DQO-PRO Tutorial

Success-Calc

A PowerPoint Tutorial

by

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DQO-PRO Background

- ***DQO-PRO*** provides answers for three objectives:
  1. Determining the rate at which an event occurs,
  2. Determining an estimate of an average within a tolerable error, and
  3. Determining the sampling grid necessary to detect “hot spots”

- This tutorial shows how it can be used to calculate the number This of environmental or QA or QC samples needed for some example objectives involving **your personal** Data Quality Objectives.

QA and QC Samples Assess Environmental Samples

- **QA and QC samples are used to provide an assessment of the kinds and amounts of bias and/or imprecision in the data that is obtained from the environmental samples.**

- **QA samples typically are blind samples to the analyst while QC samples have known values.**
  - Thus, QA and QC samples are used to assess the collection and measurement system in a similar way that environmental samples are used to assess the portion of the environment from which they come.

QA and QC Samples Assess Environmental Samples (continued)

- Therefore, representative environmental samples are collected and analyzed to form conclusions about a particular site, and representative QA or QC samples are analyzed to form conclusions about the system that measures the environmental samples.

- This similarity in environmental sample usage and QA or QC sample usage is often not appreciated or even recognized.

What are Some Basic MQOs?

- **What percentage of false positives and false negatives are you willing to accept?**

- **Most other factors considered will affect the amounts of false positives and false negatives in a project.**

False Positives

What are some of the most important criteria in environmental analytical data?

- Isn't one of them an assurance that analytes have been correctly concluded to be present from the data?
  - When incorrect conclusions are made the result is **False Positives**.
    - The wrong analytes are concluded to be present.
    - This can result in severe consequences to clients.

False Negatives

Correctly concluding from analytical data that analytes are absent from samples is also from important.

- Incorrect conclusions when analytes are really present result in **<u>False Negatives.</u>**
  - False negatives commonly occur from poor recovery of analytes from environmental matrices or interferences.
  - Minimization of false negatives is important with risk assessment data and regulatory agencies.

False Positives / False Negatives

SAMPLE CONCLUSION	PRESENT	ABSENT
PRESENT	✓	False-Positive (Type I) Error
ABSENT	False-Negative (Type II) Error	✓

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Method Blanks

- **Method Blanks** are used to demonstrate the absence of False Positives in analytical data.

- They do **NOT** help to measure the presence of False Positives caused by misidentification of analytes!!

Method Spikes

- **Method Spikes (Matrix Spikes)** are used to demonstrate the absence of <u>False Negatives</u> in analytical data.
  - Most laboratories have this kind of data for analytes analyzed by various methods.

Note: Method Blanks and Method Spikes cover **<u>all</u>** sources of lab errors. Additional QC samples are needed to distinguish between different sources of lab errors or sampling errors; ***Practical QC*** (an inexpensive program available separately from Instant Reference Sources) helps to determine which of these you need for specific purposes.].

Current Use of QA and QC Samples

How do laboratories, their industrial clients and regulatory agencies typically use data from method blanks and method spikes?

Current Use of QA and QC Samples

- Isn't it to demonstrate that false positive and false negative conclusions are not occurring in the data from the analytical/preparation batch with which these QA or QC samples are associated?
  - Used this way isn't that just one or two data points with a sample set?
  - Are one or two data points statistically significant? (You know they are not).

Statistics of Typical Batch Sample Data

- For example, if a laboratory analyzes two spiked QC samples with a day's batch of environmental samples, there is only a <u>10% probability</u> of detecting false negatives with a 95% confidence level if they occur at a rate of up to 5%.

- Likewise, there is only a <u>5% probability</u> of detecting false positives with a 95% confidence level if they occur at a rate up to 5% when only one method blank is run with a day's batch.

Are Your Assumptions Wrong?

- An implicit assumption that the environmental samples analyzed in conjunction with a method blank and one or two spiked method blanks (or matrix spikes) do not contain false positives or false negatives because the accompanying one or two QA or QC samples did not contain them is <u>not necessarily correct</u>.

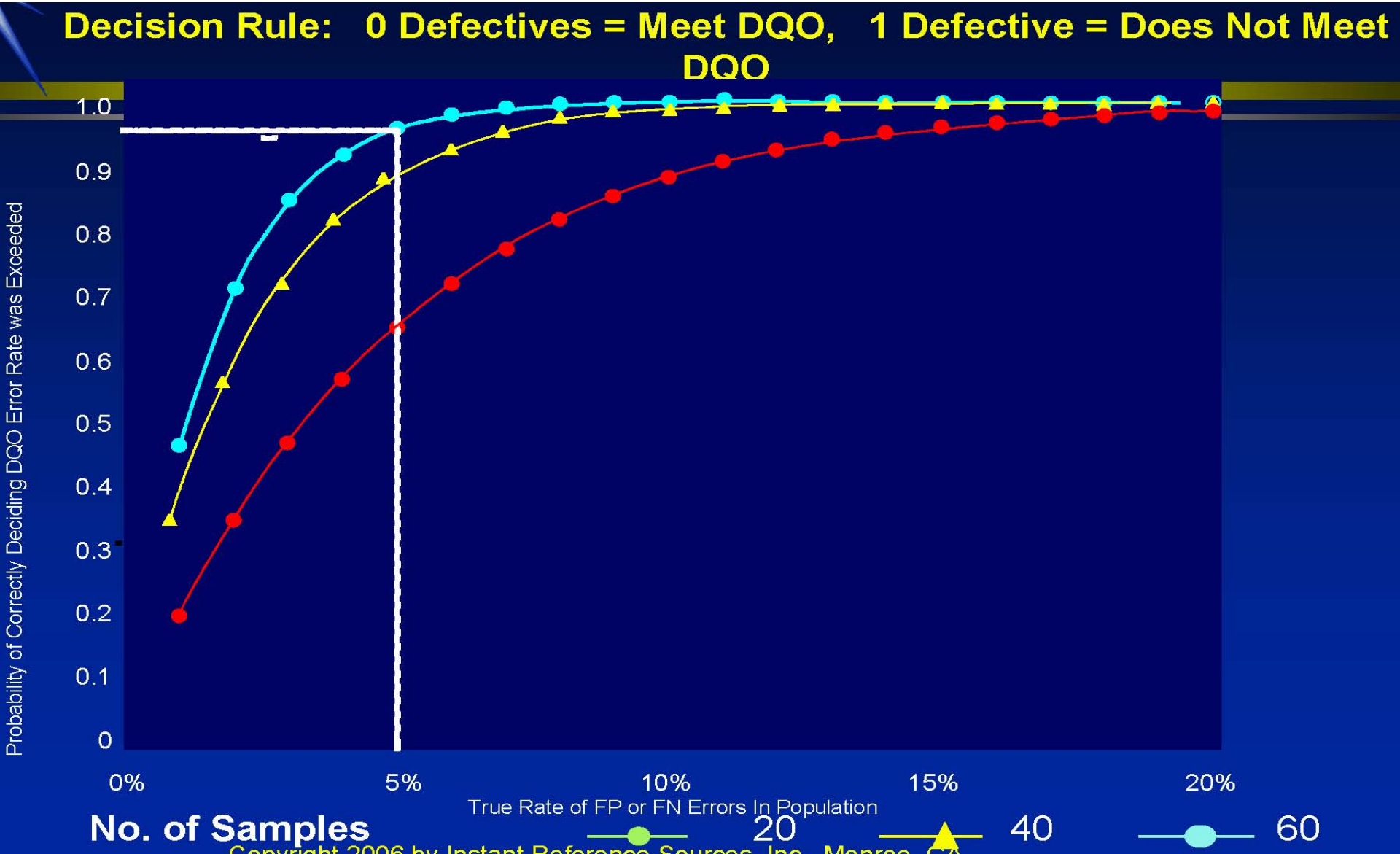
- **Thus, the present way of assessing QA and QC data contains a basic flaw that is not usually recognized.**

Statistical Use of QA/QC Data

If the data from method blanks and method spikes that laboratories have could be used statistically, what would it mean?

- That there is X probability that there will be no more than Y% false positives (or false negatives) in the samples associated with a particular QA or QC data set.
  - **Wouldn't that be more useful than the present way which provides no statistical conclusions?**

Power Curves Can Estimate Numbers of QC Samples



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Statistical Use of QA/QC Data

- **How can a statistical treatment of available QA or QC data better characterize environmental analytical programs better programs?**

1. **The probability of not exceeding a selected rate of occurrence of false positives or false negatives would be known;**
   - e.g., we want a 99% probability that there will be no more than 5% false positives using Method 8270. How many method blanks are needed? (ANSWER: 90)
   - What if we decreased the confidence level to 90%? (ANSWER: 45)
   - What if we changed the rate of false positives to 10% and the confidence level to 95%? (ANSWER: 29).

These answers were obtained using Success-Calc as you'll see in a minute.

Statistical Use of QA/QC Data

- **How can a statistical treatment of available QA and QC data better characterize environmental analytical programs?**

2. The number of QA or QC samples needed to assure that a desired rate of false positives or negatives would be detected could be compared with the number analyzed.

- Furthermore, if the actual number of QA or QC samples was less than the desired number, the increase in rate or decrease in probability could be calculated.
- Using the example from the previous slide, what if only 20 method blanks actually were run? (ANSWER: a 65% probability of not exceeding 5% false positives or an 88% probability of not exceeding 10% false positives).

Statistical Use of Data & DQOs

- **How Else Could Method Blanks and Method Spike QA or QC Data be Used Statistically?**

3. Regulators, engineers, project directors, etc. could plan sampling and analytical projects so that they will generate statistically valid data that will demonstrate whether false positives and false negatives are probable (or not) at some selected rate of occurrence.

  – This is a statement of a Method Quality Objective.

Measurable Failure of DQOs

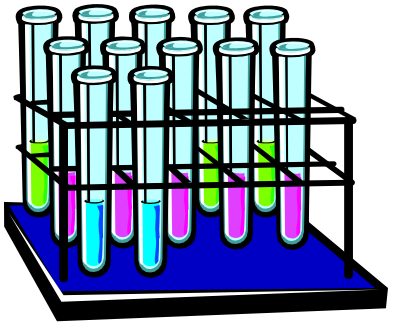
- **How Else Could Method Blanks and Method Spike QA or QC Data be Used Statistically?**

4. If a MQO is <u>not</u> achieved (i.e., the rate of false positives or false negatives in a data set are higher than desired) then the degree to which it failed can be calculated.

- For example, there may only be a 50% probability that one analyte has no more than a 5% false positive rate of occurrence in a particular EPA Method 8270 data set, while others meet the 99% probability MQO.
- **Wouldn't that be very important to know?**

Success-Calc Uses

- ***Success-Calc*** **is used to determine the number of samples needed to detect a specified characteristic in a population of samples.**



  - For example, it may be used to calculate the number of QA or QC samples (such as method blanks or matrix spikes) needed in order to assure that no more than a specified rate (e.g., 5%) of false positive or false negative detections will occur in the environmental samples associated with the QA or QC samples.

Success-Calc Uses

- **Success-Calc may also be used to calculate the number of samples needed to assure detection of any other characteristic of interest that occurs in more than a specified portion of the population.**
  - For example, the percent contamination of a sampling site.

- **In addition, Success-Calc also calculates the maximum and minimum proportions corresponding to the observed (sample) proportion.**
  - For example, the maximum and minimum rate of false positives and false negatives that could occur in samples.

Inputs to Success-Calc

- **Inputs include:**
  - **the maximum percentage of the selected characteristic that is allowed to go undetected,**
  - **the desired probability of detecting that characteristic if it occurs in more than the maximum percentage specified, and**
  - **how many samples, if any, that will be allowed to fail the specified criteria.**

Success-Calc Assumptions

- **Assumption**
  - Each sample (including QA or QC samples) is representative of the sample population they are being used as substitutes for.
    - This means that all <u>significant criteria</u> involving the analyses must remain constant during the time period, or the project, for which the statistical calculations are made:
      - This may include analysts, instrumental conditions, methods, matrix, standards, etc.
  - **<u>However, the time period can be days, weeks, or months as long as the above conditions are met.</u>**

Success-Calc Calculations

- This calculator does NOT calculate the number of samples needed to estimate the frequency at which a characteristic occurs;

- Rather, it calculates the number of samples required to decide when the true frequency of occurrence exceeds some predefined frequency using a specified decision rule.

Where Can Extra QA or QC Samples Come From?

- **An important point is that many of the QA, QC or environmental samples needed for a statistical population are available (or can easily be made available); they are just not used this way now.**

- **Thus, increased <u>costs</u> associated with large numbers of samples may not be necessary – they may, in fact, be *minimal or even reduced* with proper planning.**

All Significant Parameters Must Remain Constant

- **The key to obtaining a statistically useable population of sample data within a window of time is that all significant parameters that can affect analytical method performance must remain constant.**

- **Significant parameters may include the instrumentation and method, the analyst, <u>and the matrix</u> (e.g. soil, wastewater, etc.).**

Can Data from Multiple Instruments or Analysts be Pooled?

- Laboratories can usually readily document the consistent use of instrumentation and an analyst for a given period of time or for a specific project.
- Therefore, the answer may be yes **if** documentation exists that show the pooled data over a given period of time is not statistically different when one or more instruments or one or more analysts are used with a given method and matrix.
  - The consequence of being wrong with either of these assumptions is that the rates of false positives or false negatives will be underestimated.

Equation Used With Success-Calc and Low Frequency Occurrences

If the frequency of the characteristic which is desirable to detect is less than 10% the following equation is used:

n = nL(alpha)/nL(1-Y)

where: alpha = 1 - the desired confidence;

Y = the frequency to detect (this must be less than 10%).

The equation is based on the exponential distribution and assumes that the characteristic to be detected occurs very infrequently, as opposed to the binomial, which can tolerate any frequency from 0 to 100%.

The reference for this approach is information available from EPA on "Xmax and the Exponential Distribution Model in the Development of Tolerance Intervals". This information is used in conjunction with guidance on evaluating gas pipelines for PCB contamination, but is currently not published.

Equation Used With Success-Calc and >10% Frequency Occurrences

If the frequency of the characteristic which is desirable to detect is more than 10%, we must use the binomial equation and iteratively solve for an appropriate n. In this case:

$$Pr = n!/r!(n - r)!*q(n - r)*pr$$

where n = the number of samples in a sample collection

r = the number of samples with the characteristic to be detected

p = the true percentage of the population with the characteristic to be detected

q = the true percentage of the population without the characteristic to be detected

q = 1-p.

Decision Rules With *Success-Calc*

The last portion of the ***Success-Calc*** program determines the minimum and maximum percentage of the population with the chosen characteristic given that some number of samples collected indicated the presence of this characteristic.

This calculation is analogous to setting an upper and lower confidence level for a mean.

