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Non-Detectable Natural Elements in Aqueous and Solid-Phase Geological Samples Are Often Well Below One-Half the Detection Limit

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Abstract

There are many opinions and options for numerically handling chemical analyses less than the human artifact of a detection limit. All have implicit assumptions about what cannot be currently measured.

For geological samples such as rock and natural water containing natural elements, there are no "zero" concentrations, but instead many-orders-of-magnitude ranges of concentrations. In light of this, logarithmic distributions show that, in most cases, the concentrations less than detection will be frequently (>90%) also less than one-half the detection limit. Cases where analyses show most values may lie just below the detection limit can still cumulatively have most values less than one-half the detection limit. Therefore, the usage of one-half the detection limit for geologic samples of rock and natural waters is typically an overwhelmingly safe assumption for most samples, and there can be detectable information in a related dataset when this assumption may not be safe.

1. Introduction

Here is a dangerous debate to wade into: how should values below the human limitation of detection limits be handled numerically? There are many opinions and options as an Internet search will reveal, including:

- assume a below-detection sample is at detection;
- assume a below-detection sample is at one-half the detection limit;
- assume a below-detection sample is at 1/1.41 (1/square root of 2) of the detection limit;
- assume a below-detection sample is zero; and
- if significant portions of the related dataset are above detection, assume a regression curve based on these detectable samples to values below detection.

Obviously, there is no way to know the correct assumption from the list above because the concentration is below our current ability to detect it. In some cases, the arbitrary choice is based on what is desired for a dataset in general, like an overestimation or an underestimation of the mean and variance of the dataset. In some cases, the arbitrary choice is dependent on the unknown statistical distributions like a Gaussian (normal) or triangular distribution between zero and the detection limit.

After decades of watching these ongoing arguments, it is time to add my opinion in this matter. At MDAG, one-half the detection limit is almost always used for geological samples like rock and natural waters. This is because in most cases the probability is greater than 90% (>90%) that a value below detection will also be below one-half the detection limit, and when it is not the remainder of the related dataset may highlight that.

2. No Visible Geological Sample of Rock or Water Has a Zero Concentration of Most Natural Elements

If you can see a sample of rock or natural water, then it will likely contain at least some atoms of every natural element in the Periodic Table. There is no zero concentration of any natural element in most geologic samples. Thus, assuming zero will always be wrong for these samples and will underestimate the true concentration. This foreshadows the importance of logarithmic scales, discussed in Section 3 below.

One mole of an element contains roughly $6x10^{23}$ atoms. In 1 g of multi-element rock or in 1 mL of natural water with many dissolved elements, the total number of atoms varies with the proportions of the elements. For simplicity and as a gross estimate, let's say 1 g of rock or 1 mL of water contains somewhere around 10^{22} atoms (an order of magnitude here and there does not change the reality).

According to general crustal abundances, gold has an average abundance of about 0.001 ppm. This means that 1 g of rock with the average gold content still contains approximately 10^{13} atoms of gold. This is far from zero, although not economic at current bullion prices! The rarest natural element is astatine with an average crustal abundance around 10^{-20} ppm. For this natural element alone, there could plausibly be zero atoms in small geologic samples (<~1kg), but not for the remaining elements.

In natural waters, background concentrations of gold have been reported around 0.001 ppb. Thus, even 1 mL of natural background water can contain roughly 10^{10} atoms of gold. This is far from zero.

Therefore, concentrations in geological samples of rock and water do not have zero concentrations of natural elements, except for perhaps the rarest element in small samples. In turn, this means their concentrations can range across many orders of magnitude, which leads to the importance of logarithmic scales discussed next.

3. Logarithmic Scales for Showing the Orders-of-Magnitude Possible Variations in Concentrations of Natural Elements

As explained in Section 2 above, concentrations of natural elements in rock and water can span many orders of magnitude but do not reach zero except in extreme circumstances. As a result, the graphical plotting of natural elements below detection should not be from zero up to detection (e.g., Figure 3-1), but from many orders of magnitude below detection up to detection (e.g., Figure 3-2).

For simplicity of illustration, the current detection limit for a natural element is set at 1 ppm. One-half the detection limit is 0.5 ppm. Probabilities of values (the probability density function), or the number of concentrations in a related dataset, below detection are assumed here to be Gaussian ("normal") on a logarithmic basis ("lognormal", typical of geological samples). Nevertheless, many other similar statistical distributions will lead to the same overall conclusion. Based on Section 2 above, the distribution or probability of this element is not 1 ppm down to zero (Figure 3-1), but instead from 1 ppm down to some value orders-of-magnitude lower (Figure 3-2).

