

# LIMITING SITE SOIL CHARACTERIZATION TO CONSEQUENTIAL CONTAMINATION

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## ABSTRACT

Contamination in an abundance that is sufficient to threaten human health or the environment is herein termed consequential contamination. The most common approach to sample plan design inherently assumes that the absence of discovered contamination is sufficient evidence to conclude the absence of consequential contamination. This assumption is indefensible if it can be reasoned that consequential contamination might exist between sampling locations. Small areas of discontinuous contamination, e.g. hot spots, would reasonably be expected at uncontrolled dump sites, industrial sites, when defining the spatial limits of contamination at any site, and when determining the effectiveness of a cleanup that relies on excavation and removal of contaminated soil. In these instances, it is prudent that both soil characterization and rules for decision making minimally ensure greater than a 50 percent chance of responding to the reasonably conceivable smallest hot spot of consequential contamination. An approach to create, evaluate and defend sample plan designs for these and similar situations is described.

**Keywords:** composite, incremental, soil, sample, multi increment, number, many increments, contamination, hot spot

## 1. INTRODUCTION

Contamination in an abundance that is sufficient to cause the average concentration ( $C_{ave}$ ) of a soil mass or a surface area to exceed a related risk-based limiting concentration or regulatory standard ( $C_{index}$ ) is consequential contamination. A method is presented that calculates the minimum number of locations ( $\underline{n}$ ) required to be represented by sampling when the reasonably smallest footprint of consequential contamination is present. Such a footprint is called a consequential hot spot. The value  $\underline{n}$  is managed by the action concentration,  $C_{act}$ , which is a user selected value less than  $C_{index}$  that, if equaled or exceeded, indicates the possible presence of consequential contamination. For example, if  $C_{index}$  limits cancer risk to  $10^{-5}$ , the action concentration,  $C_{act}$ , may be selected as the concentration that would limit cancer risk to  $10^{-6}$ . Taking action when  $C_{act}$  is exceeded provides a prescribed level of assurance the area average does not exceed  $C_{index}$ . It will be seen that selecting  $C_{act}$  ten times lower than  $C_{index}$  reduces  $\underline{n}$  by an order of magnitude.

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This approach focuses on providing reasonable assurance that hot spots inadvertently not represented in the sampling effort are inconsequential to decision making. Typically, in hot spot scenarios, a large number of samples are needed to apply nonparametric statistical methods or statistical methods that are based on the Central Limit Theorem. The approach presented herein requires considerably fewer samples and provides a defensible level of confidence for the often presumed, yet seldom defensible, expectation that undiscovered contamination is inconsequential.

The number of locations that must be represented in a sampling effort depends on: 1) the remediation goal or regulatory concentration ( $C_{index}$ ); 2) an action concentration ( $C_{act}$ ) that, if equaled or exceeded, would indicate a possible exceedance of  $C_{index}$ ; 3) the size of the smallest hot spot that can reasonably exist and also cause a soil mass or area average concentration to exceed  $C_{index}$ ; and 4) the hypothesized contaminant distribution within such a hot spot. The method being presented has evolved over several decades as it has been used by the author for site assessments and to develop characterization and cleanup verification plans for uncontrolled dump sites, mine sites and industrial sites. Several example applications are presented and discussed.

## **2. MATERIAL AND METHODS**

### **2.1 Background**

The most common approach to sample plan design inherently assumes that the absence of discovered contamination is sufficient evidence to conclude the absence of consequential contamination. However, finding no contamination is insufficient to verify this supposition. This incorrect perception is generally based on an indefensible belief that common sense, judgment, experience, or incomplete technical argument is sufficient to support the decision.

Most sampling efforts are formulated to estimate the mean concentrations of contaminants of concern. Such estimates are required to perform quantitative risk assessments and for comparisons to remediation goals or regulatory limits. Commonly applied statistical methods rely on the Law of Large Numbers and Central Limit Theorem. Taken together, these constitutive rules of statistics guarantee that repeated measurements of contaminant mean concentration, with each measurement determined using the results of sampling at  $n$  random locations, will be normally distributed and centered on the true mean *if  $n$  is sufficiently large*. Unfortunately, it is impossible to know if a solitary consequential hot spot exists between sample collection locations in an otherwise clean area. Hence, in a single sampling event, there is no assurance that any assumed or derived  $n$  is sufficient.