Success-Calc Equations for Upper and Lower Confidence Levels

The equations for calculating the lower confidence level (LCL) and upper confidence level (UCL) for the binomial distribution are:

$$LCL = \{1+((n-r+1)*F(1-alpha/2;2n-2r+2,2r)/r)\}^{-1}$$

$$UCL = \{1+((n-r)/(r+1)*F(1-alpha/2;2r+2,2n-2r))\}^{-1}$$

where

F = the F statistic with the above specified degrees of freedom

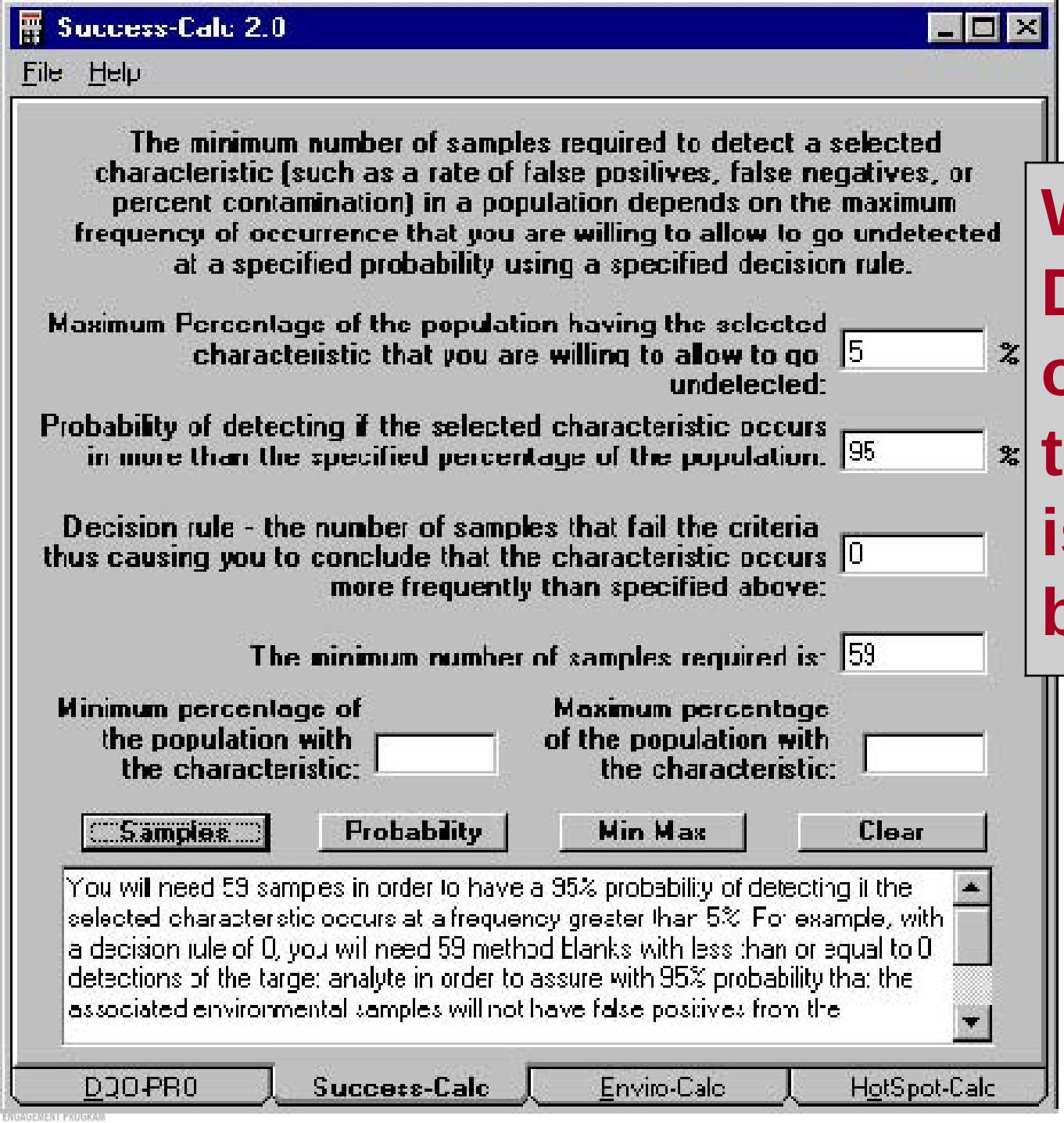
n = the number of samples collected

r = the number of samples with some characteristic (r in the earlier equations)

-1 = exponentiate the result to the negative 1

Problem 1. Use *Success-Calc* to Calculate Numbers of Method Blanks Needed

- ***Success-Calc*** **can be used to estimate the number of QA or QC samples needed for a desired objective.**
  - **Estimate the number of method blanks needed in order to assure, with 95% confidence, that no more than 5% false positives would be in the QC data, thus inferring that the same assessment would be true for the associated environmental samples.**



With a Decision rule of zero (0), the answer is 59 method blanks.

59 is a lot of Method Blanks

- **Maybe 59 is too many method blanks for a particular project, especially if it only involved, for example, 30 samples.**

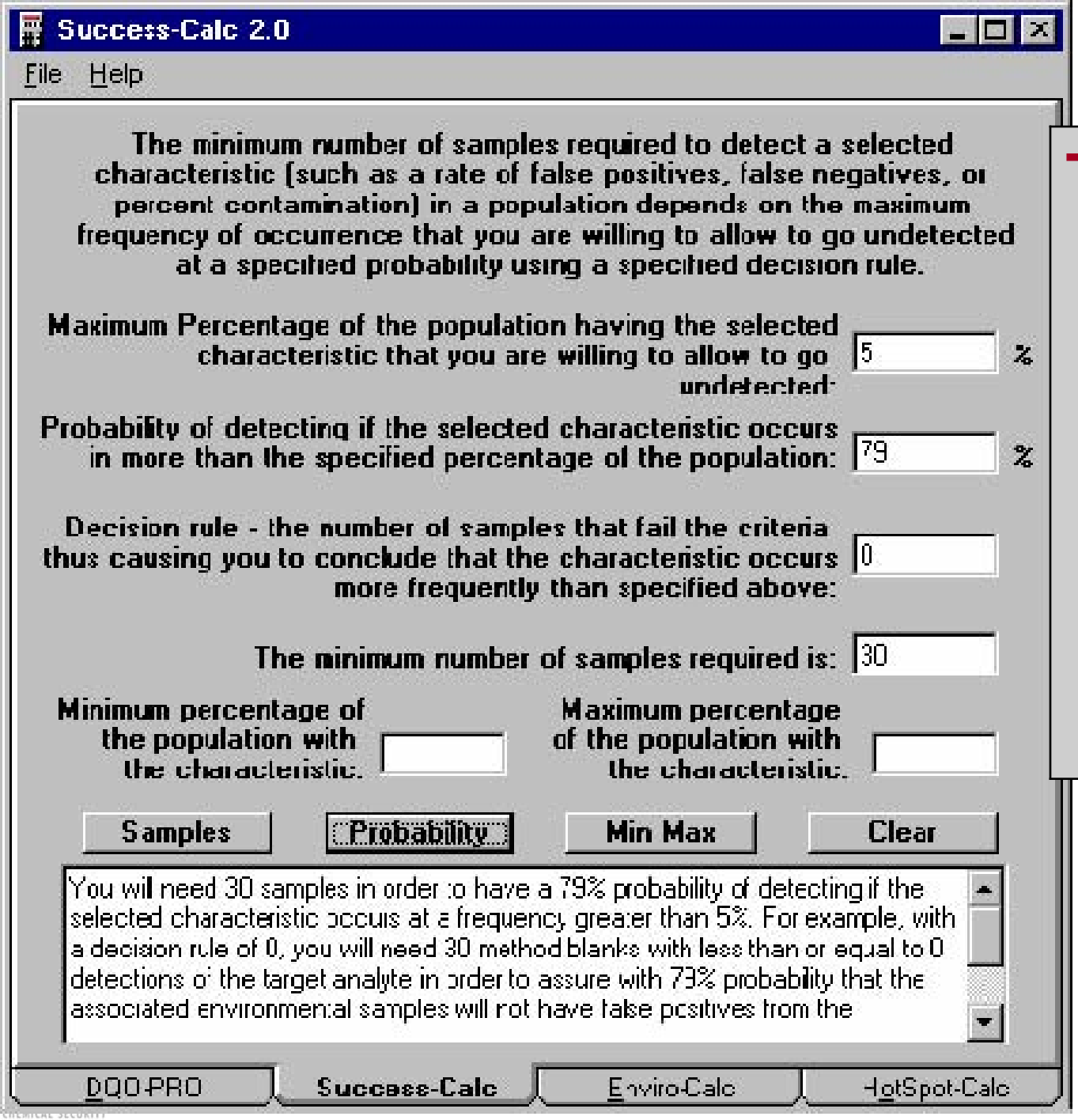
- **But, remember, the 59 method blanks do NOT <u>all</u> have to be analyzed with the samples in a specific single project.**
  - **They can be analyzed over a time period in which significant analytical parameters do not change - that could be over numerous months.**

Labs Usually Have This Data

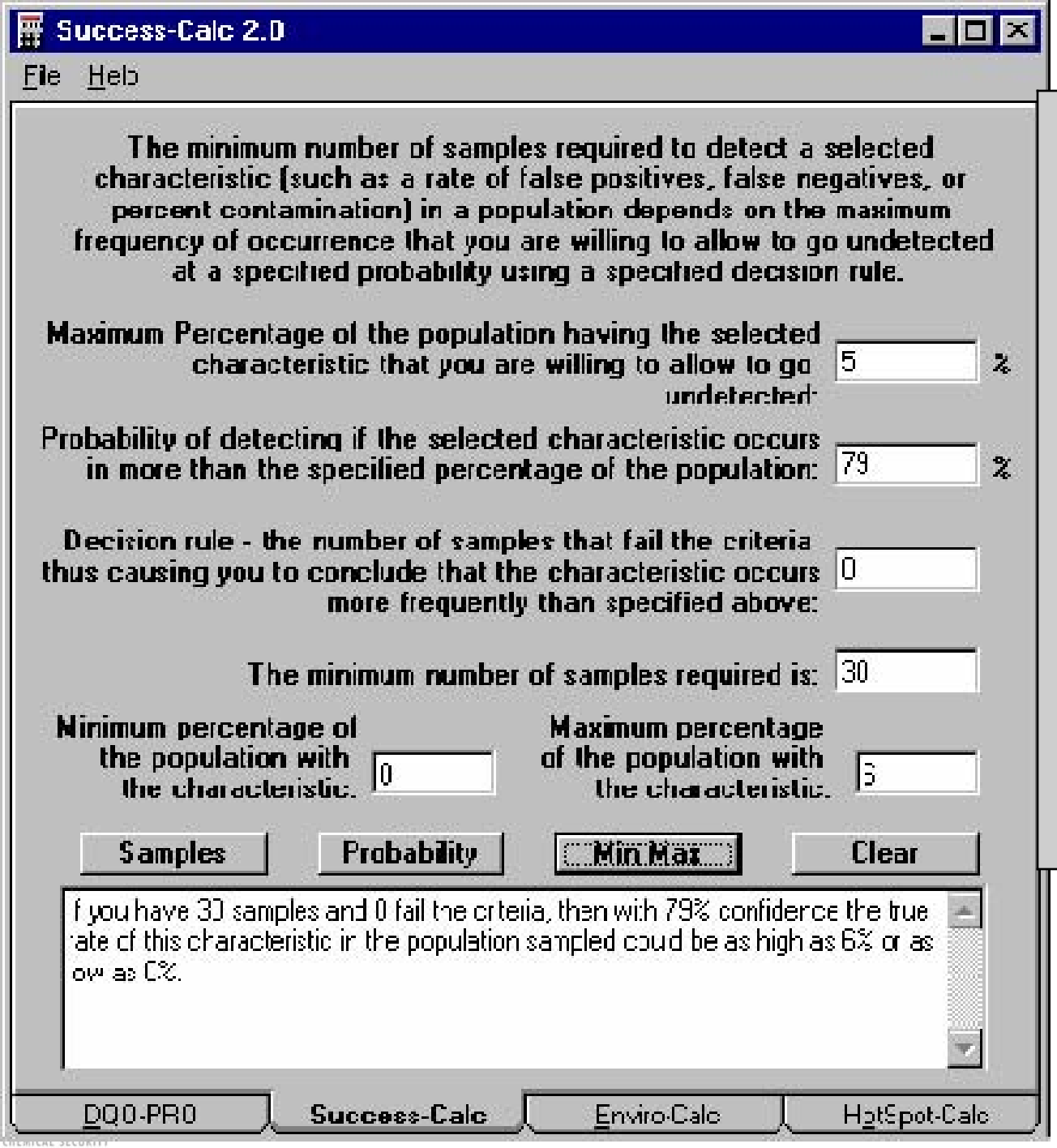
- The key is to obtain the data you need over a period of time that (1) includes the environmental samples of your project, and (2) where all significant parameters that can affect the Data Quality Assessment (DQA) criteria being used remain essentially the same during that period of time.
- Labs usually have this data but they may not store it in a way that can easily be extracted and added to a statistical pool of similar data. ASK for it.

Problem 2. What if There Are Not Enough QC Samples?

- What if only half of the desired QC samples were available?
  - Replace number of samples **"n"** with 30 and click on the button labeled "Probability"
  - What is your confidence level of detecting a maximum rate at 5% false positives or false negatives reduced to?
  - What could the maximum rate of occurrence of false positives or negatives be?



The program recalculates the new probability reduced from 95% to 79%



Clicking on the Min Max key shows that the maximum rate increases from 5% to 6%.

Problem 3. What if There Are False Positives or Negatives in the QC Data?

There may be times when the "zero" decision rule is not attained.

- If, after a QC sample set has been analyzed there are 3 false positives or false negatives among the analyte identifications what is the identifications confidence level reduced to?
- What would the minimum and maximum possible rate of false positives or negatives be? **(Use the results from the previous slide)**

Success-Calc 2.0

File Help

The minimum number of samples required to detect a selected characteristic (such as a rate of false positives, false negatives, or percent contamination) in a population depends on the maximum frequency of occurrence that you are willing to allow to go undetected at a specified probability using a specified decision rule.

Maximum Percentage of the population having the selected characteristic that you are willing to allow to go undetected: 5 %

Probability of detecting if the selected characteristic occurs in more than the specified percentage of the population. 79 %

Decision rule - the number of samples that fail the criteria thus causing you to conclude that the characteristic occurs more frequently than specified above: 0

The minimum number of samples required is: 30

Minimum percentage of the population with the characteristic: 0

Maximum percentage of the population with the characteristic: 6

Samples | Probability | Min Max | Clear

If you have 30 samples and 0 fail the criteria, then with 79% confidence the true rate of this characteristic in the population sampled could be as high as 6% or as low as 0%.

