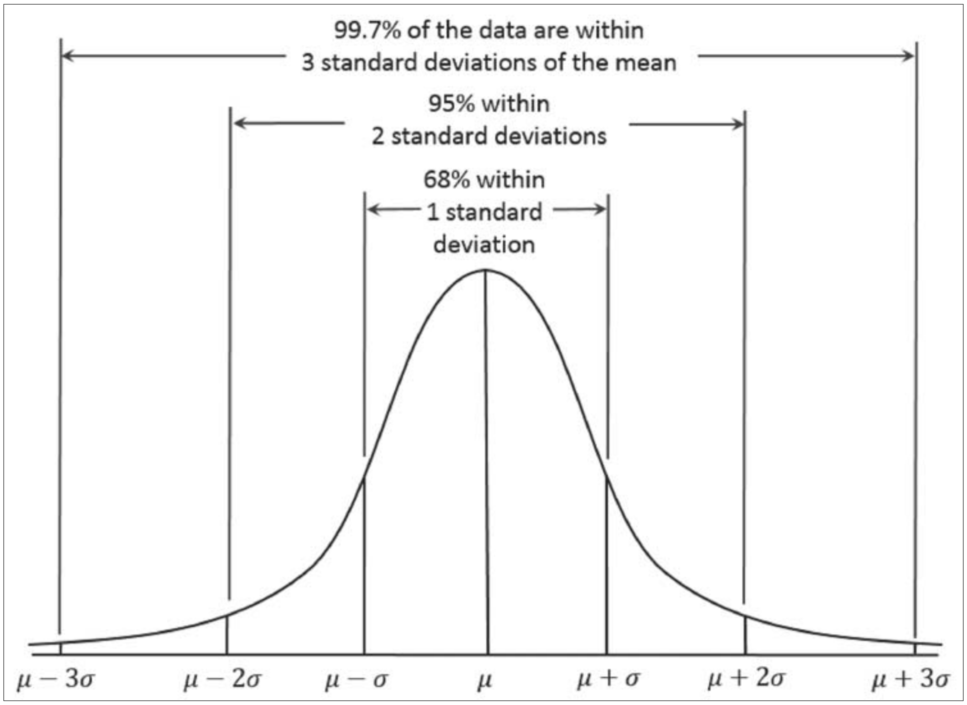

Figure 3-1. An example of a probability density function (PDF) for a normal distribution (from Wikipedia, 2018a); when the normal PDF for ENP is divided by the normal PDF for EAP, another normal PDF is obtained for NPR using propagation-of-uncertainty.

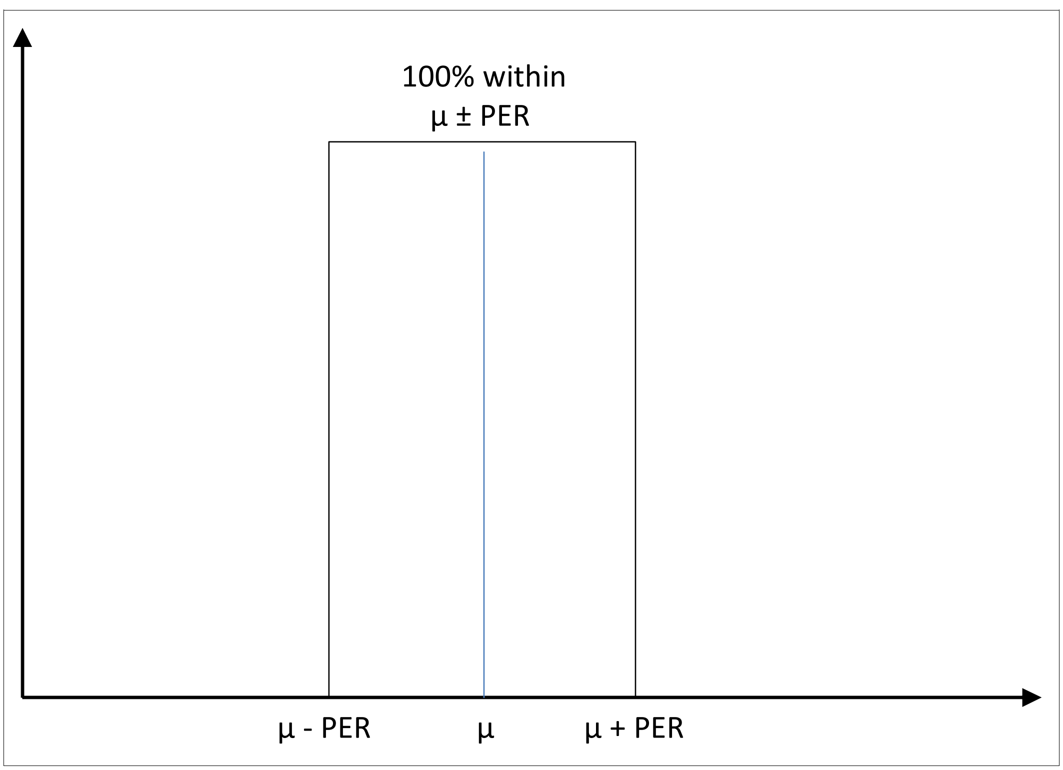

Figure 3-2. An example of a boxcar function, used for the probability density function of ENP and EAP.

- Within the range of ($\mu \pm$ PER), the probability is equal for all values. There is no normal distribution with a central "peak" value of probability like Figure 3-1.
- The reported mean (the reported analytical concentration) is in the center of the boxcar range, but is not more probable than any other concentration within the range.