This problem can be resolved by considering the nature of potentially unrepresented contamination and its associated effect on decision making. As will be discussed, both

contaminant distribution and size of the smallest consequential hot spot can be reasonably hypothesized and used to make assertions regarding the adequacy of  $\underline{n}$ .

## **2.2 Extreme Hot Spot Example**

The following example is presented to demonstrate fundamental aspects of the perception problem. Consider sampling a field suspected of containing buried explosive landmines. Needless to say, missing a single landmine is consequential. Suppose ten locations are sampled and each is found clean, i.e. no landmine. Concluding that the field contains no landmines would be inappropriate. The clarity of this conclusion is based on common sense recognition; 1) a landmine may remain undetected between sampling locations; and 2) there is an extreme human health risk associated with landmines. For these reasons it is simple to conclude that  $\underline{n}$  must be larger than ten to enable a meaningful decision regarding the potential presence of a landmine.

Unlike this landmine example, most chemical hot spots are not explosive on contact. Furthermore, ill-effects may not be deadly, are often manifested only after numerous encounters over long time periods, and may not be correctly associated with consequential contamination encounters. Consequently, common sense does not always foster a clear understanding of the need for larger  $\underline{n}$ . A more theoretical understanding is therefore required, as demonstrated with the next example.

## **2.3 Typical Hot Spot Example**

The following is a typical example of surface chemical soil contamination. It is applicable to both initial site characterization and cleanup verification.

A surface soil sampling program must be designed to acquire data needed to evaluate human carcinogenic risk caused by PCBs in a park setting. PCBs may have leaked or been dumped from transformers 30 years ago. The exposure area for use in human health risk assessment is established to be 5000 m<sup>2</sup>. Furthermore, the exposure model assumes a person will encounter all locations within the exposure area with equal probability over a long period of time. Consequently, an estimate of the mean total PCB concentration will be used to represent the exposure concentration in risk calculations.

Total PCB's exposure concentrations of 1.0 mg/kg and 0.10 mg/kg are calculated to present 10<sup>-5</sup> and 10<sup>-6</sup> carcinogenic human health risks respectively. The anticipated risk-based limiting concentration,  $C_{index}$ , is 1.0 mg/kg. To ensure this goal is attained, action will be taken to remediate the exposure area if it is discovered that the average concentration of  $\underline{n}$  randomly selected surface soil locations equals or exceeds  $C_{act} = 0.10$  mg/kg. The problem is to determine the value of  $\underline{n}$  that results in a 50 percent or greater chance that  $C_{act}$  will be equaled or exceeded if the reasonably conceivable smallest footprint of consequential contamination is the only contamination present. Hereafter such contamination is termed the smallest consequential hot spot (*SCHS*).

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The following rationale is used to select  $\underline{n}$ . First, it is reasonable to assume that the spilled or leaked transformer oil initially saturated the soil at the time of release resulting in a PCB soil concentration of about 100,000 mg/kg. Using an estimated five year half-life for PCBs, it is reasoned that the maximum concentration 30 years after release is about  $C_{max} = 1560$  mg/kg.

Chemical diffusion and mechanical dispersion cause the contaminant distribution to vary between zero and  $C_{max}$ . For calculation simplicity, assume the hot spot is circular and that the concentration decreases linearly with distance from the center. The average concentration of such a hot spot is one third of the maximum concentration, about 520 mg/kg in this example. Using this information, the hot spot size that would cause the 5000 m<sup>2</sup> exposure area to have an average concentration of 1.0 mg/kg is calculated to be 9.6 m<sup>2</sup>. This represents a reasonably conceivable smallest footprint for the *SCHS* because: 1) a hot spot with maximum concentration lower than  $C_{max}$  must be larger than the *SCHS* if it is to cause an average exposure area concentration of 1.0 mg/kg; and 2) a hot spot smaller than the *SCHS* must have a maximum concentration greater than  $C_{max}$  to cause an average exposure area concentration of 1.0 mg/kg and, based on the exponential decay model, this is not expected 30 years after the PCBs release.