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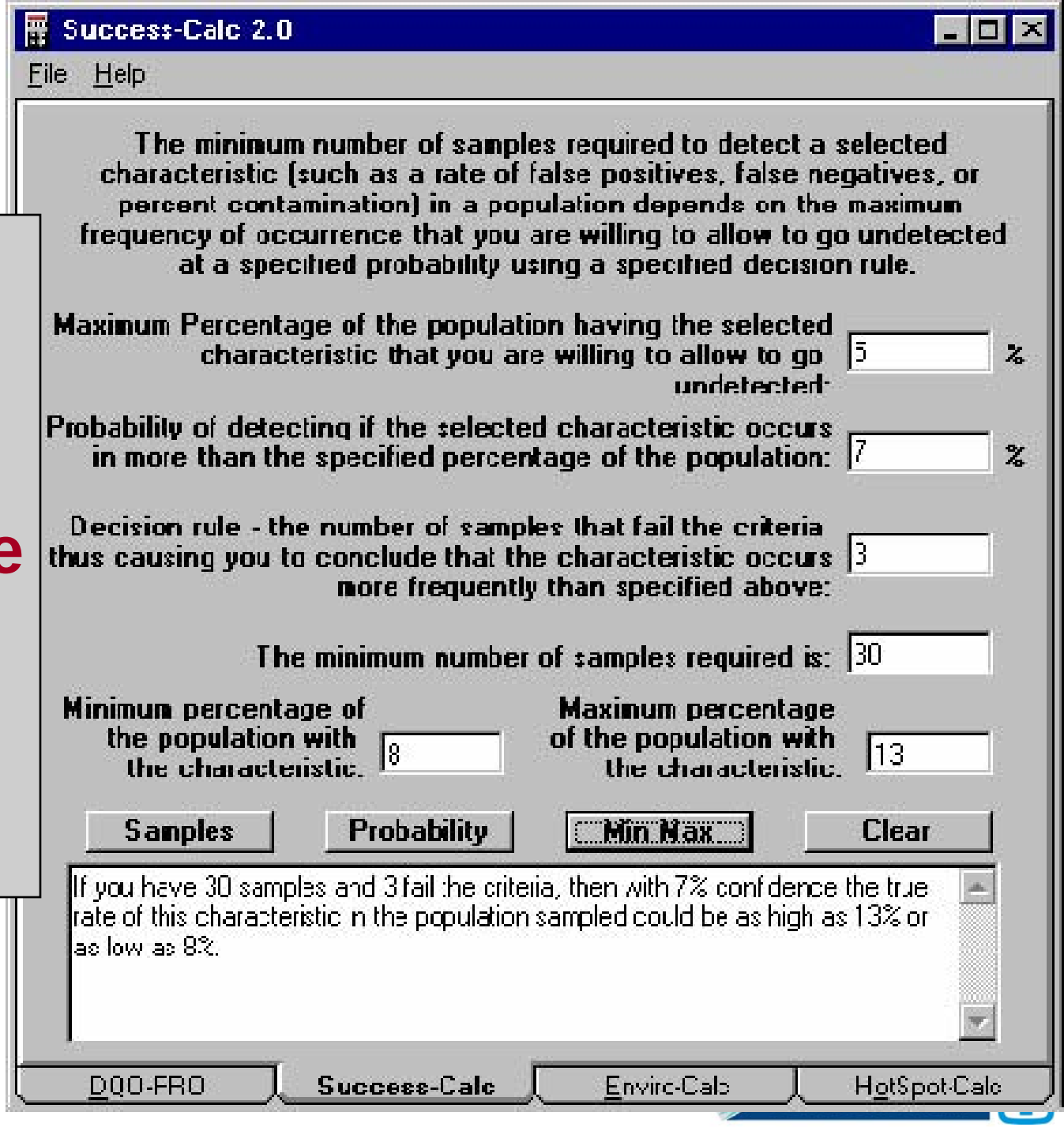
3 failures in 30 samples (decision rule = 6) reduces the probability from 79% to only 7%!

And it increases the maximum rate of false positives to13% in this example.



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Success-Calc is Powerful

- **This is the most sophisticated program of the triad yet its power is made to seem trivial by the ease of its use.**
  - **With just a few clicks of your mouse key you can easily evaluate the probability of detecting any characteristic you want to in a group of samples as long as the selected samples meet the criteria that they represent the same opportunity for detection of the same characteristic as the environmental samples do.**

Thank You!

- **We hope this tutorial will help you to understand better how to use *Success-Calc*. It is only a tool to help you estimate success.**
- **This program can be used to estimate how many samples it should take to detect a characteristic of interest in a sample population with the assumption that the samples you use will have the same opportunities of detection of that characteristic as your test samples.**
- **The purpose of *Success-Calc* is to help you make informed decisions. If you don't like the answers you get and choose to use fewer numbers of samples, that's okay. It's your decision and the purpose of *Success-Calc* is to help you make informed decisions whatever they may be.**

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Enviro-Calc

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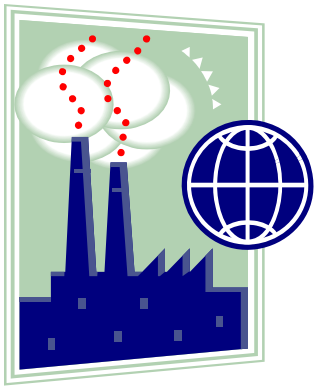
DQO-PRO Background

- ***DQO-PRO*** provides answers for three objectives:
  1. Determining the rate at which an event occurs,
  2. Determining an estimate of an average within a tolerable error, and
  3. Determining the sampling grid necessary to detect “hot spots”.
- This tutorial shows how it can be used to calculate the number of environmental samples needed for some example objectives involving **your personal** Data Quality Data Objectives.

Analytical Methods Affect Sampling

- Ways in which sampling can affect the analysis of environmental samples are typically direct and usually very clear.



- However, it is the relationship in the opposite direction that can influence the number of environmental samples needed

Analytical Methods Affect Sampling

- The analytical methods selected will influence not only the number of environmental samples that are needed, but also the amount of sample (i.e., volume or weight) and the way it is preserved if it is not analyzed immediately in the field.

- Both the amount of a sample to be collected and the way in which it is to be preserved (i.e., pH, temperature, protection from light, heat, air, etc.) influence the sampling procedures.

Analytical Methods Affect Sampling

- Thus, the effects of analytical procedures on sampling are as important as the effects of sampling procedures on the analysis.

- This is why plans for sampling and analysis are co-dependent.

- When sampling and analytical plans are developed independently of each other, the probability of obtaining data that will meet your objectives is significantly reduced.

Which Method(s) Should You Use?

- There are methods for each of the major types of pollutants.
- Metals
  - Other inorganics(cyanides, anions, etc.)
  - Volatile organics
  - Semivolatileorganics
  - Nonvolatile organics

Which Method(s) Should You Use?

- There are methods for various matrices:
  - Drinking water
  - Industrial waste waters
  - Soils, sludges, solid and liquid wastes
  - Ambient air
  - Indoor air

Which Method(s) Should You Use?

- Methods also vary by performance
  - Some are more sensitive than others
  - Some have more analytes they have been validated for
  - Some are more selective than others
  - Some have less expensive detectors than others and
  - Some have longer holding times than others.

Calculating Numbers of Environmental Samples Needed

- Numbers of environmental samples needed for many projects that involve random sampling can be calculated.
- Statistical equations may be used when the purpose of environmental sampling is to estimate the average concentration of target analyte(s) within the study boundaries.
- These types of samples are often used for fluid matrices such as air and water.

Numbers of Samples Based on Average Pollutant Concentration

- The equation $n = (z\sigma p/e)^2$ was recommended by ACS and published in "Principles of Environmental Analysis" (L. H. Keith, et. al., Anal. Chem.,1983).
  - It includes the assumption that pollutants are distributed over the entire study boundaries.
- The objective is assumed to be to determine the average concentration of the pollutants.
- The resulting characterization is for the site as a whole.

Numbers of Samples Based on Average Pollutant Concentration

- However, the equation recommended by ACS does not consider the number of samples you have in order to estimate variability.

- Therefore, a similar approach was used with other equations in **Enviro-Calc** which allow an iterative determination of the number of samples needed to meet objectives for tolerable error and confidence in estimating a mean concentration.

Equations Using Standard Deviation

- Equations for determining the number of samples needed to estimate a mean concentration when variability is estimated in absolute terms using the SD are:
  - First Pass

$$n = [Z(1\text{-alpha}/2)*SD/d]^2$$

  - Second Pass

$$n = [t(1\text{-alpha}/2)*SD/d]^2$$

Equations Using Relative Std. Dev.

- Equations for determining the number of samples to estimate a mean concentration when variability is estimated in relative terms using the coefficient of variation (relative standard deviation) are:
  - First Pass

$$n = [Z(1\text{-}alpha/2)*CV/d(r)]^2$$

  - Second Pass

$$n = [t(1\text{-}alpha/2)*CV/d(r)]^2$$

Equation Term Definitions

Z = the standard normal deviate from the Z distribution using alpha for a two-tailed distribution;

SD = the standard deviation for a sample set;

d = the amount of error tolerable in the estimate of the average in absolute terms (e.g., 4 mg/L);

(r) = the amount of error tolerable in the estimate of the average in relative terms (e.g., 5%); and,

2 = square the previous product.

Variability Affects Numbers of Samples

- When the decision of "what" and “how” to sample is complete, then a decision as to "how" the samples will be analyzed is necessary because the RSD or the SD for the method that will be used must be known or estimated.
- Analytical methods often significantly differ in the amount of variability they introduce in the data.
  - Variability is usually method, analyte and matrix specific. It is also concentration specific and the RSD usually increases as the analyte concentration level decreases.

Variability Affects Numbers of Samples

- Total variability consists of all the sources of variability in the chain of events that include sampling, sample preservation, sample preparation, sample analysis and data handling and reporting.

- In a simplistic view it can be divided into components from (1) sampling and (2) analysis.
  - Variability from sampling activities (including the heterogeneous distribution of the analytes in the environmental matrix) are usually much larger than the variability from analytical activities.

Variability Affects Numbers of Samples

- Unfortunately, variability data from sampling is often not available and we are left with only the published variability of the measurement system (typically obtained by using a reagent water matrix under the best analytical conditions).

- In addition, observed variability is usually larger than the true variability because observed variability includes variability in the population around the mean (sampling variability) plus the variability of the analytical measurement system.

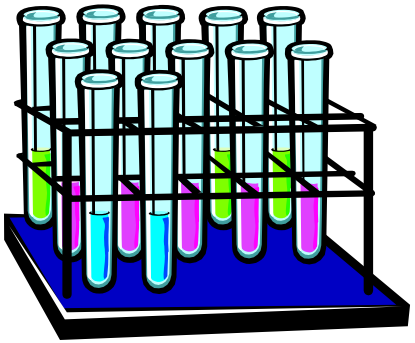
Example of How Method Variability Affects Numbers of Samples

- Most environmental analytical methods accommodate multiple pollutants.

- A list of pollutants covered by a particular method may range from half a dozen analytes to several hundred of them.
  - Exceptions involve some methods for elements (involving atomic absorption spectrophotometers), cyanide, ammonia, etc.

Example of How Method Variability Affects Numbers of Samples

- It is clear that the numbers of samples to be collected depends, in part, on the method that will be used.



- When multiple methods will be used (in order to analyze all the pollutants of interest), and the samples will be subdivided, then the number of samples to be collected will depend on the method with the largest variability (highest SD or RSD).

Example of How Method Variability Affects Numbers of Samples

- Values for SDs or RSDs may be obtained from each of the methods or in one or more publications that contain short method summaries.
  - Several sources of method summaries contain all info needed to decide which method would be best.
  - Each contains SDs or RSDs, detection levels, instrumentation required, interferences, sample collection and preservation, brief description of the method and the matrices for which it is used, reference source, etc.
- Help you quickly and easily find the info needed to calculate how many samples are needed and which method is the best for your DQOs.

Example of How Method Variability Affects Numbers of Samples

- Enviro-Calc is an easy to use computer program that calculates the number of samples needed based on the iterative equations discussed above. It uses the familiar user interface of a calculator.

- Programmed using Windows Visual Basic, it is one of a trilogy of computer programs used to help you calculate the number of samples needed to meet your specific objectives.

Example of How Method Variability Affects Numbers of Samples

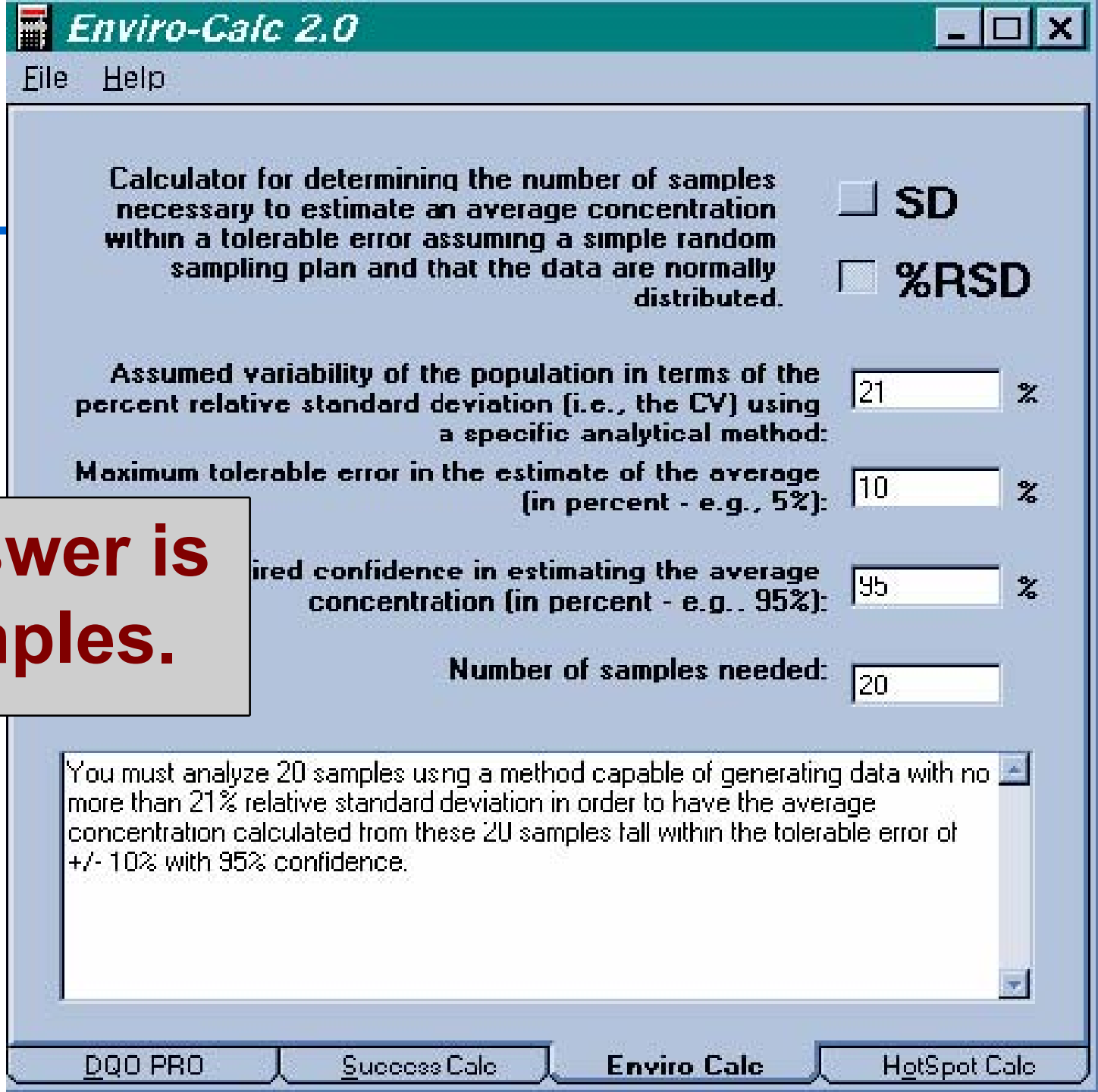
EPA Method	RSD
1625	21%
625	34%
8270	34%
8040	24%

RSDs are for pentachlorophenol in water at a concentration of 100 ug/L.
They were calculated from published SDs in the EPA methods.