NPR is ENP divided by EAP (Equation 1-1), but the shapes of the "input" distributions for ENP and EAP are notably different in this case (compare Figures 3-1 and 3-2). There are no simple propagation-of-uncertainty equations for estimating the distribution of NPR from the PER-based boxcar numerator and boxcar denominator. Thus, Monte Carlo simulations were used to estimate the distribution of NPR with boxcar ENP and EAP in Section 4.2.

4. Uncertainties in NPR Values based Propagation-of-Uncertainty with Normal and Boxcar Distributions of ENP and EAP

4.1 Normal Distributions of ENP and EAP

As discussed in Section 3.1 and Equation 3-4, the standard deviation of the normal distribution for NPR can be calculated from the standard deviations of ENP (Section 1.1) and EAP (Section 1.2). The important question is: what is the probability that a sample with an NPR above the criterion of 2.0 may actually be less than 2.0? If the probability is relatively high, then a criterion of 2.0 is not reliable.

This can be addressed by looking at various examples and scenarios. For example, Figure 4-1 shows nine examples, although only three are apparent due to overlapping lines. All nine samples have an NPR = 2.0, right at the 2.0 criterion, based on ENP/EAP = 100/50, 10/5, and 1.0/0.5. As a result, there is a 50% probability that NPR is actually less than 2.0 in all nine samples. The overlapping lines show that the absolute values of ENP and EAP do not affect the probabilities.

In contrast, the probabilities are different that all nine samples have an NPR such as less than 1.7, although reported as 2.0 (Figure 4-1). Samples with RSDs (Equation 3-1) of 0.20, which means the standard deviation is 20% of the reported ENP and EAP, have a larger probability of having an NPR less than 1.7 (around 30%) than samples with RSDs of 0.05 for ENP and EAP (around 1.7%). Thus, the increase in RSDs and standard deviations by a factor of 4 (from 0.05 to 0.20) for ENP and EAP increased the probability of NPR<1.7 by a factor of about 18.

Similar observations can be made for samples with NPR values of 1.0, 2.0, and 4.0 (Figure 4-2). In these cases, the visually apparent "spreading" in probabilities increases as NPR increases for the same RSD.

The preceding examples were based on samples with identical RSD values for both ENP and EAP. However, it is more likely that these two parameters will have different RSDs, and thus many different NPR standard deviations and RSDs may be encountered. Nevertheless, as a general statement, the RSD of NPR is consistently greater than the RSD of ENP and the RSD of EAP (Figure 4-3). This shows that mathematical division in the NPR calculation increases the relative uncertainty in NPR above that of either ENP or EAP.

There is a special case of differing RSDs, due to the commutative property in the summation of Equation 3-4. For example (Figure 4-4), where the RSD for ENP is one value (e.g., 0.20) and the RSD for EAP is another (e.g., 0.05), then the standard deviation from Equation 3-4 remains the same if the RSD values were switched (e.g., RSD_{ENP} = 0.05 and RSD_{EAP} = 0.20).

Finally, some realistic examples are informative, where RSD varies with the analytical value (e.g., Thompson, 1988). At high concentrations of ENP and EAP, the RSDs can be expected to be small, perhaps as low as 0.05 (5% of reported value) but this value is not typical. In contrast, at low concentrations of ENP and EAP, the RSD is typically higher. The RSD has been observed around 1.0 (100% of reported value) or higher, close to the lower detection limits of about 0.01%S for sulphur and around 3 kg/t for NP. We will now consider six of these more realistic samples (Table 4-1).

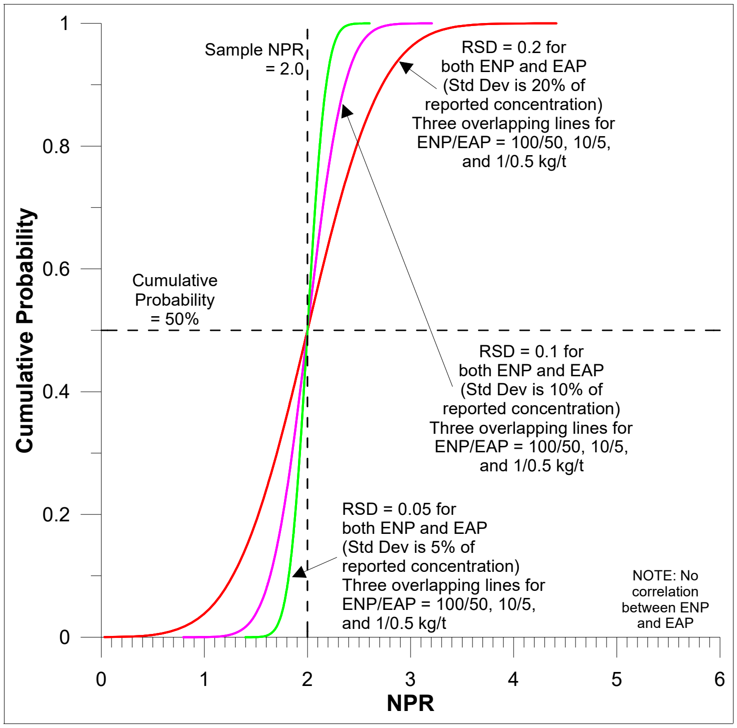

Figure 4-1. An example of nine samples all with a reported NPR of 2.0, with relative standard deviation (RSD) resulting in differing cumulative distribution functions; RSDs are identical for ENP and EAP.