Notice the small "window" of probability, or the very low number of samples in the related dataset, that lies between detection and one-half detection in Figure 3-2. Therefore, any natural element that is below the human artifact of a detection limit is very likely also below one-half the detection limit also. For the four examples shown in Figure 3-2, more than 90% are also below one-half detection, with the rightmost example with a mean value of 1/10th the detection limit and a standard deviation of 0.5 log cycles having 92% below one-half detection.

By focussing on the right side of Figure 3-2, there is a way to know if many below-detection samples in a related dataset might lie within the narrow range between detection and one-half detection. The "clue" to this is when several samples within a dataset are above detection and seem to be increasing in number as concentrations decrease towards detection.

An example of this in Figure 3-3 shows that 40% of samples were above the detection limit and were also suggesting that most of the remaining 60% were likely just below detection. The peak number of samples in this hypothetical example was placed at 0.75 ppm, halfway between detection and one-half detection. Nevertheless, in this example, about 60% of all the samples below detection were also below one-half detection (in total, ~40% above detection, ~24% between detection and one-half detection, and ~36% below half detection). Thus, even when many samples might lie between detection and half detection, based on the related detectable samples, the lognormal distribution can show that cumulatively most non-detectable samples are also less than half the detection limit.

Therefore, the usage of one-half the detection limit for natural elements in geologic samples of rock and natural waters is typically an overwhelmingly safe assumption for most samples, and there can be detectable information in the related dataset when this assumption may not be safe.