Problem 1. How many samples are needed for a method with RSD of 21%?

- How many water samples would be needed for 100 ug/L (avg.) samples of pentachlorophenolto not exceed a maximum tolerance error of +/-10% and a 95% confidence level if EPA Method 1625 was used?

(RSD = 21%)



The answer is 20 samples.

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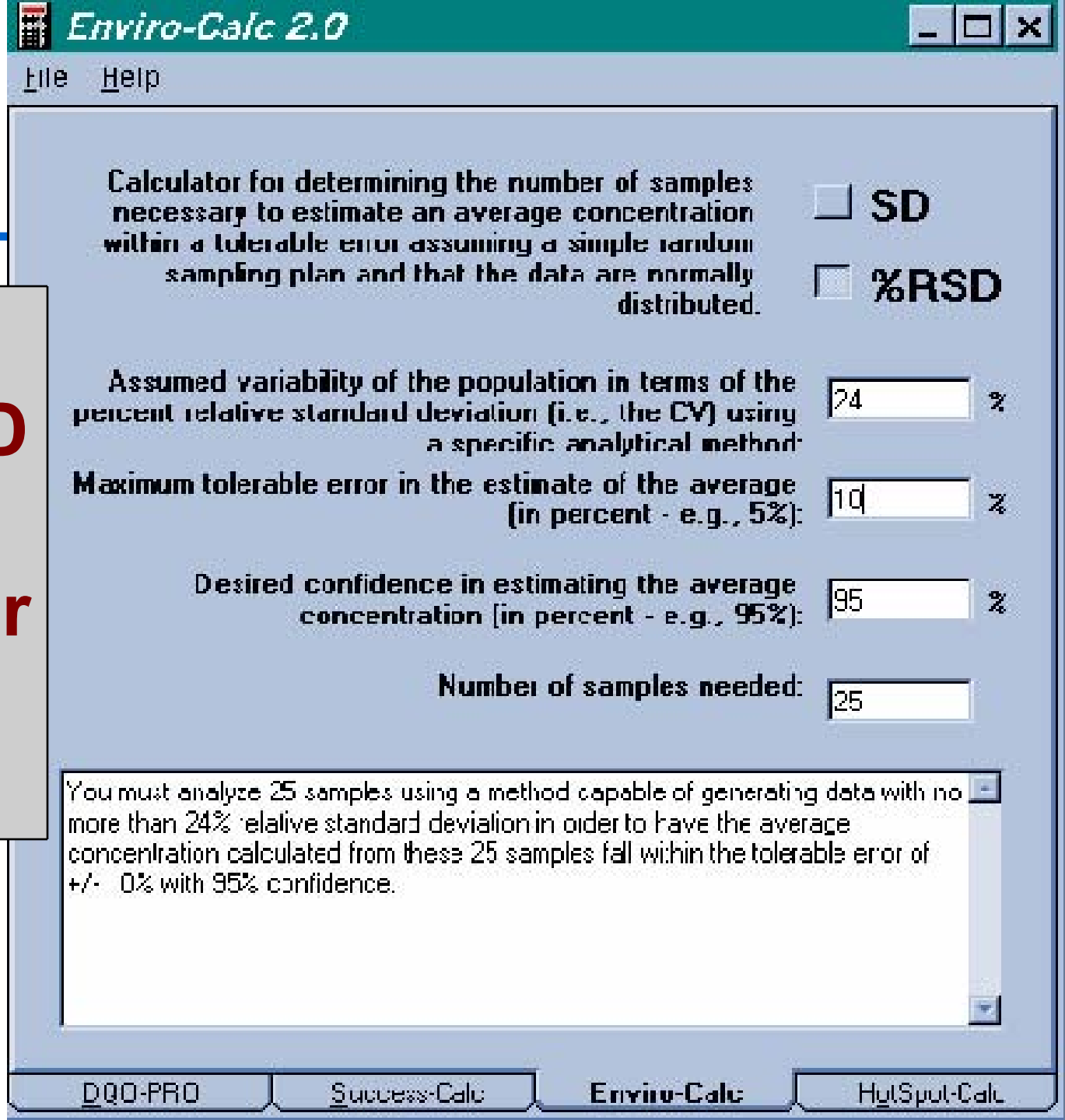
Problem 2. How many samples are needed for a method with RSD of 24%?

- How many samples would be needed for 100 ug/L (avg.) samples of pentachlorophenol to not exceed a maximum tolerance error of +/-10% and a 95% confidence level if EPA Method 8040 was used?

(RSD = 24%)

With a larger RSD of 24%, the answer is 25 samples.



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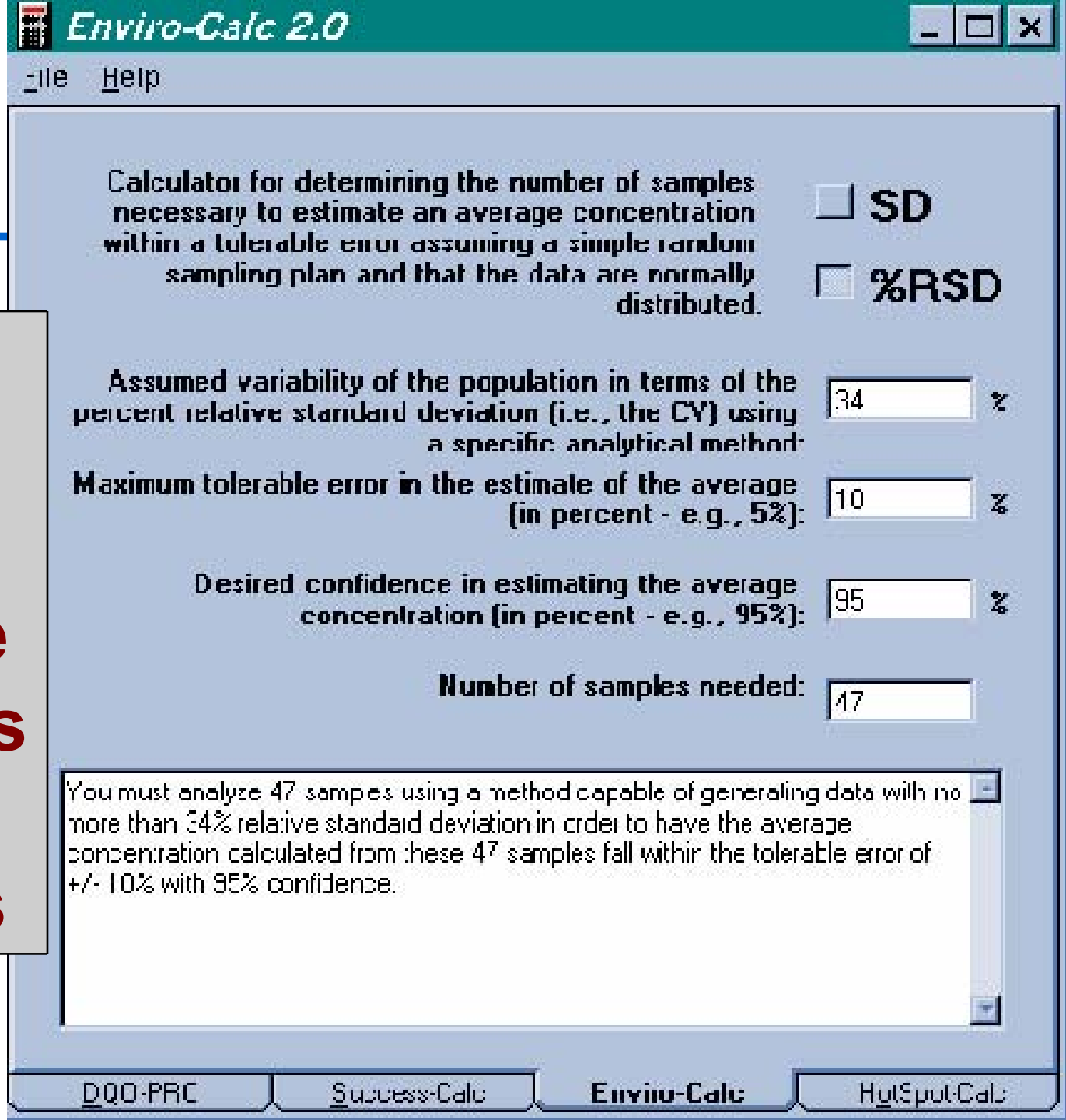
Problem 3. How many samples are needed for a method with RSD of 34%?

- How many samples would be needed for 100 ug/L (avg.) samples of pentachlorophenol to not exceed a maximum tolerance error of +/-10% and a 95% confidence level if EPA Method 625 or 8270 was used?

(RSD = 34%)

With a larger RSD of 34%, the answer is 47 samples



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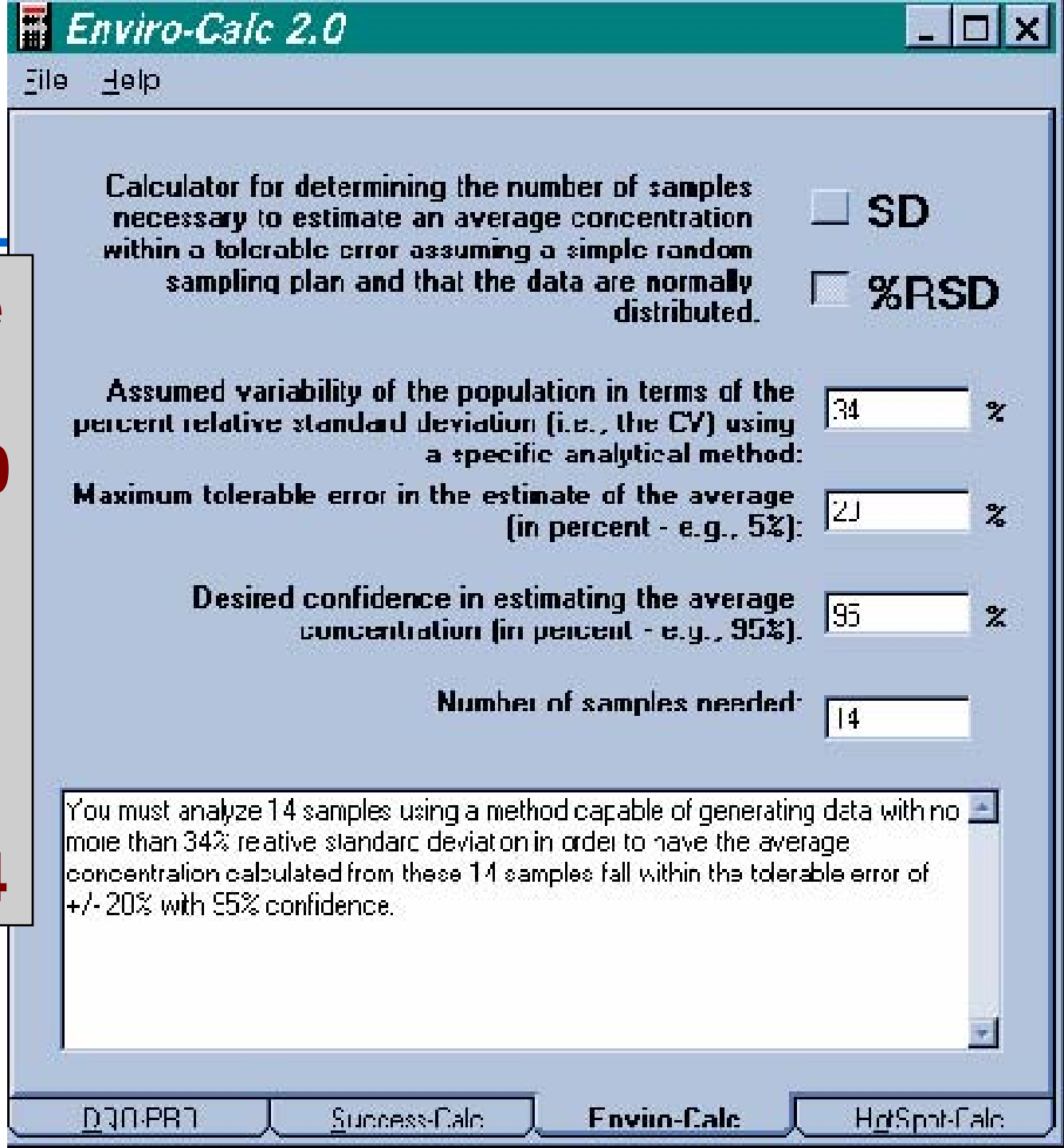
Problem 4. What is the effect of changing the tolerable error?

- How many samples would be needed for 100 ug/L (avg.) samples of pentachlorophenol to not exceed a maximum tolerable error of +/-20% and a 95% confidence level if EPA Method 625 or 8270 was used?
- What is the effect if the maximum tolerable error is changed to +/-5% with a 95% confidence level.