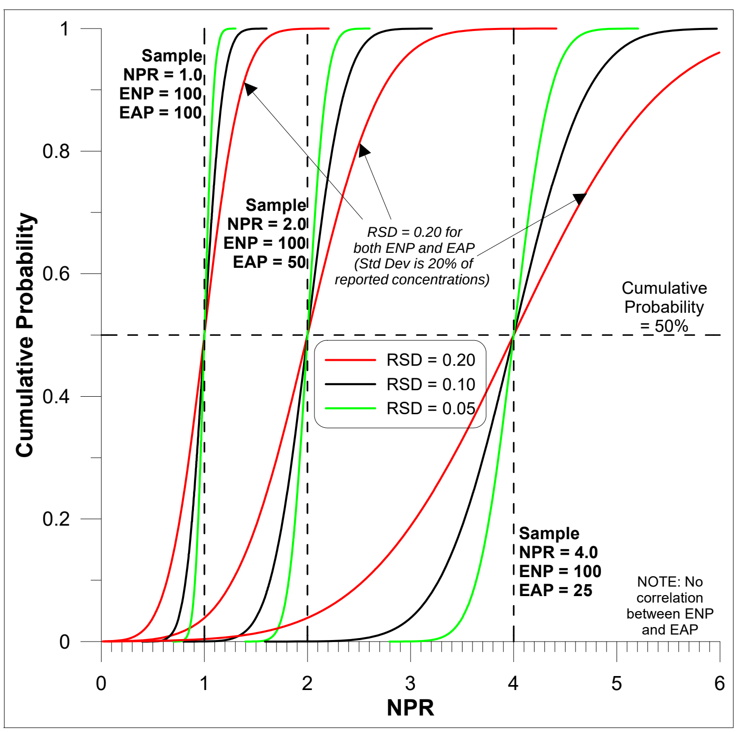

Figure 4-2. An example of nine samples with three each having a reported NPR of 1.0, 2.0, and 4.0; with relative standard deviation (RSD) resulting in differing cumulative distribution functions at each of the NPR values.

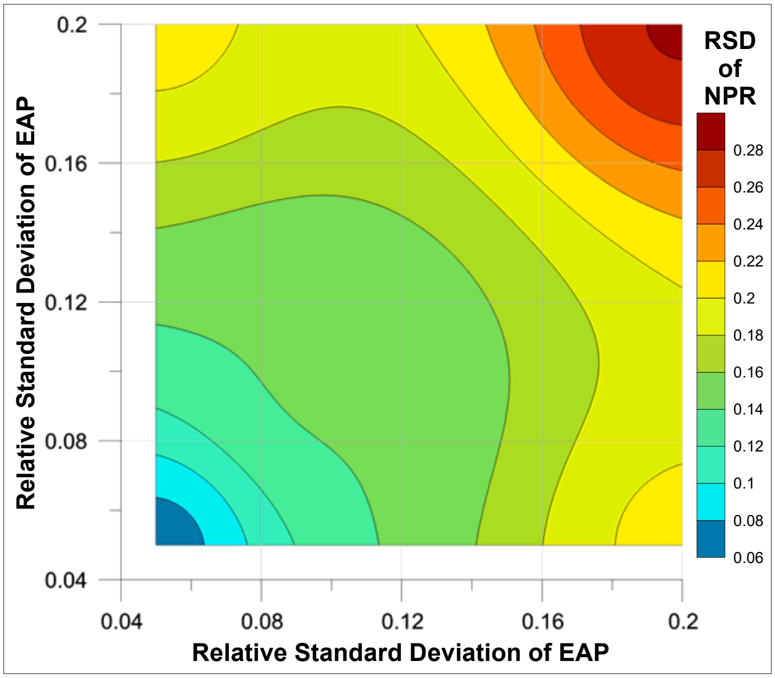

Figure 4-3. A contour plot showing the RSD of the calculated NPR exceeds the RSDs of the corresponding ENP and EAP.

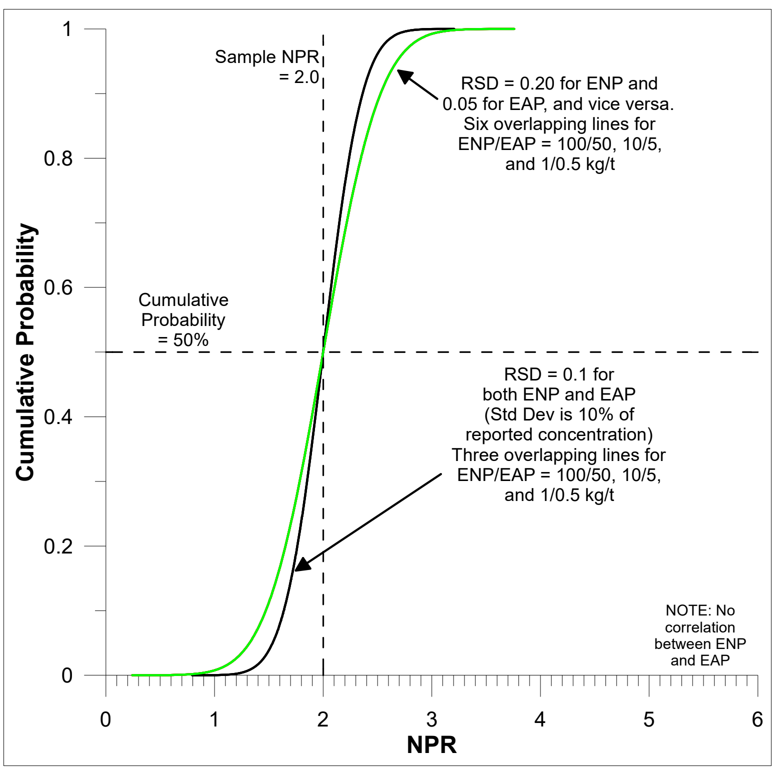

Figure 4-4. An example of nine samples all with a reported NPR of 2.0, with relative standard deviation (RSD) resulting in differing cumulative distribution functions; RSDs are different for ENP and EAP (compare to Figure 4-1).