It is desired to limit the chance of erroneously declaring the exposure area clean to less than 50 percent if the *SCHS* is present. In other words, the problem is to determine the value of  $\underline{n}$  that results in a 50 percent or greater chance that  $C_{act}$  will be equaled or exceeded if the *SCHS* is the only contamination present.

The number of samples required for application of methods that rely on the Central Limit Theorem of Statistics is exceptionally large. This is because a large number of the sampled locations must occur within the *SCHS* if it represents the only contamination present. For this example, 1/520 is the probability that a randomly selected location will fall within the footprint of the *SCHS*. This is the ratio of the hot spot area to the site area. The number of locations that occur within the hot spot when  $\underline{n}$  random samples are collected has a binomial distribution. It is calculated that 20560 random sampling locations are needed for a 95 percent chance that 30 or more will occur within the *SCHS*. When the  $\underline{n}$  is small, there is a good chance the hot spot will be missed altogether. For this example, when  $\underline{n}=30$  there is about a 95 percent chance of completely missing the *SCHS*. This leads to the conclusion that it is unreasonable to represent a sufficient number of sample locations to ensure confident statistical inferences using methods that rely on a large number of these locations falling within the *SCHS*. A method that depends on a smaller number of sample locations is developed next.

It is desired to determine the value for  $\underline{n}$  that will result in a 50 percent or greater chance that the average concentration of  $\underline{n}$  randomly selected locations is greater than or equal to  $C_{act}$  when the *SCHS* represents the distribution of site PCBs. The method is developed and examples given in subsequent sections. Application of the method results in the expectation that  $\underline{n} = 392$  locations will be sufficient to achieve this objective. The

average total PCBs concentration of the 392 locations may be practically determined as the calculated average of eight independent composite sample measurements. For this example, each composite will be comprised of 49 equal-mass soil specimens (8 samples x 49 locations = 392 locations), collected at either randomly selected locations or at the nodes of 7x7 square grids. If grids are used, the node spacing of each grid will be the largest that results in at least 49 nodes within the exposure area.

A calculated average total PCBs concentration equal or exceeding 0.10 mg/kg would be an indication that consequential contamination, i.e. contamination that causes the mean concentration to equal or exceed 1.0 mg/kg, may be present. Therefore, action would be prudent if the average of the eight composite samples equals or exceeds 0.10 mg/kg.

## **2.4 Terminology, Application and Method Development**

The method presented herein controls the risk of erroneously declaring an area or soil mass clean when the smallest footprint of consequential contamination, the *SCHS*, is present. It does this by selecting the number of sampling locations necessary to ensure a 50 percent or greater chance that the average concentration of the selected locations will exceed  $C_{act}$  if the decision unit contamination distribution is characterized by the *SCHS*.

Herein the following terminology is used:

**Contaminant:** An analyte or compound; a risk normalized value that represents several analytes or compounds, such as TEQ for dioxin-like compounds; or an indicative measurement, such as gamma radiation.

**Area or Volume of Concern ( $A_c$ ):** Typically the smallest exposure area or volume used in risk assessment and that is associated with the contaminant. This may also be the smallest area or volume used in the development of a regulatory limit for the contaminant.

**Consequential Contamination ( $C_{index}$ ):** The lowest mean contaminant concentration within  $A_c$  that presents an unacceptable risk to human health or the environment.

**Smallest Consequential Hot Spot (*SCHS*):** The reasonably smallest footprint of contamination that, if present within  $A_c$ , would cause  $C_{index}$  to be equaled or exceeded. Sampling this hot spot sufficiently to support good decision making is what drives the sampling effort. A hypothesized distribution for contamination within the *SCHS* is used to determine the number of locations within  $A_c$  that must be represented.

**Maximum Concentration ( $C_{max}$ ):** Maximum concentration that can reasonably exist in  $A_c$ .

**Action Concentration ( $C_{act}$ ):** The average concentration of the contaminant that has equal or better than 50 percent probability of exceedance when the *SCHS* is present and  $\underline{n}$  random locations within  $A_c$  are sampled.