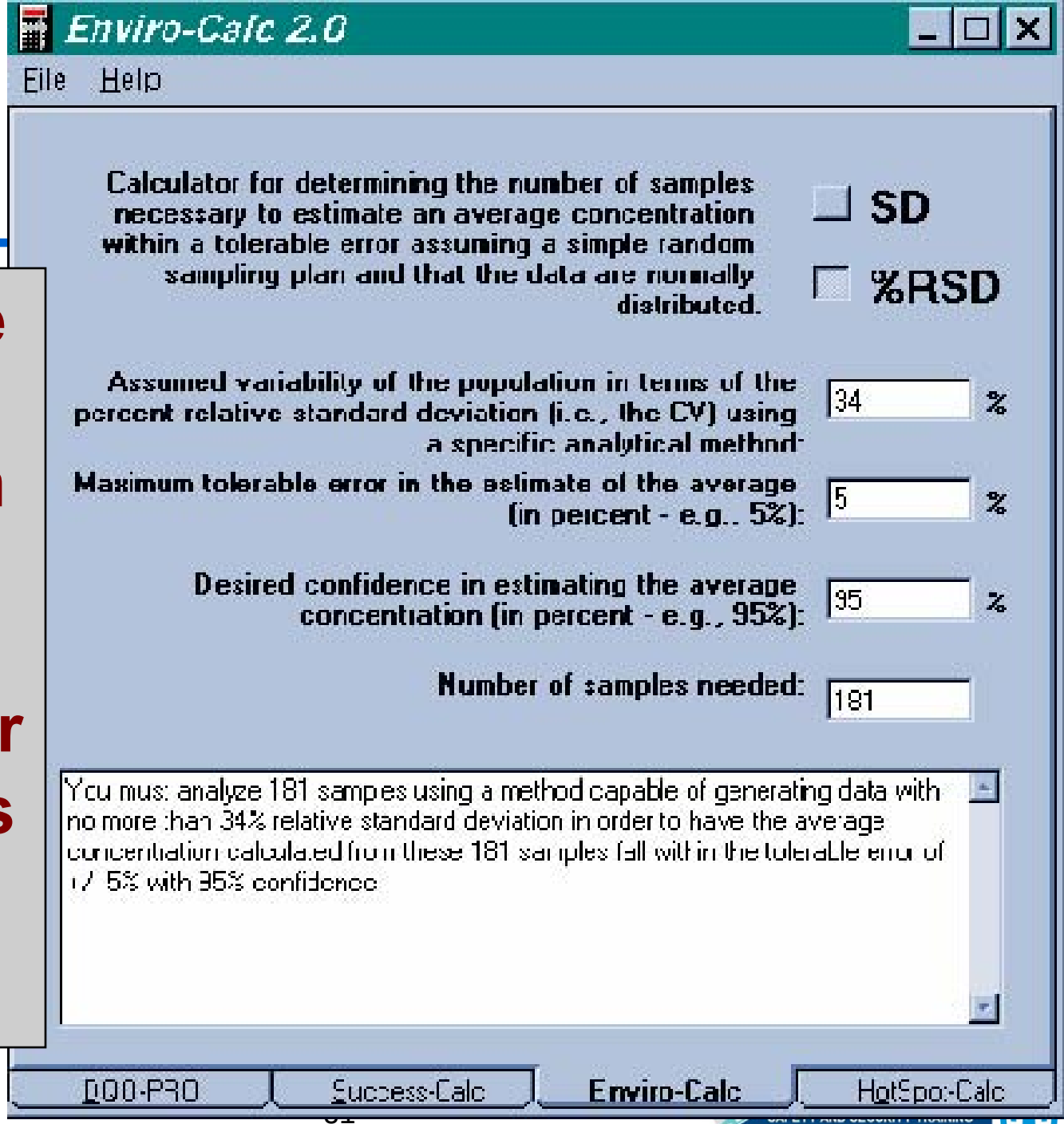
(RSD = 34%)

Doubling the Tolerable Error from 10 to 20% reduced the number of samples from 47 to 14



CSP
CHEMICAL SECURITY ENGAGEMENT PROGRAM

Halving the Tolerable Error from 10 to 5% Increased the number of samples from 47 to 181



Problem 5. What is the effect of changing the confidence level?

- How many samples would be needed for 100 ug/L (avg.) samples of pentachlorophenol to not exceed a maximum tolerance error of +/- 5% and a 90% confidence level if EPA Method 625 or 8270 was used?

(RSD = 34%)

- What if the confidence level is 99%?
- What if the confidence level is only 50%?

Enviro-Calc 2.0

File Help

Calculator for determining the number of samples necessary to estimate an average concentration within a tolerable error assuming a simple random sampling plan and that the data are normally distributed.

☐ SD

☐ %RSD

Assumed variability of the population in terms of the percent relative standard deviation (i.e., the CV) using a specific analytical method: 34 %

Maximum tolerable error in the estimate of the average (in percent - e.g., 5%): 5 %

Desired confidence in estimating the average concentration (in percent - e.g., 95%): 90 %

Number of samples needed: 127

You must analyze 127 samples using a method capable of generating data with no more than 34% relative standard deviation in order to have the average concentration calculated from these 127 samples fall within the tolerable error of +/- 5% with 90% confidence

CQD PRO | Success Calc | Enviro Calc | Ho:Spo: Calc

Decreasing the Confidence Level from 95% to 90% decreased the number of samples from 181 to 127

Enviro-Calc 2.0

File Help

Calculator for determining the number of samples necessary to estimate an average concentration within a tolerable error assuming a simple random sampling plan and that the data are normally distributed

☐ SD

☐ %RSD

Assumed variability of the population in terms of the percent relative standard deviation (i.e., the CV) using a specific analytical method: 34 %

Maximum tolerable error in the estimate of the average (in percent - e.g., 5%): 5 %

Desired confidence in estimating the average concentration (in percent - e.g., 95%): 99 %

Number of samples needed: 311

You must analyze 311 samples using a method capable of generating data with no more than 34% relative standard deviation in order to have the average concentration calculated from these 311 samples fall within the tolerable error of +/- 5% with 99% confidence.

DQO-PRO | Success-Calc | Enviro-Calc | HotSpot-Calc

Increasing the Confidence Level from 95 to 99% Increased the number of samples from 181 to 311

Problem 6. What is the effect of Pushing the limits of the equations?

- How many samples would be needed for a 95% confidence level to estimate an average concentration of 500 ng/L of an analyte using a method in which the Standard Deviation was 100 ng/L and the maximum tolerance level is 50 ng/L?

Enviro-Calc 2.0

File Help

Calculator for determining the number of samples necessary to estimate an average concentration within a tolerable error assuming a simple random sampling plan and that the data are normally distributed.

☐ SD

☐ %RSD

Assumed variability of the population in terms of the percent relative standard deviation (i.e., the CV) using a specific analytical method: 34 %

Maximum tolerable error in the estimate of the average [in percent - e.g., 5%]: 5 %

Desired confidence in estimating the average concentration [in percent - e.g., 95%]: 99 %

Number of samples needed: 311

You must analyze 311 samples using a method capable of generating data with no more than 34% relative standard deviation in order to have the average concentration calculated from these 311 samples fall within the tolerable error of +/- 5% with 99% confidence.

DQO-PRO | Success-Calc | Enviro-Calc | HotSpot-Calc

The answer is 18 but what if the Max. Tolerable Error is increased to 100 ng/L? or to135 ng/L?

Tolerable Error Should <u>not</u> Exceed 75% of the SD or RSD

- Using the previous example: when the maximum tolerable error is increased from 50 ng/L to 100 ng/L then the number of samples calculated decreases from 18 to 8.

- When the maximum tolerable error is increased to 135 ng/L then the number of samples increases to 90 - a change of direction from decreasing to increasing numbers.

Enviro-Calc 2.0

File Help

Calculator for determining the number of samples necessary to estimate an average concentration within a tolerable error assuming a simple random sampling plan and that the data are normally distributed

☐ SD

☐ %RSD

Assumed variability of the measurement population in terms of the standard deviation using a specific analytical method: 100

Maximum tolerable error in the estimate of the average (in same units as SD): 100

Desired confidence in estimating the average concentration (in percent - e.g., 95%): 95 %

Number of samples needed: 8

You must analyze 8 samples using a method capable of generating data with no more than 100 units of standard deviation in order to have the average concentration calculated from these 8 samples fall within the tolerable error of +/- 100 units with 95% confidence. The tolerable error is approaching the level of variability in the population where sample size calculators are imprecise so use the estimated number of samples with caution.

DQO PRO | Success Calc | Enviro Calc | HotSpot Calc

Note the Warning Text that appears when the Maximum Tolerable Error Equals or Exceeds the RD or RSD.

Chemical SAFETY AND SECURITY TRAINING

WARNING

Do not use estimates from Enviro-Calc when the maximum tolerable error equals or exceeds the standard deviation or relative standard deviation.

What Other Warnings are Applicable?

- Up to this point only the variability in data from the analytical method has been considered.

- What about other sources of variability in data from environmental samples?

Estimates Based Only on Analytical Variances Will Be Wrong

- Remember that calculations of estimated numbers of samples needed based only on analytical method SDs or RSDs will result in **underestimated** numbers of samples because only the analytical variances are considered.
  - In fact, variances from the sampling operations are usually **larger** than those from the analytical operations.
- Thus, to obtain more accurate estimates of numbers of samples needed, SDs or RSDs from **overall sampling and analysis operations** should be used.

Then How is Enviro-Calc Useful?

- In the preceding examples Enviro-Calc served to evaluate the relative number of samples that would be needed for a desired tolerable error and confidence level from four different EPA methods.

- If you preferred EPA Method 8040, perhaps because it is a less expensive (but also less specific) method using GC/ECD, the number of samples needed based on analytical RSD was 25.

Then How is Enviro-Calc Useful?

- Thus, Enviro-Calc was useful by providing information that showed EPA Method 8040 would require about 20% more samples than the most precise and more expensive method (EPA Method 1625).
- Assuming that you do not have information on the RSD of the sampling components, how can you estimate how many samples you need to accommodate total variability using Method 8040?

Then How is Enviro-Calc Useful?

- There is no good answer. A rule of thumb is that you could estimate that the variability of sampling is at least two to three times the analytical variability.

- If we assumed that the total variability of sampling and analysis for Method 8040 was about 50 to 75%, how many samples would be needed to provide data with a 95% probability of a tolerable error that won't exceed +/-10% when the concentration of pentachlorophenol is 100 ug/L?

Enviro-Calc 2.0

File Help

Calculator for determining the number of samples necessary to estimate an average concentration within a tolerable error assuming a simple random sampling plan and that the data are normally distributed.

SD

%RSD

Assumed variability of the population in terms of the percent relative standard deviation (i.e., the CV) using a specific analytical method: 50 %

Maximum tolerable error in the estimate of the average (in percent - e.g., 5%): 10 %

Desired confidence in estimating the average concentration (in percent - e.g., 95%): 95 %

Number of samples needed: 99

You must analyze 99 samples using a method capable of generating data with no more than 50% relative standard deviation in order to have the average concentration calculated from these 99 samples fall within the tolerable error of +/- 10% with 95% confidence.

DQO-PRO | Success-Calc | Enviro-Calc | HotSpot-Calc

About one hundred samples would be needed if we assumed that the RSD of sampling and analysis was about 50%.

Chemical SAFETY AND SECURITY TRAINING

Enviro-Calc 2.0

File Help

Calculator for determining the number of samples necessary to estimate an average concentration within a tolerable error assuming a simple random sampling plan and that the data are normally distributed.

SD

%RSD

Assumed variability of the population in terms of the percent relative standard deviation (i.e., the CV) using a specific analytical method: 75

Maximum tolerable error in the estimate of the average (in percent - e.g., 5%): 10

Desired confidence in estimating the average concentration (in percent - e.g., 95%): 95

Number of samples needed: 219

You must analyze 219 samples using a method capable of generating data with no more than 75% relative standard deviation in order to have the average concentration calculated from these 219 samples fall within the tolerable error of +/- 10% with 95% confidence.

DQO PRO | Success Calc | Enviro Calc | HotSpot Calc

Over two hundred samples would be needed if we assumed that the RSD of sampling and analysis was about 75%.

Chemical SAFETY AND SECURITY TRAINING

Advantages of *Enviro-Calc*

- The great advantage lies in your ability to make rapid assessments of DQO or project objective changes.

- Often initial objectives cannot be met due to budget or time constraints, inability of the method to perform at its published levels (matrix effects, interferences, etc.).

- You can quickly assess (either before or after samples have been analyzed) the consequences of missed DQOs and determine the consequences to either the maximum tolerable error or the confidence level would be if fewer samples were analyzed.

Advantages of *Enviro-Calc*

- For example, if only 10 samples were able to be analyzed using Method 8040, then:
  - at the same 95% confidence level the maximum analytical tolerable error would increase from 10% to 18% and the total tolerable error would range from about 37% to 55% (assuming 50 -75% RSD) or,
  - at the same 10% tolerable error the analytical confidence level would decrease from 95% to 77% and the total confidence level would range from about 45% to 31% (assuming 50 -75% RSD, respectively).

How Were These Estimated Determined?

- The estimates on the previous slide were determined simply by leaving one of the two parameters (tolerable error or RSD) alone and varying the other until the answer was estimated to be 10 samples.

- This is very **quick and easy** to do.

Advantages of *Enviro-Calc* (cont.)

- With this kind of information, people can readily assess their DQOs and modify them as needed to meet time and budget limitations.

- In addition, when evaluating reports of analytical data, if the minimum numbers of samples were not available for your DQOs, you can quickly calculate the approximate confidence levels that the data have for a desired tolerable error in the data.

- This enables you to make a rapid assessment of whether the data will be useful or not for your specific needs.

Thank You!

- We hope this tutorial will help you to understand better how to use *Enviro-Calc*. It is only a tool to help you estimate how many samples you need to meet your specific goals.
- This program should be used to determine the number of samples needed to estimate an average analyte concentration in a specific matrix using a specific method.
- It's purpose is to help you make informed decisions. If you don't like the answers you get and choose to use fewer numbers of samples, that's okay. It's your decision and the purpose of *Enviro-Calc* is to help you make informed decisions whatever they may be.

DQO-PRO Tutorial - HotSpot-Calc

Dr. Lawrence H. Keith, Director of Environmental Chemistry
Environmental & Chemical Safety Educational Institute
Monroe, Georgia USA

- This Tutorial is based on the DQO-PRO Version 2
- The program was written by Dr. Keith and two other scientists (G.L. Patton and P.G. Edwards) at Radian International LLC for the U.S. Government.
- DQO is free and may be copied and freely distributed.
- (Basis for Equations are found on the HELP tab of DQO-PRO Main Page)

DQO-PRO Background

DQO-PRO provides answers for three objectives:

1. determining the rate at which an event occurs,
2. determining an estimate of an average within a tolerable error, and
3. determining the sampling grid necessary to detect "hot spots".