Table 4-1. Realistic examples of samples with reported NPR values significantly above 2.0, yet with some probability of being less than 2.0 based on their relative standard deviations

NPR	ENP (kg/t)	EAP (kg/t)	RSDs of ENP and EAP	RSD of NPR	Probability that NPR is below 2.0
2.2	100	45.45	0.05	0.07071	10%
	44	20	0.10	0.1414	26%
	2.2	1.0	1.0	1.414	47.5%
3.0	300	100	0.05	0.07071	<0.001%
	100	30	0.10	0.1414	0.3%
	3.0	1.0	1.0	1.414	40.7%

Three of the realistic samples (Table 4-1) have reported NPR values of 2.2 (10% above the criterion of 2.0 and thus often considered "safe"). For both ENP and EAP, each sample has an RSD of 0.05, 0.10, or 1.0. Remarkably, for these samples with reported NPR values of 2.2, the probabilities that their NPR is actually less than 2.0 is: 10% for ENP of 100 kg/t, 26% for ENP of 44 kg/t, and nearly 48% for ENP of 2.2 kg/t.

The remaining three realistic samples have reported NPR values of 3.0 (Table 4-1), significantly higher than the criterion of 2.0. For both ENP and EAP, each sample has an RSD of 0.05, 0.10, or 1.0. For these samples with reported NPR values of 3.0, the probabilities that their NPR is actually less than 2.0 is: negligible for ENP of 300 kg/t, 0.3% for ENP of 100 kg/t, and nearly 41% for ENP of 3.0 kg/t.

In summary, normal distributions of uncertainty in ENP and EAP result in normal or lognormal distributions of uncertainty for NPR. Based on a criterion of 2.0 separating net-acid-generating from net-acid-neutralizing samples, all hypothetical samples with a reported NPR of exactly 2.0 have a 50% probability of being less than 2.0. Furthermore, samples with a reported NPR of even 2.2 have at least a notable 48% probability of actually being less than 2.0 when the relative standard deviations (RSD) of ENP and EAP are at least 1.0. These RSD values are typical of ENP and EAP close to their lower detection limits. Also at the reported NPR of 2.2, the probability of a sample's NPR being less than 2.0 decreases from 48% to 10% as the RSD decreases to 0.05, typical of very high values far above the lower detection limit. In comparison, at a reported NPR of 3.0, the probability rises above 40% as concentrations of ENP and EAP generally decrease and RSD increases above 1.0, compared with above 48% at NPR 2.2. The probability of NPR actually being less than 2.0 when reported as 3.0 was negligible at an RSD of 0.05.

4.2 Boxcar Distributions of ENP and EAP

As discussed in Section 3.2 and Figure 3-2, the step-like boxcar function is very different from the normal distribution (Figure 3-1). It is like "all-or-nothing", with zero probability outside the ±PER range.

There are no simple propagation-of-uncertainty equations for boxcar inputs as there are for normally distributed inputs (Equations 3-3 and 3-4). Therefore, 5000 randomly selected ENP and EAP values, within their boxcar distributions, were used for each Monte Carlo simulation to estimate the probability distribution of the resulting NPR.

With three samples having a reported NPR of 2.0, their corresponding NPR probability distributions show that increasing values of the same PER, for both ENP and EAP, from ±5% to ±20%, naturally increases the "spread" of the probability (Figure 4-5).

Another observation from Figure 4-5 becomes more apparent at higher PER, like ±20%. For these distributions of equal PER for ENP and EAP, the lognormal distribution is a slightly better fit than the normal distribution for NPR, although they are close. The medians are consistently slightly lower than the means, and the minimum and maximum values show some "tailing" at higher values. For example, the red distribution in Figure 4-5 has a minimum of about 0.66 below the mean and median, but a maximum of about 0.96 above the mean and median.

This may be the result of the Central Limit Theorem that indicates that the sum of statistically independent and identically distributed variables, not necessarily normally distributed themselves, trends towards a normal distribution. However, in this case, a variant of the Central Limit Theorem may apply where the mathematical division of two non-normally-distributed numbers with equal PER tends towards the lognormal distribution.

As a general statement, any sample with an NPR of 2.0 and with equal boxcar distributions of ENP and EAP have a roughly 50% probability of being less than 2.0 (Figure 4-5). This is similar to normally distributed uncertainty at NPR 2.0 (Figures 4-1 and 4-4).

When PER values of ENP and EAP differ, the distributions change but the 50% probability of being less than 2.0 do not (Figure 4-6). In this case, the higher the PER for ENP, relative to the PER for EAP, the more the NPR distribution approaches a boxcar shape itself. The red distribution in Figure 4-6 displays a boxcar distribution equal to 25%, or:

$$PER_{NPR} = PER_{ENP} + PER_{EAP} \quad \text{(Eq. 4-1)}$$

However, when the PER for EAP is relatively higher, a skewed triangular distribution appears (the green distribution in Figure 4-6), which is not lognormal. This is different from normal distributions where switching RSDs for ENP and EAP had not effect due to the commutative property of Equation 3-4. Nevertheless, for all three non-normal NPR distributions in Figure 4-6, the mean and median remain around 2.0, so there is roughly a 50% probability for all three that their NPR may be less than 2.0.

The relative "spreading" effect of probability, from PER values for ENP greater than PER for EAP, can be seen also be seen at NPR 1.0 and 4.0 (Figure 4-7). Furthermore, the asymmetry when non-equal PER values are switched for ENP and EAP, which is not seen for normal distributions, can be seen by comparing Figures 4-7 and 4-8.