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**Number of Represented Locations ( $\underline{n}$ ):** The number of locations within  $A_c$  that must be represented by sampling to provide at least a 50 percent chance that  $C_{act}$  is exceeded when the *SCHS* is present.

**Average Concentration ( $C_{ave}$ ):** The average concentration of contaminant at  $\underline{n}$  random locations within  $A_c$ .

The minimum number of samples,  $\underline{n}$ , and  $C_{act}$  are most commonly determined given  $C_{index}$  and an estimate of  $C_{max}$ . The following process is applied to each contaminant of concern and the largest  $\underline{n}$  selected for sample plan design.

1. Determine  $C_{index}$ . Human or ecological risk assessment may be applied to establish the concentration for an exposure area,  $A_c$ , that results in unacceptable risk.  $C_{index}$  often differ for surface and subsurface conditions and also for different exposure areas or subareas. The values for  $\underline{n}$  will be accordingly different.
2. Determine the reasonable  $C_{max}$  within  $A_c$ . Estimating  $C_{max}$  requires a degree of understanding and modeling of contaminant release events. Technical understanding of fate and transport mechanisms may be applied to hypothesize a reasonable dispersion model from which  $C_{max}$  may be calculated. Alternatively, a simple exponential decay model may be applied using 1) a published decay constant; 2) an estimate of the time since chemical release; and 3) a reasonable estimate of the maximum soil concentration at the time of the release. Maximum concentrations obtained by analysis of samples from within  $A_c$  would expectedly be lower than the true maximum since the true maximum occupies a very small soil volume and will likely be missed by sampling. Therefore maximum concentrations obtained by analysis of samples from within  $A_c$  should not be used to represent  $C_{max}$ . However, because such measurements are expectedly lower than  $C_{max}$ , they may aid in evaluating the adequacy of the hypothesized  $C_{max}$ .
3. Calculate the ratio of  $C_{max}/C_{index}$ .
4. Select an acceptable combination of  $C_{act}/C_{index}$  and determine  $\underline{n}$  from Table 1 or Equation 1. This is an iterative process that ends when an acceptable combination of  $\underline{n}$  and  $C_{act}/C_{index}$  is found.  $C_{act}$  is the most reasonably altered variable. However, in some situations  $C_{index}$  may be increased thereby accepting a greater human or ecological risk in exchange for lower  $\underline{n}$ , or to explain the benefit of reduced risk gained by using a larger  $\underline{n}$ .  $C_{max}$  must not be altered unless the previous estimate is determined to be erroneous.
5. The value for  $A_c$  is generally an exposure area or a volume of soil established by risk assessment and associated with  $C_{index}$ .<sup>2</sup>
6. Design the sampling plan to include soil collection at  $\underline{n}$  random locations in  $A_c$  and expect to take action if the calculated average of measured concentration exceeds  $C_{act}$ . Care should be taken to control errors introduced by sample collection, processing and measurement to assure the contribution of these errors

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<sup>2</sup>  $A_c$  may be subdivided and a disproportionate risk assigned to the subdivided areas while ensuring the sum of risks remain unchanged. A different  $C_{index}$  results for each subarea. This technique can help to justify the use of different sampling densities within subareas of  $A_c$ .

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to decision-making uncertainty is less than that attributable to the process just described.

The values in Table 1 were generated by computer simulation of sampling events. Equation 1 fits the data in Table 1 limited to the significant digits used in the table and rounded to the nearest whole number. Table 1 and Equation 1 provide values that are sufficiently accurate for their intended use as presented in this paper. Uncertainty in this method is expected to be governed by uncertainty in the estimates of  $C_{index}$  and  $C_{max}$ . The uncertainty in the estimate of  $C_{max}$  may not be as great as the uncertainty attributable to  $C_{index}$  derived by risk assessment. Consequently, it is expected that method uncertainty will typically be governed by  $C_{index}$  uncertainty.

*Table 1.* The Value  $n$  that Provides a Greater Than 50 Percent Chance that  $C_{ave}/C_{index}$  Exceeds  $C_{act}/C_{index}$  in the Presence of the Smallest Consequential Hot Spot (SCHS).