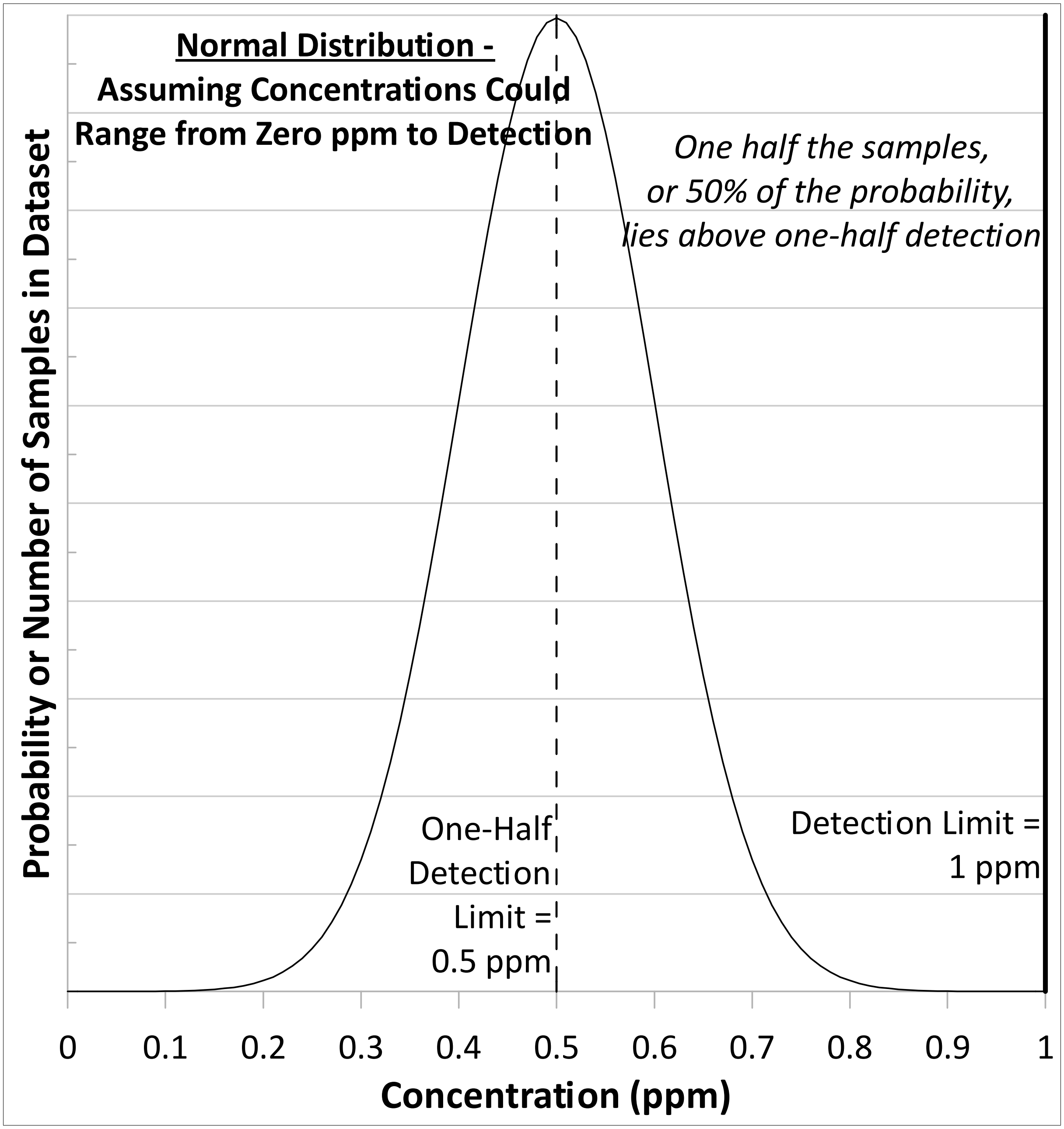

Figure 3-1. A common view of below-detection probability or number of samples in a related dataset, with a concentration range of zero to detection, which does not apply to natural elements.

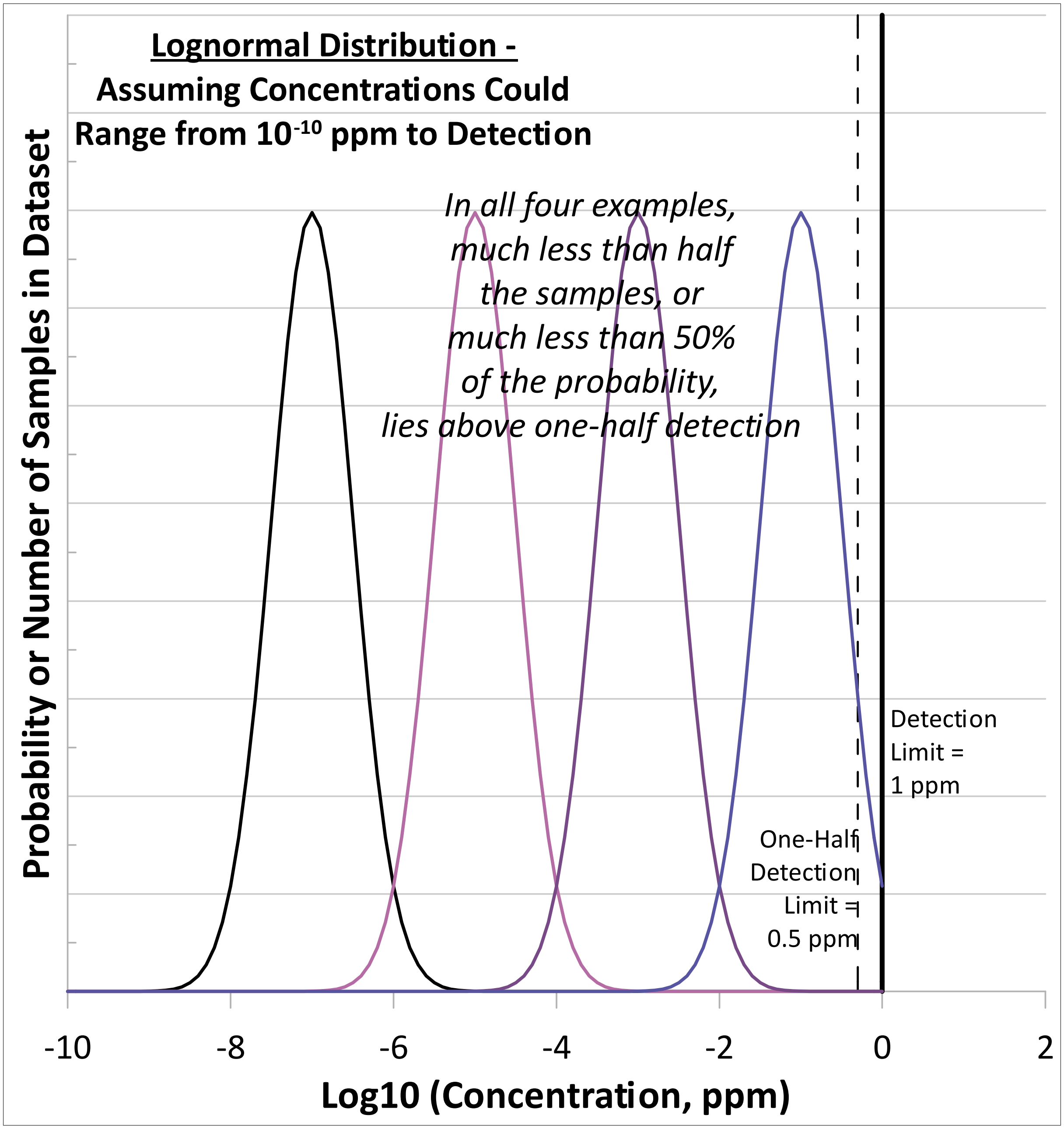

Figure 3-2. A more realistic view of below-detection probability or number of samples in a related geologic dataset of rock or water, with a potential concentration that is orders of magnitude below detection applying to natural elements.