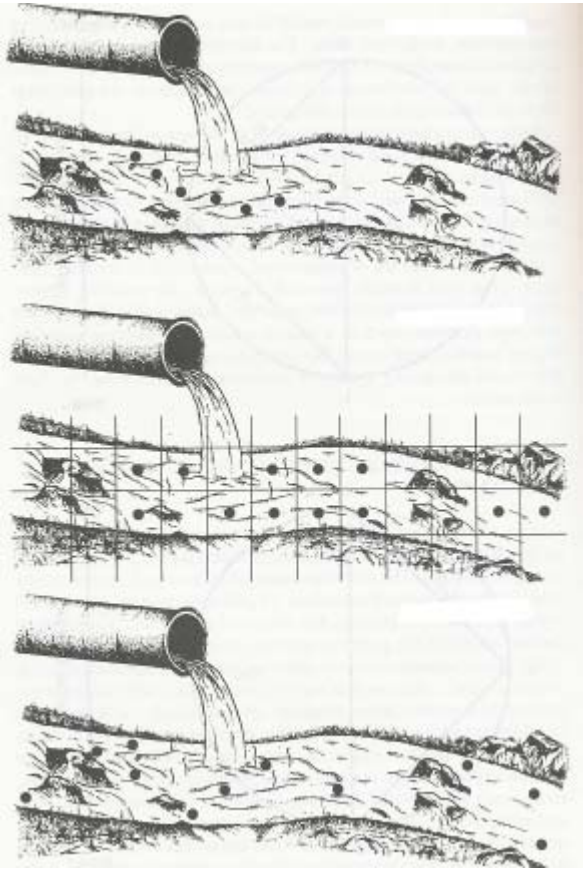
- This tutorial shows how it can be used to calculate the number of samples needed for some example objectives involving a sampling grid for systematic sampling.

Basic Sampling Types - Review

- There are many different types of sampling
  (stratified sampling, random sampling at sites judgmentally chosen etc).

- But they are all combinations or variations of three basic types of sampling:
  1. Systematic Sampling
  2. Random Sampling,
  3. Judgmental Sampling

Representative sampling is a great challenge- sampling types



Judgmental Sampling

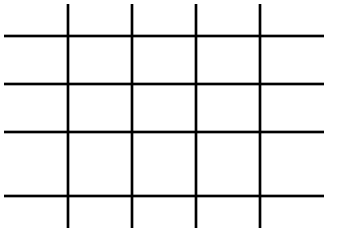
Systematic Sampling

Random Sampling

From: *Environmental Sampling and Analysis.* 1991 Larry Keith

Systematic Sampling

- Systematic sampling typically involves placing a grid over a map, or marking the sampling site, and then collecting samples at every node where the lines cross or in the center of each grid. Various shaped grids are used.



- The most common shapes are triangles, squares, or rectangles

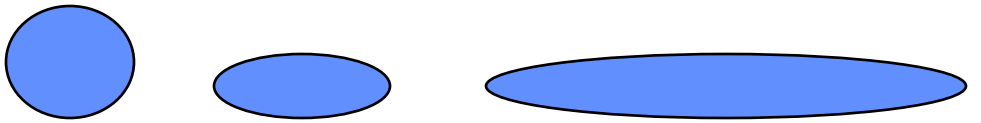
Systematic Sampling

- Systematic sampling using a grid is usually used with contaminated land-based sites.

- It may be used to collect samples of soil from a landfill, to drill wells to collect samples of groundwater, or to collect aqueous sediments from the bottom of a lake or the sea.

HotSpot - Calc Assumptions

- HotSpot-Calc is designed to determine the grid spacing needed to detect the presence of a single hot spot of a specified size and shape with a specified probability of **missing** the hot spot. It is based on the following key assumptions:



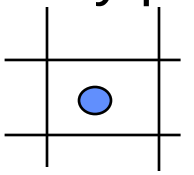
1. That the hot spot is circular, short elliptical or long elliptical in shape;
2. That sample measurements are collected on square, rectangular, or triangular grids;
3. That the definition of a "hot spot" is clear and agreed to by all decision makers; and,
4. That there are no classification errors (i.e., that there are no false-positive or false-negative measurement errors).

Hot Spot Sampling Objectives

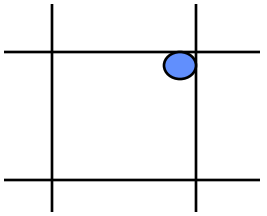
- The primary objective of hot spot sampling is to determine if localized areas of contamination exist.
  - These localized areas of contamination may be due to spills, leaks, buried waste, or any number of other events where contamination might be confined to a relatively small area.
  - A single site might have multiple hot spots of different origins.

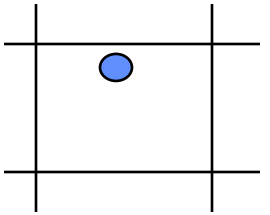
Systematically Sampling a Grid

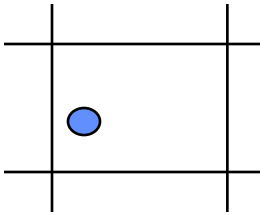
- Basically, hot spot sampling involves performing a systematic search of a site for "hot spots" of a certain specified shape and area.
  - The search is conducted by sampling every point on a two-dimensional grid.



  - Samples are usually taken either in the center of every grid or randomly within every grid area.

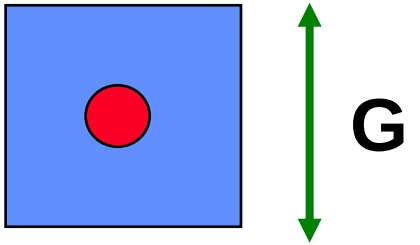






Calculating Numbers of Samples

The number of samples required for hot spot sampling is the number of samples required to sample **all grid areas** at the site for the selected grid spacing. The number of samples required for a **square grid** is approximated by the equation:



$$n = A/G^2$$

where,

n = number of samples,
A = area to be sampled, in the square of the units for G
G = grid spacing.

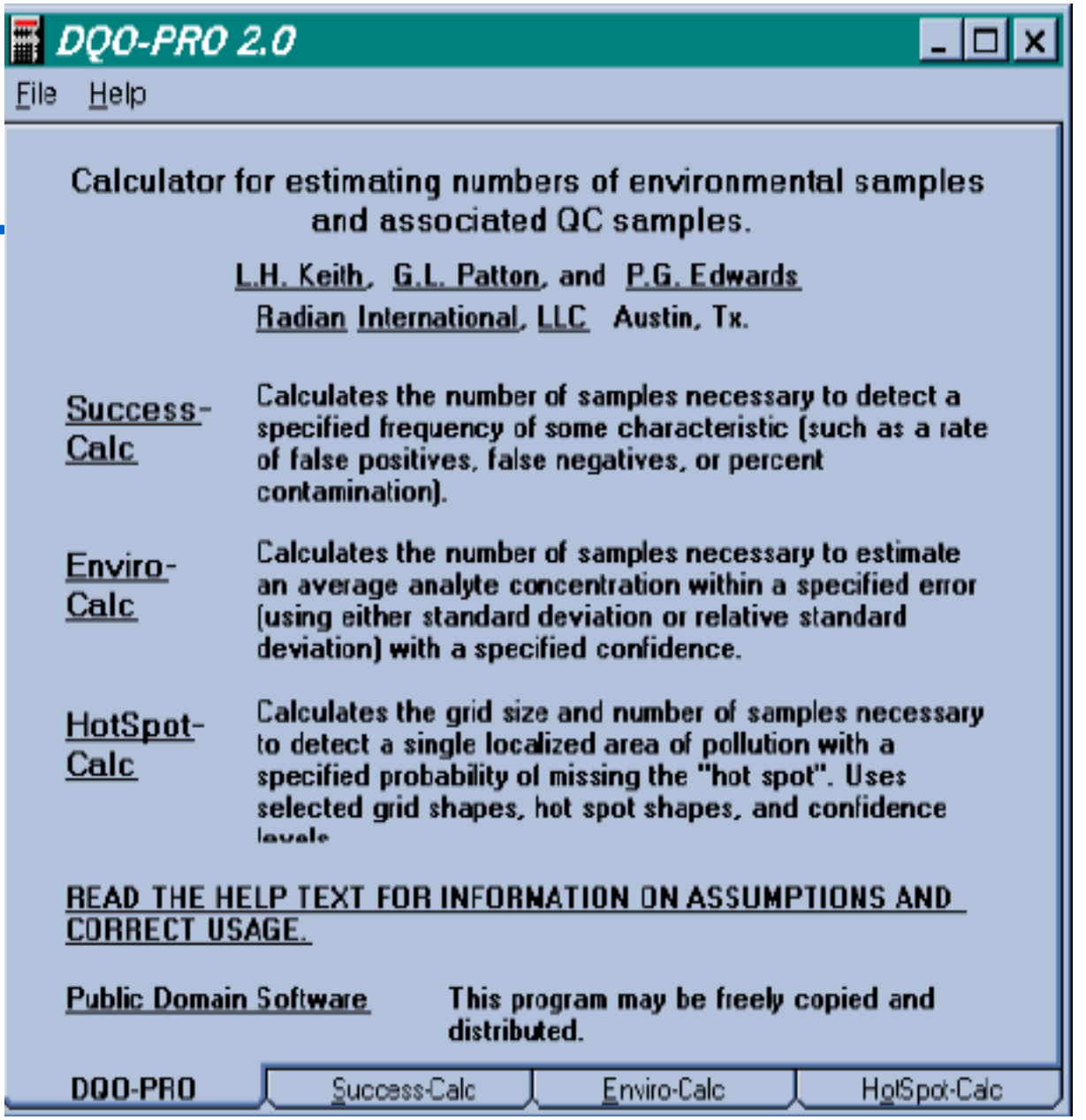
HotSpot - Calc Probability

- The probability of finding a hot spot is determined as a function of the specified size and shape of the hot spot, the pattern of the grid, and the relationship between the size of the hot spot and the grid spacing.

- HotSpot-Calc is programmed based on the probability of **missing** a hot spot if one exists rather than on the probability of finding one.

- **The Opening Screen of DQO-PRO**

- Underlined Words are Hyperlinked to Programs, Help or Definitions



HotSpot-Calc

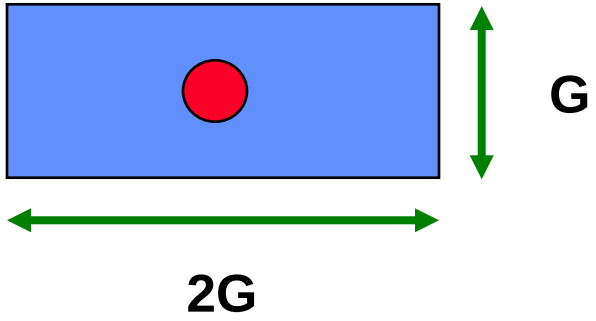
- HotSpot-Calc is used to determine the grid size needed to detect the presence of a single localized spot of pollutants (“hot spot”) of a specified size and shape with a specified probability of missing its detection if it is present.

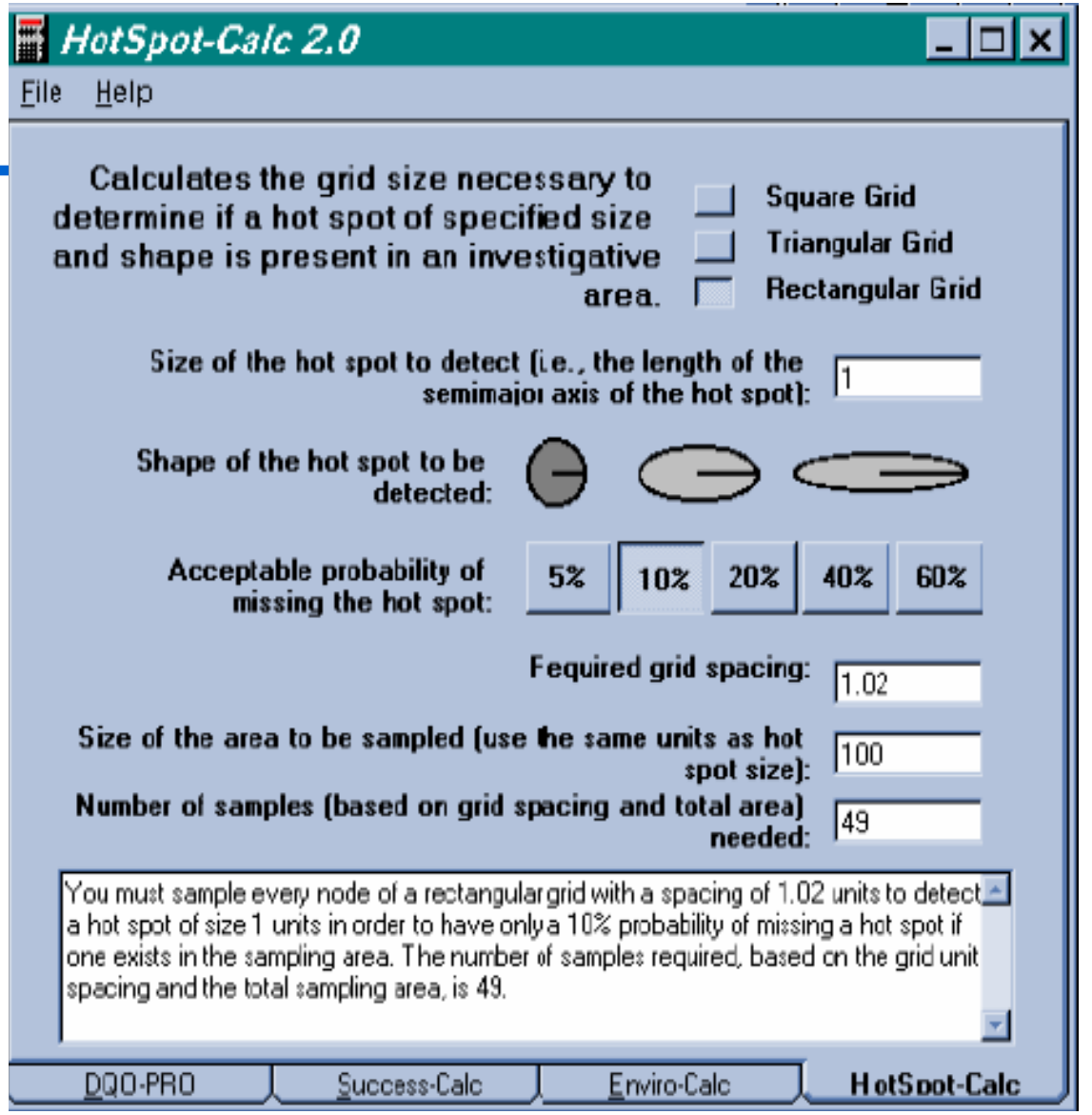
- Once the grid size is calculated, then the number of samples needed are automatically calculated by dividing the sampling area by the square of the grid size

Inputs to HotSpot-Calc

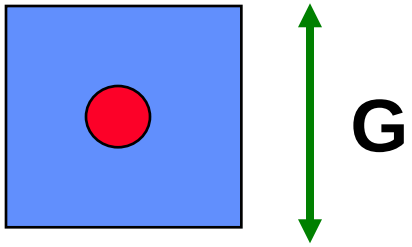
- The shape of the grid that will be used
  - (e.g., triangle, square or rectangle),
- The size and shape of the spot
  - (e.g., circle, ellipse, or long ellipse),
- The acceptable probability of **missing** it
  - (e.g., 10%, 20%, etc.), and
- The size of the area to be sampled
  - (e.g., 100 square meters, 2 square miles, etc.).