		$C_{act}/C_{index}$										
		0.95	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0
$C_{max}/C_{index}$	$n$ That Provides Greater Than-50% Chance that $C_{ave}/C_{index}$ Exceeds $C_{act}/C_{index}$ in the Presence of the Smallest Consequential Hot Spot											
<b>1000000</b>	2000000	970000	530000	400000	340000	310000	290000	270000	260000	250000	230000	
<b>100000</b>	200000	97000	53000	40000	34000	31000	29000	27000	26000	25000	23000	
<b>10000</b>	20000	9700	5300	4000	3400	3100	2900	2700	2600	2500	2300	
<b>1000</b>	2000	970	530	400	340	310	290	270	260	250	230	
<b>100</b>	200	97	53	40	34	31	29	27	26	25	23	
<b>10</b>	20	10	5	4	3	3	3	3	3	3	2	
<b>3</b>		3	2	1	1	1	1	1	1	1	1	

$$n = \frac{C_{max}}{C_{index}} \left( 0.764 \left[ \frac{-0.102}{LN\left(\frac{C_{act}}{C_{index}}\right)} \right]^{1.21} + 0.233 \right) \quad (1)$$

## 2.5 Sampling Design

A properly processed composite sample that is comprised of  $n$  specimens, collected from within  $A_c$  from node locations of a randomly oriented grid or from random locations, is an effective and cost efficient method to represent large numbers of sampling locations. Replicate composite samples that cumulatively are comprised of a total of  $n$  specimens may be used rather than a single composite sample. Use of replicate composite samples reduces the effect of analytical uncertainty on decision making and sometimes is necessary to represent a large  $n$  with manageable sample mass. Appropriate processing, including homogenization and subsampling, is required to ensure that each test aliquot is representative of the composite sample mean contaminant concentration. Fundamental Error is described by Pierre Gy and may be used to help define the minimum mass of the

field sample (Pitard, 1993). An iterative process of grinding the composite sample and subsampling is often necessary to maintain fundamental error when test aliquots are expected to be small.

To evaluate the effectiveness of composite sample processing, a field spike must be introduced to each sample and the recovery ( $R$ ) and relative percent difference ( $RPD$ ) of the spike in subsamples determined. The spike should be added to the field sample in a manner intended to mimic a single potentially contaminated field specimen. Composite sample homogeneity is generally considered sufficient if the error introduced to decision making by inhomogeneity is less than that introduced by the laboratory analytical methodology. Hence, proper homogenization and subsampling should result in  $R$  and  $RPD$  that are statistically indistinguishable from values measured at the bench in accordance with laboratory analytical procedures. To ensure this level of quality, the recovery of the field spike should be routinely 80 percent or greater. Likewise, the  $RPD$  of totally independent subsamples should routinely be less than 30 percent.

It is sometimes difficult to develop a homogenization and subsampling procedure that routinely achieves the field spike  $R$  and  $RPD$  limits of 80 percent and 30 percent respectively. However, a successful procedure that is tailored to soil type and condition is always achievable. As a word of caution,  $RPD$ 's often misleadingly achieve the 30 percent upper limit. This is because when processing is inadequate the spiked chemical remains predominantly as a hot spot in the sample and is missed in subsampling. Therefore, it is necessary to process the sample sufficiently to ensure that both  $R$  and  $RPD$  limits are routinely achieved. A pilot study is recommended to initially evaluate a proposed homogenization and subsampling procedure and it should be repeated whenever the soil physical characteristics change in a manner that may significantly affect the process. Furthermore, field spike  $R$  and the  $RPD$  of two subsamples should be evaluated for each sample. Corrective action must be taken to improve the homogenization process if  $R$  or  $RPD$  limits are not always achieved.

## **2.6 Historical Development of the Relationship between $n$ , $C_{max}/C_{index}$ and $C_{act}/C_{index}$**

The author developed the following relationship to establish a defensible reason to sample at  $N$  locations during the remedial investigation of the Krejci Dump Site (Gemperline 1993, Gemperline 1994, BOR 1994).

$$N = \frac{\log(\alpha)}{\log\left(1 - 3\frac{C_{index}}{C_{max}}\left(1 - \frac{C_d}{C_{max}}\right)^2\right)} \quad (2)$$

$C_d$  is the reporting limit of the screening or laboratory procedure.