As with normal distributions, the Monte Carlo simulations for boxcar distributions can be compiled into cumulative distribution functions (e.g., Figure 4-9). This allows probability estimations for the realistic samples discussed next.

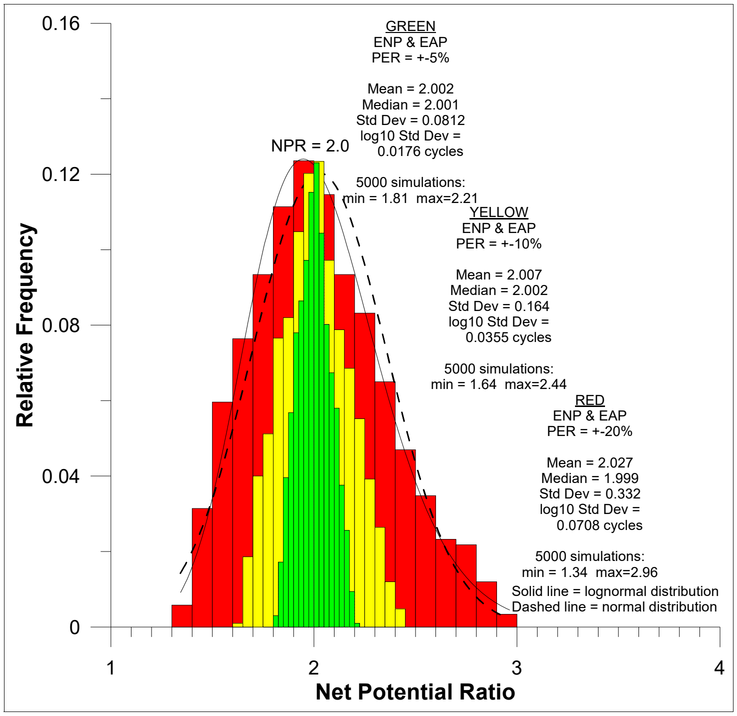

Figure 4-5. An example of three samples all with a reported NPR of 2.0, with differing cumulative distribution functions caused by variations in the boxcar PER and with PER identical for ENP and EAP.

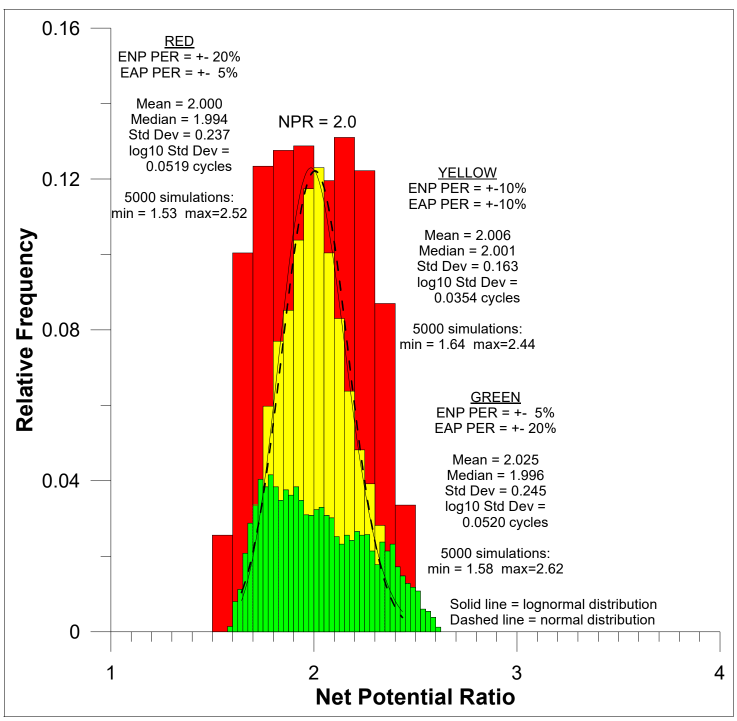

Figure 4-6. An example of three samples all with a reported NPR of 2.0, with differing cumulative distribution functions caused by variations in the boxcar PER and with PER different for ENP and EAP.

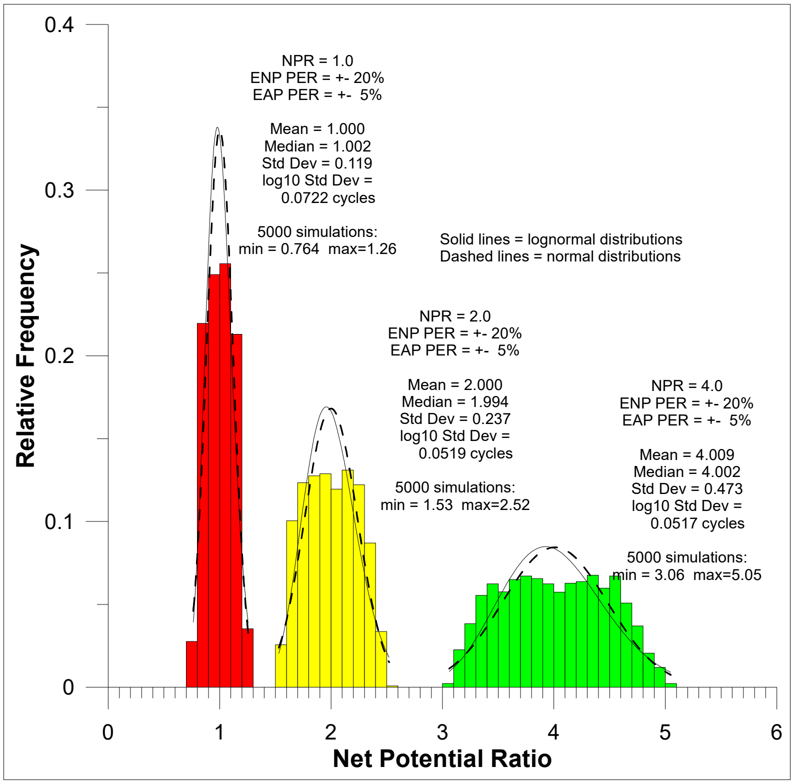

Figure 4-7. An example of three samples with a reported NPRs of 1.0, 2.0, and 4.0, and PER values for ENP and EAP of ±20% and ±5%, respectively.