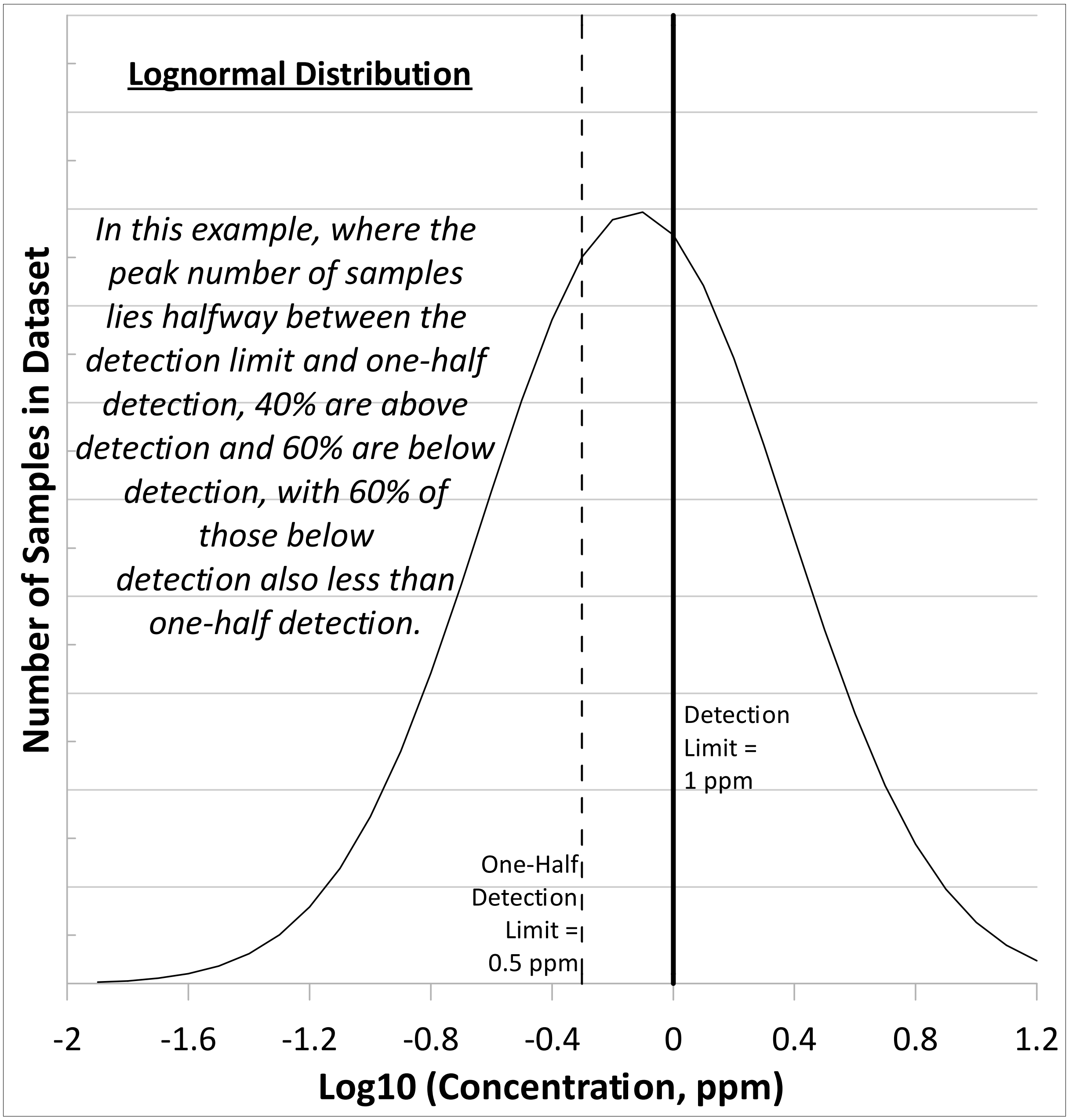

Figure 3-3. An example of a related dataset where the above-detection values suggest the value of the peak number of samples lies just below detection, and yet cumulatively about 60% of the non-detectable values still lie below one-half the detection limit.