Equation 2 estimates the number of discrete samples ( $N$ ) required to provide a 1-  $\alpha$  probability that at least one sampling location is from within the detectable area of the



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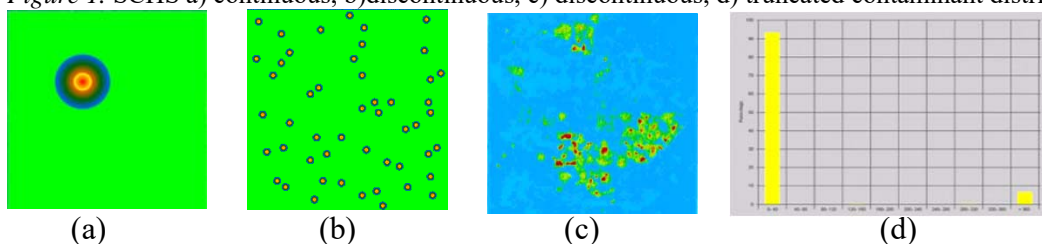
*SCHS*. The equation is valid for conditions where  $N$  decreases as  $C_{max}$  approaches  $C_{index}$ . This condition is satisfied when  $C_d/C_{index}$  is less than 4/9 (Gemperline, 1994). Application also requires that the detectable hot spot area must also be less than or equal to the Site area.

Equation 2 was developed to indicate the possible presence of the *SCHS* using field screening methods, primarily for the purpose of having a defensible reason for selecting  $N$ . However, there are several shortcomings to this approach. First, any quantifiable concentration would indicate the possible presence of the *SCHS*. Second, the rate of false positive decisions cannot be established or easily controlled. Third,  $C_d$ 's for field screening methods were often much higher than risk-based remediation goals and therefore they cannot be used to characterize large low concentration consequential hot spots. Fourth, the numbers of samples required to ensure one sampled location was from within the *SCHS* were sometimes very large. Finally, the smallest consequential hot spot may be discontinuous, so finding a discrete location with an elevated concentration may erroneously be interpreted as indicating a *SCHS* location.

A risk-based composite sampling methodology was developed to overcome the above problems. The approach uses low detection limit laboratory methods and requires a user selected action level,  $C_{act}$ .  $C_{act}$  is both greater than the method quantitation limit and less than the concentration indicative of unacceptable risk,  $C_{index}$ . Furthermore, it combines specimens collected at  $n$  locations into a single composite sample. Consequently, rather than estimating the mean concentration for purposes of risk assessment by mathematically averaging discrete measurements, it used mechanical homogenization to create a uniform concentration representative of the mean. This approach helps alleviate the problems discussed in the previous paragraph. First, quantifiable concentrations exceeding  $C_{act}$ , rather than the mere detection of contaminant, will indicate the possible presence of the *SCHS*. Second, the rate of false positive decisions can be controlled by adjusting the proximity of  $C_{act}$  to  $C_{index}$ . Third, the use of analytical methods that have reporting limits less than  $C_{act}$  would reasonably ensure characterization of large low concentration consequential hot spots. Fourth, the number of analytical samples is greatly reduced because the locations are not individually sampled and tested. Finally, the composite nature of the sample eliminates the possibility that measured contaminant concentration at a discrete location is misinterpreted as being unique.

The potential discontinuous nature of the *SCHS* is important because it helps to explain this methods indifference to random sampling and grid sampling. The selection of samples from the nodes of a randomly created grid is nearly as effective a design as random location selection for application of the concepts presented in this paper. Until now the *SCHS* has been portrayed as shown on Figure 1, a circle with the concentration decreasing with increasing distance from its center. Figures 1a, 1b and 1c all represent the same Site contaminant distribution. A truncated histogram depicting the site distribution is shown on Figure 1d. The contaminant concentration is portrayed as decreasing linearly from red to green, except for Figure 1c. On Figure 1c the contaminant concentration is portrayed as decreasing from red to blue.