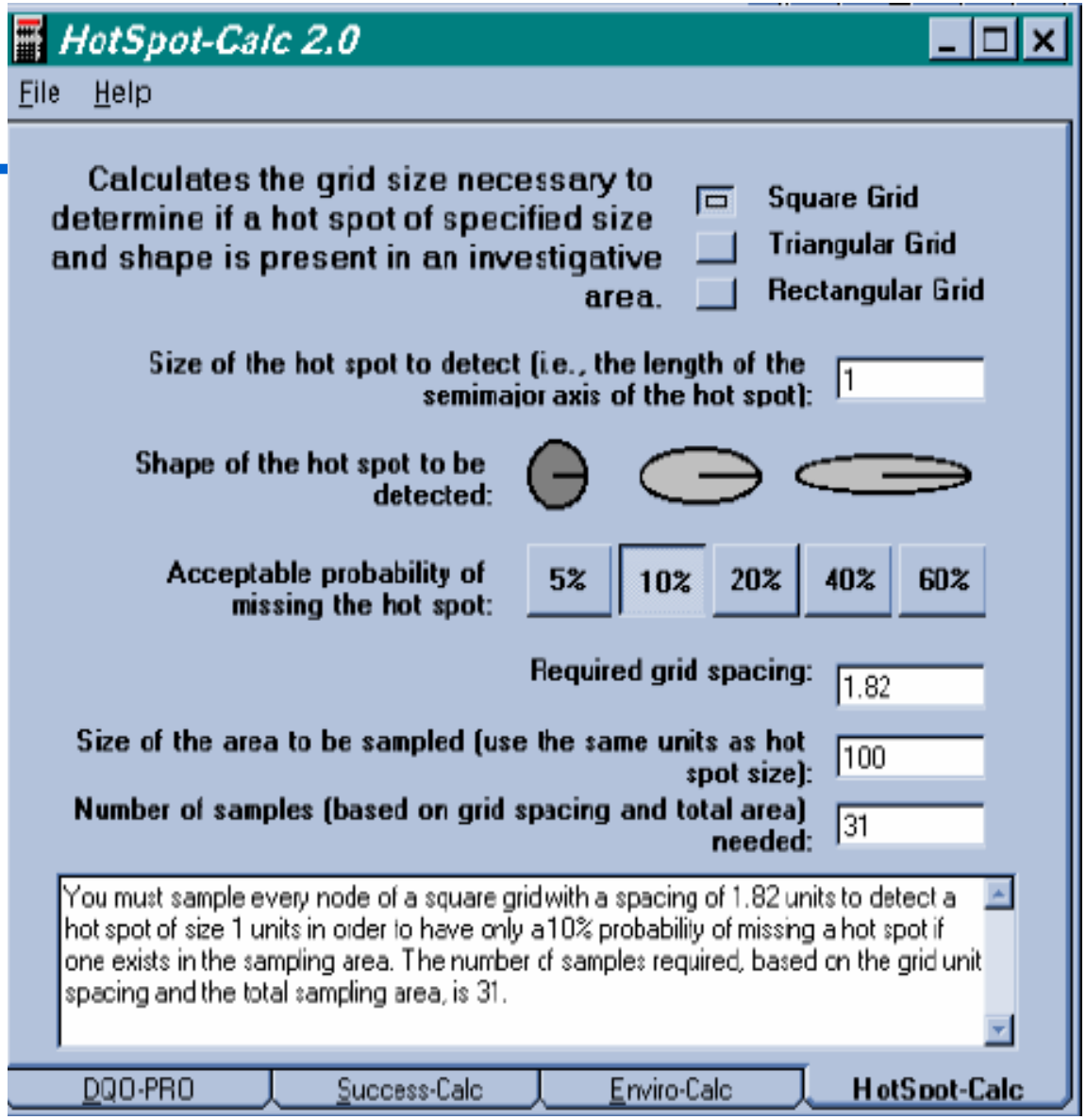
- Assume a Rectangular Grid, a Round Spot, and a 10% Probability of Missing the Hot Spot



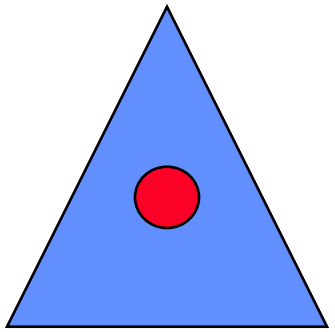


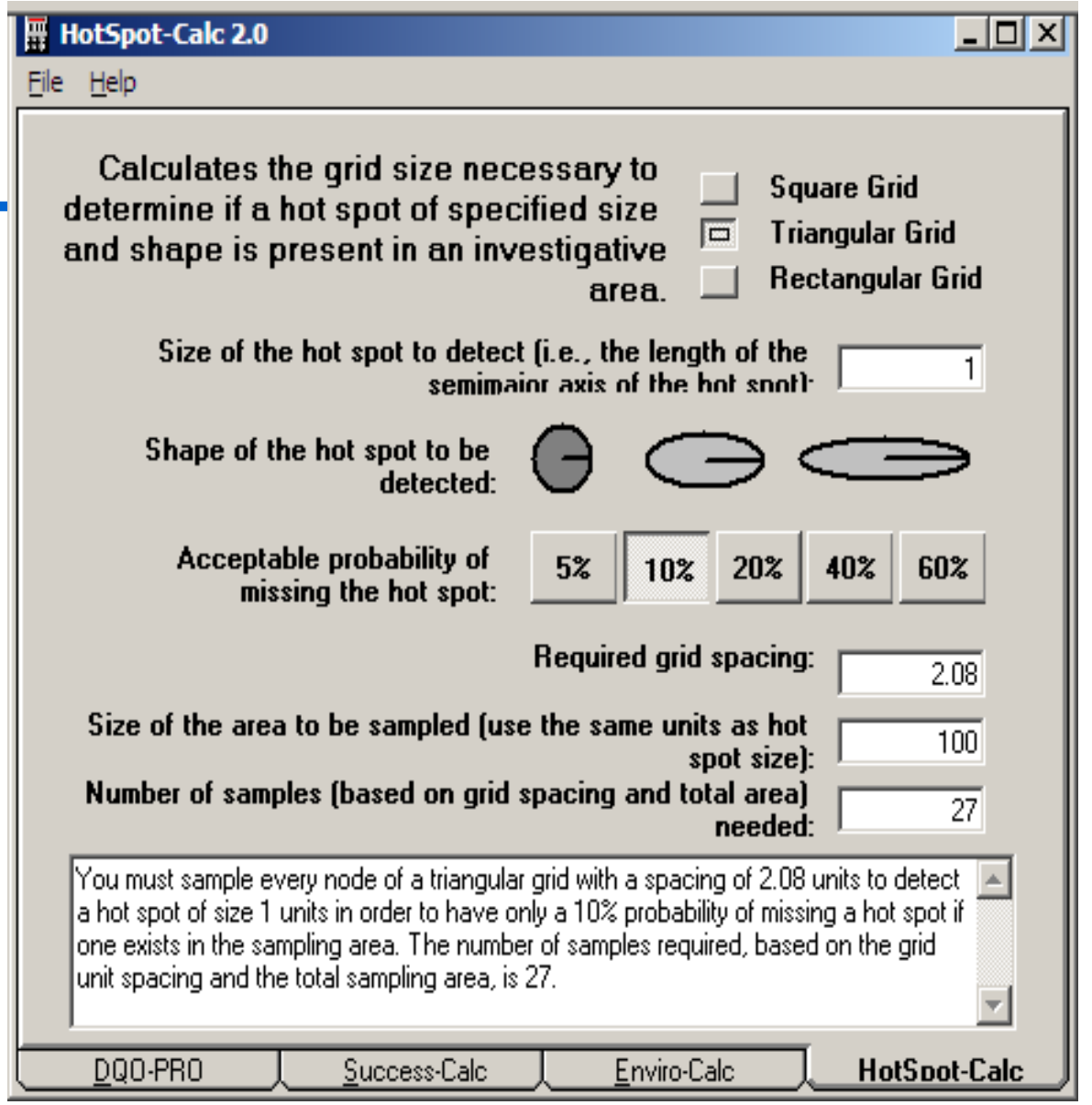
- What if the Grid is Changed to a Square?





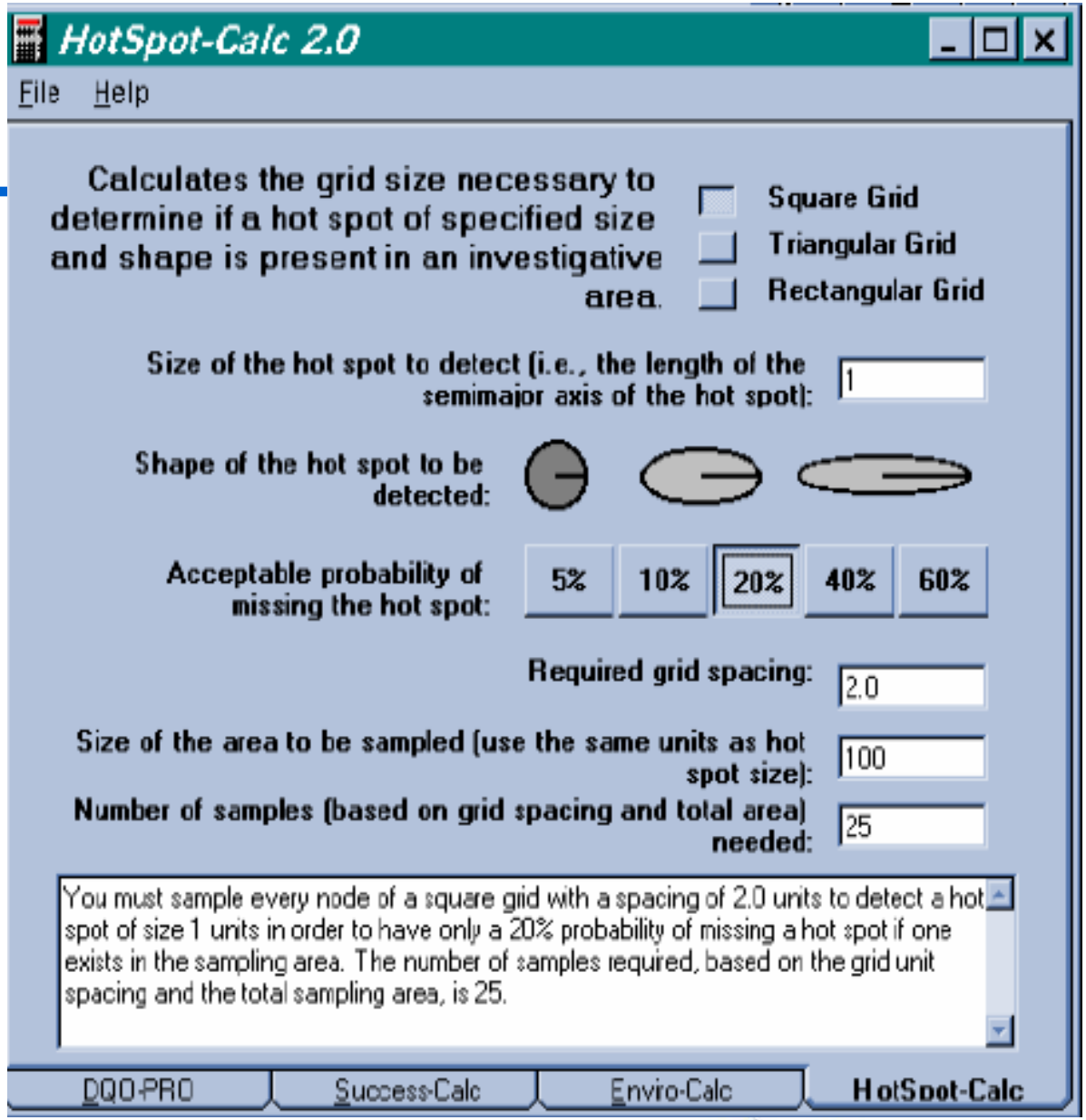
- What if the Grid is Changed to a Triangle?