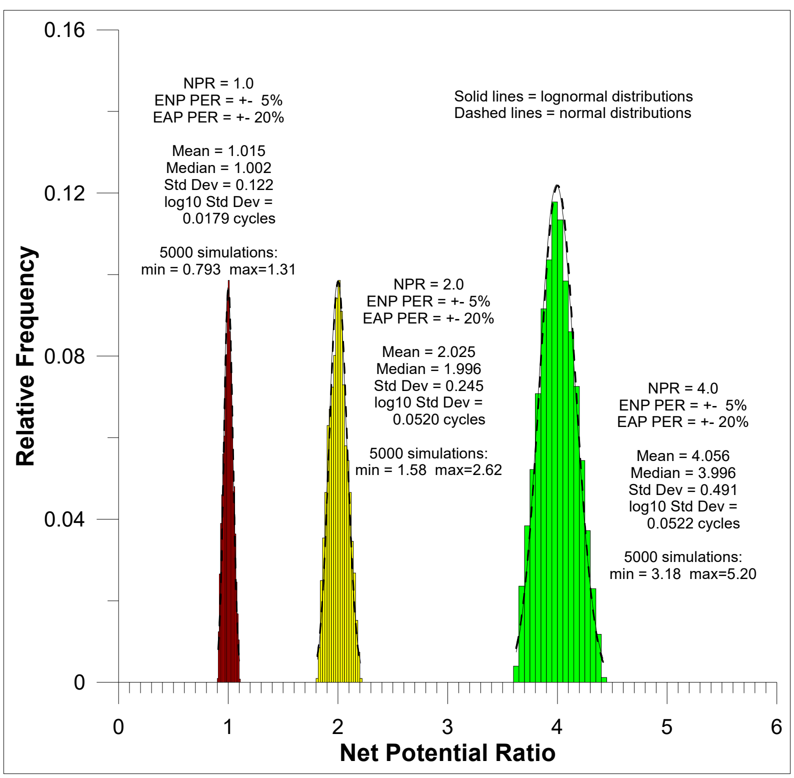

Figure 4-8. An example of three samples with a reported NPRs of 1.0, 2.0, and 4.0, and PER values for ENP and EAP of ±5% and ±20%, respectively.

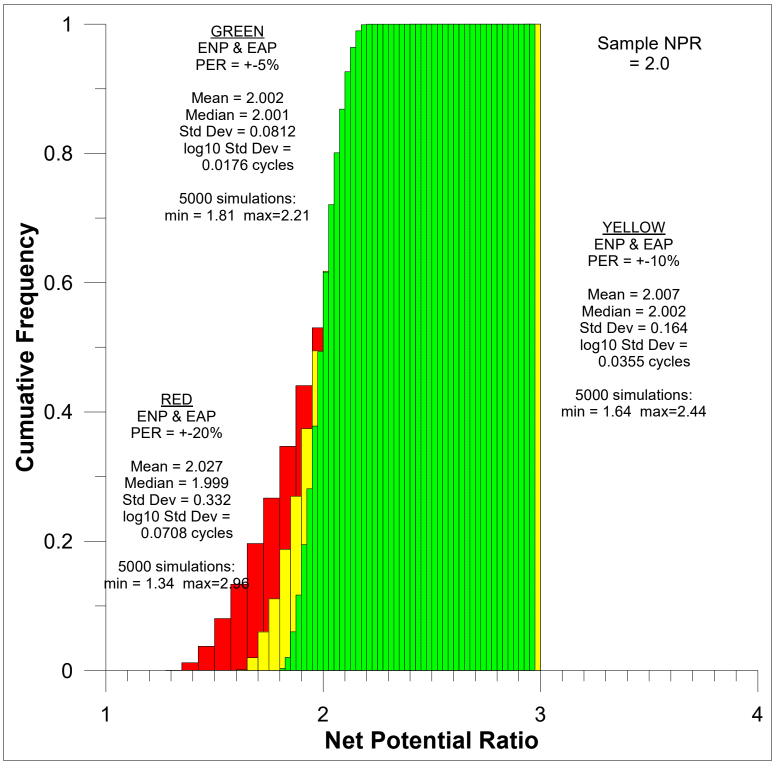

Figure 4-9. Cumulative distribution functions corresponding to Figure 4-5.

As with normal input distributions where RSD varies with the analytical value (Table 4-1), some realistic examples for boxcar distributions are examined here (Table 4-2). At high concentrations of ENP and EAP, the PER values can be expected to be small, perhaps as low as 5% of the reported value. In contrast, at low concentrations of ENP and EAP, PER can be much higher. A PER of 100% or higher of the reported value ENP and EAP could be expected close to the lower detection limits of about 0.01%S for sulphur and around 3 kg/t for NP. An additional consideration, not encountered with normal distributions, is the asymmetry of switching PER values of ENP and EAP with boxcar distributions. This needed additional hypothetical samples to examine (Table 4-2) compared with normal distributions (Table 4-1).