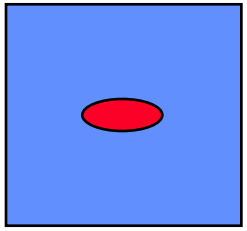


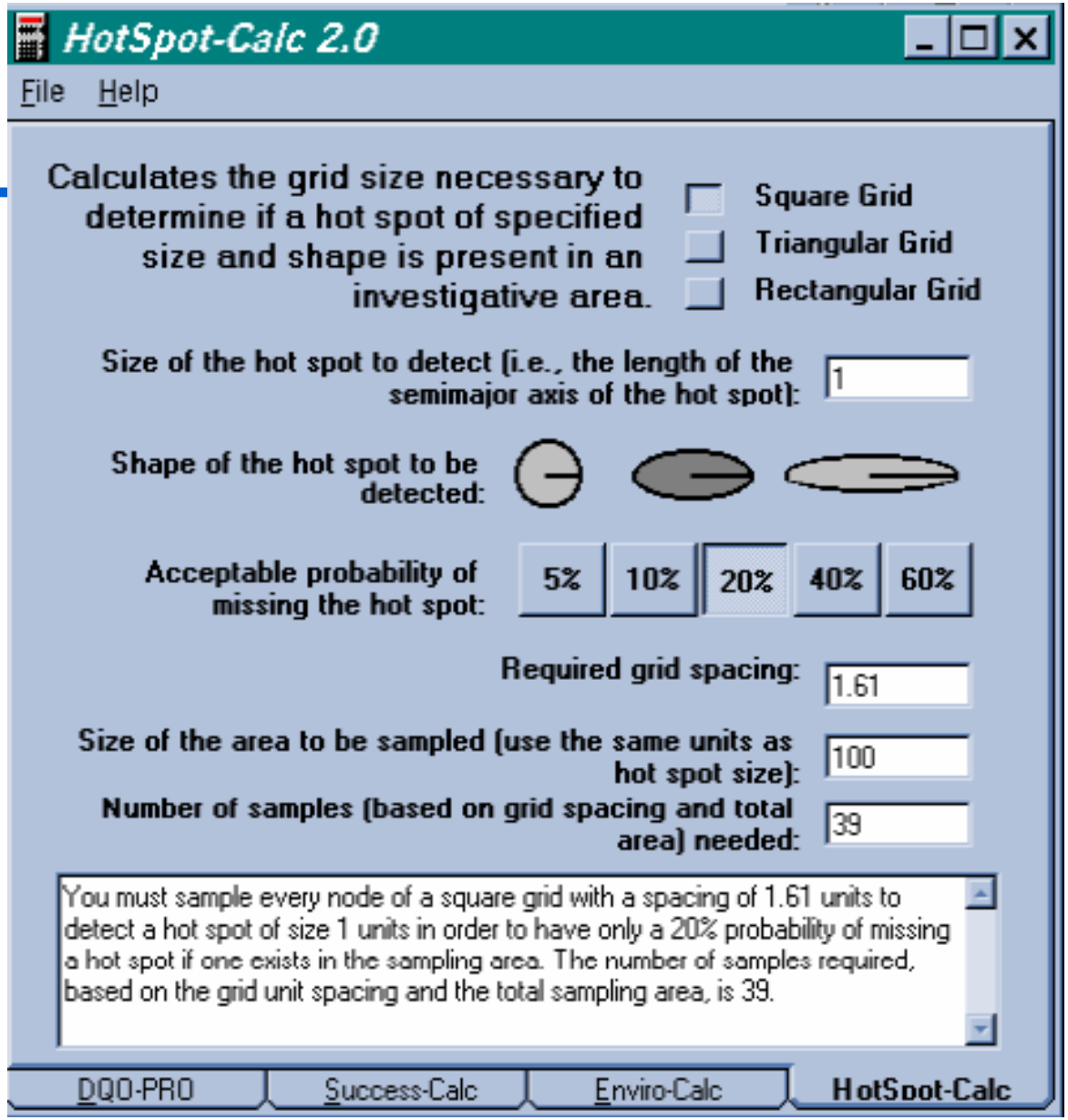
Increased Probability of Miss to 20%

- Using a Square Grid, What if the Acceptable Probability of Missing a Hot Spot was Increased?
- Doubling the Probability of missing the spot only decreased the number of samples needed by 6.



- **What if the Hot Spot was an Ellipse Instead of Circular in Shape?**
- **Then the number of samples increased from 25 to 39.**





Problem 1. What is the Effect of <u>Decreasing Size</u> of a Spot on Numbers of Samples Needed?

- Assume a Square Grid
- Assume the minimum size of a hot spot you are willing to miss is a circle with a radius of 5.0 meters.
- Assume a Probability of Missing a Hot Spot, if one existed, of 60%
- Assume a Sampling Area of 500 square meters.
- How many samples are required?

Problem 1. What is the Effect of Decreasing Size of a Spot on Numbers of Samples Needed?

- How many samples are needed if the size of the spot is decreased from a radius of 5 meters to a radius of 4 meters?
  - If the radius is decreased to 3 meters?
  - If the radius is decreased to 2 meters?
  - If the radius is decreased to 1 meter?
  - If the radius is decreased to 0.5 meter?
- Use HotSpot-Calc to see the effects of these changes.

Problem 2. What is the Effect of <u>Decreasing the Probability</u> of Missing a Spot on Numbers of Samples Needed?

- Assume a Square Grid
- Assume the minimum size of a hot spot you are willing to miss is a circle with a radius of 2.5 meters.
- Assume a Probability of Missing a Hot Spot, if one existed, of 60%
- Assume a Sampling Area of 4000 square meters.
- How many samples are required?

Problem 2. What is the Effect of Decreasing the Probability of Missing a Spot on Numbers of Samples Needed?

- How many samples are needed if the probability of missing a hot spot is decreased from 60% to 40%?
  - Decreased to 20%
  - Decreased to 10%
  - Decreased to 5%

- Use HotSpot-Calc to see the effects of these changes

Problem 3. What is the Effect of <u>the shape of a Spot</u> on Numbers of Samples Needed?

- Assume a Square Grid
- Assume the minimum size of a hot spot you are willing to miss is a circle with a radius of 1.0 meters.
- Assume a Probability of Missing a Hot Spot, if one existed, of 10%
- Assume a Sampling Area of 500 square meters.
- How many samples are required?

Problem 3. What is the Effect of the <u>shape of a Spot</u> on Numbers of Samples Needed?

- Assume the shape of the hot spot is an ellipse instead of a circle. How many samples are needed?

- Assume the shape of the hot spot is a long ellipse; how many samples are needed?

Problem 4. What is the effect of the <u>shape of the grid</u> on numbers of samples needed?

- Assume a Square Grid
- Assume the minimum size of a hot spot you are willing to miss is a circle with a radius of 1.0 meters.
- Assume a Probability of Missing a Hot Spot, if one existed, of 5%
- Assume a Sampling Area of 1000square meters.
- How many samples are required?

Problem 4. What is the effect of the <u>shape of the grid</u> on numbers of samples needed? (continued)

- What is the effect of changing the shape of the grid from a square to a triangle?
- What is the effect of changing the shape of the grid to a rectangle?
- Keeping the input to the rectangle the same, change the shape of the hot spot from a circle to an ellipse.
  - What happens?
  - Is this a bug in the program?

The Effects of Shapes

Four facts become apparent when various shapes and probabilities are assessed:

1. The number of samples needed increases as the size of the spot which is acceptable to miss decreases.

2. The number of samples needed increases as the acceptable probability of missing a hot spot decreases,

3. If the hot spot is circular fewer numbers of samples are needed than when it is elliptical and, the longer the horizontal axis is in the ellipse the larger is the number of samples that will be needed for a given probability and grid shape.

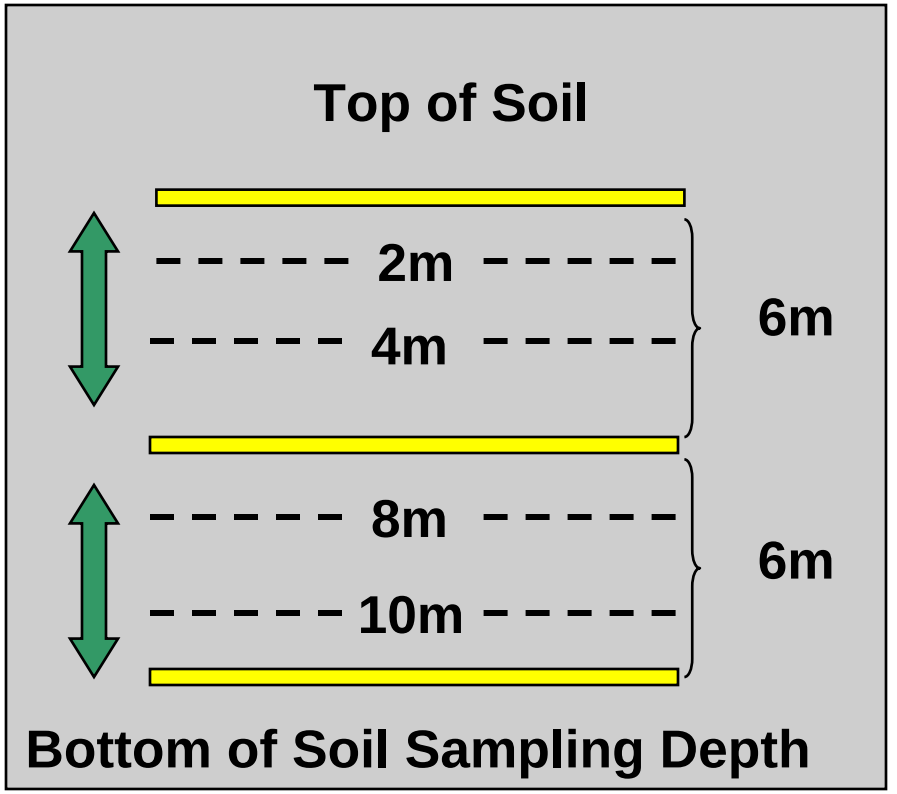
4. A triangular grid is the most efficient and a rectangular grid is the least efficient for finding a hot spot using the same assumptions.

Three Dimensional Use

HotSpot-Calc does not provide confidence in detecting a three dimensional hot spot; it only works on a two dimensional plane. However, if a three-dimensional grid is desired then multiple layers of the two-dimensional grid may be used for an estimate.

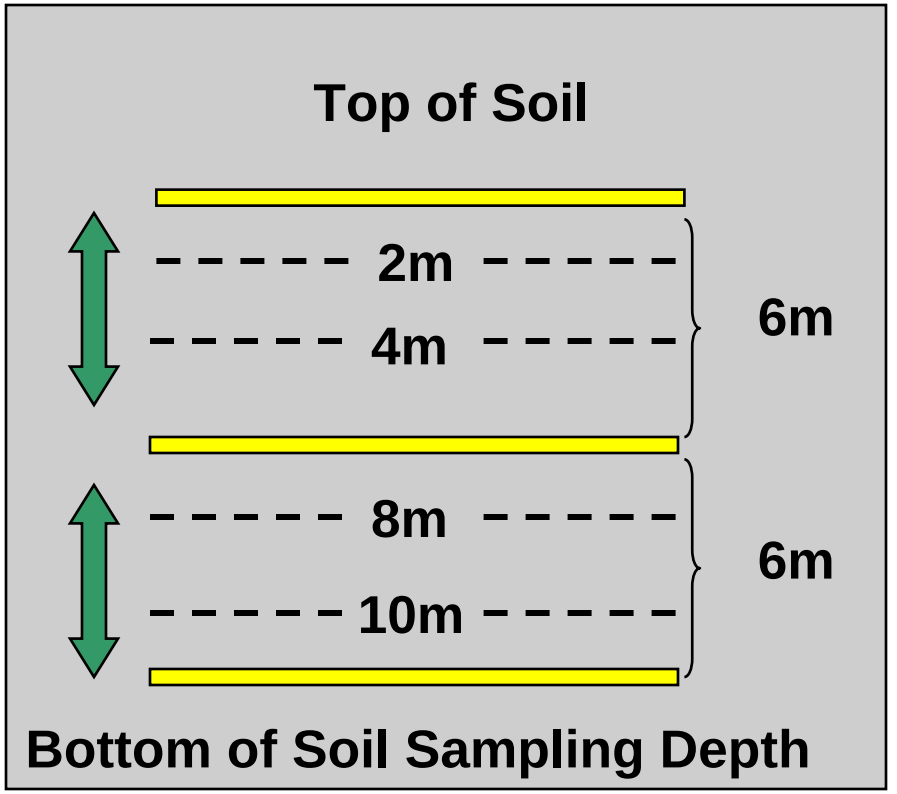
- In a 3-D application, however, there is no allowance for the three dimensional shape of the hot spot (i.e., whether it is a round sphere or an elongated sphere or some other shape).

A Three Dimensional Example



- Consider a 3-D example where **HotSpot-Calc** estimated that a 20 sampling point grid was needed.
- How many samples would be needed if holes were bored 12 meters deep and samples were collected every 6 meters?

A Three Dimensional Example



- The answer is that 60 samples would be needed for this three dimensional application.
- 20 from the top,
- 20 from the middle,
- 20 from the bottom level.

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60 samples total.

Answers to 1. What is the Effect of Decreasing Size of a Spot on Numbers of Samples Needed?

- Assume a Square Grid
- Assume the minimum size of a hot spot you are willing to miss is a circle with a radius of 5.0 meters.
- Assume a Probability of Missing a Hot Spot, if one existed, of 60%
- Assume a Sampling Area of 500 square meters.
- How many samples are required? **Answer: 3**

Answer to 1. What is the Effect of Decreasing Size of a Spot on Numbers of Samples Needed?

- How many samples are needed if the size of the spot is decreased from a radius of 5 meters to a radius of 4 meters? **Answer: 4**
  - If the radius is decreased to 3 meters? **Answer: 7**
  - If the radius is decreased to 2 meters? **Answer: 16**
  - If the radius is decreased to 1 meter? **Answer: 62**
  - If the radius is decreased to 0.5 meter? **Answer: 245**
- Use HotSpot-Calc to see the effects of these changes.

Answer to 2. What is the Effect of Decreasing the Probability of Missing a Spot on Numbers of Samples Needed?

- Assume a Square Grid
- Assume the minimum size of a hot spot you are willing to miss is a circle with a radius of 2.5 meters.
- Assume a Probability of Missing a Hot Spot, if one existed, of 60%
- Assume a Sampling Area of 4000 square meters.
  - How many samples are required? **Answer: 79**

Answer to 2. What is the Effect of Decreasing the Probability of Missing a Spot on Numbers of Samples Needed?

- How many samples are needed if the probability of missing a hot spot is decreased from 60% to 40%? **Answer: 113**
- Decreased to 20% **Answer: 160**
- Decreased to 10% **Answer: 194**
- Decreased to 5% **Answer: 231**

- Use HotSpot-Calc to see the effects of these changes

Answer to 3. What is the Effect of the shape of a Spot on Numbers of Samples Needed?

- Assume a Square Grid
- Assume the minimum size of a hot spot you are willing to miss is a circle with a radius of 1.0 meters.
- Assume a Probability of Missing a Hot Spot, if one existed, of 10%
- Assume a Sampling Area of 500 square meters.

How many samples are required? **Answer: 151**

Answer to 3. What is the Effect of the shape of a Spot on Numbers of Samples Needed?

- Assume the shape of the hot spot is an ellipse instead of a circle. How many samples are needed? **Answer: 232**

- Assume the shape of the hot spot is a long ellipse; how many samples are needed? **Answer: 354**

Answer to 4. What is the effect of the shape of the grid on numbers of samples needed?

- Assume a Square Grid
- Assume the minimum size of a hot spot you are willing to miss is a circle with a radius of 1.0 meters.
- Assume a Probability of Missing a Hot Spot, if one existed, of 5%
- Assume a Sampling Area of 1000square meters.

How many samples are required? **Answer: 359**

Answer to 4. What is the effect of the shape of the grid on numbers of samples needed?

- What is the effect of changing the shape of the grid from a square to a triangle? **Answer: Samples increase to 283**

- What is the effect of changing the shape of the grid to a rectangle? **Answer: Samples increase to 500**

- Keeping the input to the rectangle the same, change the shape of the hot spot from a circle to an ellipse. What happens? **Answer: Grid Spacing is Incalculable from Current Parameters**

- Is this a bug in the program? **Answer: No, it is a limitation of the statistical equation used.**