In summary, step-like boxcar distributions of uncertainty in ENP and EAP are expressed as ±percentage of the reported value of ENP and EAP, with zero probability outside this range. The mathematical division to obtain NPR results in a wide range of statistical distributions of uncertainty, many non-normal, for the resulting NPR. Nevertheless, based on a criterion of 2.0 separating net-acid-generating from net-acid-neutralizing samples, all Monte Carlo simulations show that all samples with a reported NPR of exactly 2.0 have about a 50% probability of being less than 2.0, just as with normal distributions. Samples with a reported NPR of even 2.2 have significant probabilities of being less than 2.0 (≥14% probability). The exception is for very high-accuracy values of both ENP and EAP at PER levels of ±5%. In comparison, at a reported NPR of 3.0, the probability of NPR actually being less than 2.0 is negligible for most boxcar ranges examined here. However, this probability of NPR being less than 2.0 increases to about 33% when the PER of ENP approaches ±100%, which is similar to the normal-distribution probability rising above 40% as RSD increases above 1.0.

Table 4-2. Realistic examples of samples with reported NPR values significantly above 2.0, yet with some probability of being less than 2.0 based on their boxcar relative percentages (PER)

NPR	ENP (kg/t)	EAP (kg/t)	PER of ENP	PER of EAP	Probability that NPR is below 2.0
2.2	100	45.45	5%	5%	0.064%
	100	45.45	10%	10%	14%
	100	45.45	20%	5%	28%
	100	45.45	5%	20%	25%
	44	20	10%	10%	14%
	44	20	20%	5%	28%
	44	20	5%	20%	25%
	2.2	1.0	100%	100%	45%
	2.2	1.0	100%	25%	45%
	2.2	1.0	25%	100%	45%
3.0	300	100	5%	5%	<0.2%
	300	100	20%	5%	<0.2%
	300	100	5%	20%	<0.2%
	30	10	10%	10%	<0.2%
	30	10	20%	5%	<0.2%
	30	10	5%	20%	<0.2%
	3.0	1.0	100%	100%	33%
	3.0	1.0	100%	25%	33%
	3.0	1.0	25%	100%	<0.2%

5. Conclusion

This MDAG case study assumed that Effective Neutralization Potential (ENP) and Effective Acid Potential (EAP) of hypothetical samples were reliably estimated, although this is rarely the case, yet included some uncertainty as a range above and below the reported values. A sample's value of ENP (and its uncertainty) was divided by the value of EAP (and its uncertainty) to obtain the Net Potential Ratio (NPR, and its uncertainty).

There were two types of ranges of uncertainty examined here for ENP, EAP, and NPR. First, the uncertainty was viewed as normal statistical distributions centered on the reported values of ENP and EAP. The uncertainty was thus expressed as ±one or more standard deviations. For numerical reasons, this case study mostly focussed on relative standard deviations (RSD), also known as the Coefficient of Variation, which is the standard deviation divided by ENP or EAP.

The second range of uncertainty examined here was ±a percentage (PER) of the reported values of ENP and EAP, as a step-like boxcar distribution. In this distribution, all probabilities outside the ±PER range are zero, and all probabilities inside the ±PER range are equal so that there is no peak probability like a normal distribution.

Propagation-of-uncertainty (POU), also know as propagation-of-error (POE), was used with these two types of uncertainty for ENP and EAP. POU was used to learn the resulting uncertainty in NPR when the uncertainty in ENP was divided by the uncertainty in EAP. For normal distributions, this was relatively straightforward, using relatively simple equations. For boxcar distributions, Monte Carlo simulations were needed, and 5000 random calculations each were used for each boxcar example in this case study.

For normal distributions of ENP and EAP uncertainty, POU showed the resulting NPR uncertainty was a normal or lognormal distribution, but with a standard deviation greater than that of both ENP and EAP. For boxcar distributions of ENP and EAP uncertainty, the resulting NPR uncertainty resembled normal, lognormal, or less regular distributions, depending on the ratio of the PER values for ENP and EAP and the NPR value. A multiplicative variant of the Central Limit Theorem may explain some of these results.

Based on a criterion of 2.0 separating net-acid-generating from net-acid-neutralizing samples, all hypothetical samples with a reported NPR of exactly 2.0 had a 50% probability of being less than 2.0. This applied to all samples in this case study with both normal and boxcar distributions.

For normal input distributions of ENP and EAP, hypothetical samples with a reported NPR of even 2.2 had at least a notable 48% probability of actually being less than 2.0, when the relative standard deviations (RSD) of ENP and EAP are at least 1.0. These RSD values are typical of ENP and EAP close to their lower detection limits. Also at the reported NPR of 2.2, the probability of a sample's NPR being less than 2.0 decreased from 48% to 10% as the RSD decreases to 0.05, typical of very high-accuracy values far above the lower detection limit.

In comparison, at a reported NPR of 3.0, the probability of being less than 2.0 was above 40% at RSD values above 1.0, compared with above >48% at NPR 2.2. The probability of NPR actually being less than 2.0 when reported as 3.0 became negligible as RSD decreased to 0.05.

For boxcar input distributions of ENP and EAP, hypothetical samples with a reported NPR of even 2.2 had significant probabilities of being less than 2.0 (≥14% probability). The exception was for very high-accuracy values of both ENP and EAP at PER levels of ±5%.

In comparison, at a reported NPR of 3.0, the probability of NPR being less than 2.0 increased to about 33% when the PER of ENP approached ±100%. This was similar to the normal-distribution probability rising above 40% as RSD increased above 1.0. The probability of NPR actually being less than 2.0 when reported as 3.0 was negligible for most lower boxcar ranges of PER examined here.

Based on these examples, this MDAG case study showed that a "safe" NPR criterion of 2.0 to distinguish net-acid-generating from net-acid-neutralizing geologic materials was not consistently "safe" even for samples with NPR levels of 3.0. The probabilities exceeded 30% that a sample with a reported NPR of 3.0 is actually less than 2.0 when ENP and EAP are close to detection limits and/or have relatively high uncertainties. A sample with a reported NPR of 2.2 had a probability above 10% that its NPR is actually less than 2.0 at common levels of normal and boxcar uncertainty. However, the probability of NPR misclassification dropped to negligible levels when excellent and minimal uncertainty is achieved.

Therefore, in light of uncertainties that exist within constituent values of Effective Neutralization Potential and Effective Acid Potential, a Net Potential Ratio criterion of any value is not assuredly "safe" for avoiding net-acid-generating samples within about one NPR unit.

6. References

Aitchison, J. 1982. The statistical analysis of compositional data. Journal of the Royal Statistical Society, Series B (Methodological), 44, p. 139-177.

Morin, K.A. 2017a. The MDAG Dynamic ARD-Onset Simulator. MDAG Internet Case Study #48, www.mdag.com/case_studies/cs48.html

Morin, K.A. 2017b. A Case Study Revisited of Full-Scale ARD from a Waste-Rock Pile with Abundant Reactive Neutralization Potential. MDAG Internet Case Study #47, www.mdag.com/case_studies/cs47.html

Morin, K.A. 2014. Temporal Evolution of Net Potential Ratios. MDAG Internet Case Study #39, www.mdag.com/case_studies/cs39.html

Morin, K.A. 2003. Problems with acid rock drainage predictions at the Ekati Diamond Mine, Northwest Territories, Canada. IN: T. Farrell and G. Taylor, eds., Proceedings from the Sixth International Conference on Acid Rock Drainage, July 14-17, Cairns, Australia, p. 663-670. The Australian Institute of Mining and Metallurgy.

Morin, K.A. 2009a. Supplement 1: Additional Discussions on the Non-Intrinsic Nature of Neutralization Potential (NP). www.mdag.com/case_studies/Additional Discussions on the Non-Intrinsic Nature of Neutralization Potential (NP).html

Morin, K.A. 2009b. Supplement 2: Arguments on the General Superiority of Neutralization Potential (NP) Methodology Translated into Varieties of Oranges. www.mdag.com/case_studies/Arguments on the General Superiority of Neutralization Potential (NP) Methodology Translated into Varieties of Oranges.html

Morin, K.A. 1990. Problems and proposed solutions in predicting acid drainage with acid-base accounting. IN: Acid Mine Drainage - Designing for Closure, Geological Association of Canada/Mineralogical Association of Canada Conference, Vancouver, British Columbia, May 16-18, p.93-107, p.93-107.

Morin, K.A., and N.M. Hutt. 2009. On the Nonsense of Arguing the Superiority of an Analytical Method for Neutralization Potential. MDAG Internet Case Study #32, www.mdag.com/case_studies/cs32.html

Morin, K.A., and N.M. Hutt. 2008a. Field Study of Unavailable Neutralization Potential in Acidic Rock. MDAG Internet Case Study #31, www.mdag.com/case_studies/cs31.html

Morin, K.A., and N.M. Hutt. 2008b. Case Studies of Unavailable Neutralization Potential in Acid-Base-Accounting Datasets. MDAG Internet Case Study #30, www.mdag.com/case_studies/cs30.html

Morin, K.A., and N.M. Hutt. 2001a. 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. 2001b. Relocation of net-acid-generating waste rock to improve post-mining water chemistry. Waste Management, 21, p. 185-190.

Morin, K.A., and N.M. Hutt. 2000. Relocation and Submergence of Net-Acid-Generating Waste Rock for Control of Acidic Drainage: A Case Study. IN: Proceedings from the Fifth International Conference on Acid Rock Drainage, May 20-26, Denver, USA, Volume II, p. 819-825. Society for Mining, Metallurgy, and Exploration, Inc., Littleton, CO, USA.

Morin, K.A., and N.M. Hutt. 1997a. 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., and N.M. Hutt. 1997b. A comparison AMD predictions with historical records. IN: Proceedings of the Workshop on Acid Mine Drainage, 15-18 July, Darwin, Northern Territory, Australia, Australian Centre for Minesite Rehabilitation Research, p.33-44.

Morin, K.A., and N.M. Hutt, and S.G. Hutt. 1997. History of Eskay Creek Mine's waste-rock dump from placement to disassembly. Canadian MEND Report 1.44.1

Price, W.A. 2009. Prediction Manual for Drainage Chemistry from Sulphidic Geologic Materials. Canadian Mine Environment Neutral Drainage Report 1.20.1, Natural Resources Canada, dated December 2009.

Thompson, M. 1988. Variation of precision with concentration in an analytical system. Analyst, 113, p. 1579-1587.

Wikipedia.org. 2018a. Propagation of Uncertainty. Accessed February 2018 at: en.wikipedia.org/wiki/Propagation_of_uncertainty

Wikipedia.org. 2018b. Measurement uncertainty. Accessed February 2018 at: en.wikipedia.org/wiki/Measurement_uncertainty

Wikipedia.org. 2018c. Uncertainty quantification. Accessed February 2018 at: en.wikipedia.org/wiki/Uncertainty_quantification

Wikipedia.org. 2018d. Experimental uncertainty analysis. Accessed February 2018 at: en.wikipedia.org/wiki/Experimental_uncertainty_analysis

Wikipedia.org. 2018e. Compositional Data. Accessed February 2018 at: en.wikipedia.org/wiki/Compositional_data