Figure 1. SCHS a) continuous, b) discontinuous, c) discontinuous, d) truncated contaminant distribution



Grid sampling and random sampling are expected to be equally effective at characterizing randomly distributed contamination and contiguous contamination respectively. The nature of the SCHS distribution about the site is unknown. Hence, either grid or random sampling is applicable for the purposes of the method presented in this paper.

The relationship between  $n$ ,  $C_{index}$ ,  $C_{act}$ , and  $C_{max}$  presented in Table 1 were determined by computer simulation of sampling events. The computer algorithm simulated an SCHS that is completely defined by  $C_{max}/C_{index}$  with a distribution characterized as a circular hot spot with concentration decreasing linearly from its center. Five thousand computer simulated sampling events using increasingly larger  $n$  were performed to calculate  $C_{ave}/C_{index}$  for each combination of  $C_{max}/C_{index}$  and  $C_{act}/C_{index}$ . The lowest value of  $n$  that resulted in 50 percent or more  $C_{ave}/C_{index}$  exceedances of  $C_{act}/C_{index}$  were determined for each  $C_{max}/C_{index}$ . Equation 1 was fit to the results of computer simulations. Table 1 represents the values calculated using Equation 1, adjusted to indicate a maximum of two significant digits. Equation 1 and the values in Table 1 estimate  $n$  with sufficient accuracy for general application.

### 3. RESULTS

Three example applications of Table 1 are provided in this section. For simplicity, the contaminant of concern for all examples is PCB's. Examples 1 and 2 use the authors experiences at the Krejci Dump Site, a former municipal and industrial dump, to calculate  $n$  for site remediation and cleanup verification respectively. Example 3 describes selection of  $n$  applicable to either characterization or cleanup verification at a former power substation.

#### 3.1 Example 1: Krejci Dump Site Remedial Investigation – 1990 through 1996

An early version of the process just described, Risk-Based Composite Sampling, was applied to determine the number of sampling locations required to characterize surface soil (depth = 2 inches) at the Krejci Dump Site (BOR 1994, Gemperline 1993, Gemperline 1994). The following applies Table 1 to select  $n$ .

##### **Background:**

Mark C. Gemperline, Limiting Site Soil Characterization to Consequential Contamination, 26th Annual International Conference on Soil, Water, Energy, & Air, March 21-24, 2016 at the Mission Valley Marriott in San Diego, CA, AEHS Proceedings, 2016.

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The roughly 186,000 m<sup>2</sup> site is a former municipal and industrial dump and salvage located within the Cuyahoga Valley National Park in Summit County, Ohio, USA. The United States purchased the land in 1980 for management by the Department of the Interior National Park Service (NPS) and all dumping operations ceased. In 1987, it was determined that the Site constituted a threat to human health and the environment. In response to this determination, the U.S. Environmental Protection Agency (EPA) initiated an emergency removal beginning in June 1987. In November 1988, NPS completed the removal of wastes staged during the initial EPA activity, as well as the removal of some unconsolidated wastes and contaminated soil. Large quantities of debris and potentially contaminated soil remained. A remedial investigation and feasibility study ensued.

During the years of operation, from approximately 1950 to 1980, large volumes of solid and liquid waste materials were brought to the Krejci dump, where significant quantities of hazardous substances were released to the environment as a result of open dumping, spills, leaking containers, and burning. The operational history of the Site as well as testing of previously removed waste, soil, and debris showed that dump operations had resulted in PCBs releases to the environment. These releases were very likely confined to the site. Operational characteristics of the dump suggested that PCBs contamination was the result of fluid releases from electrical equipment.

The Data Quality Objective (DQO) process was employed during the planning phase of the remedial investigation (Neptune *et al.*, 1990). Conceptual models of possible worst-case contaminant distributions were developed at this early stage and cursory human health risk assessments using available information were performed to assist with the identification of data needs (BOR 1994). The site was divided into 12 decision units. Each decision unit represents a unique exposure area for human health risk assessment. The DQO process revealed that the need to discover and represent PCB hot spots would likely drive both the site characterization and future cleanup efforts.

Table 1, and the process that utilizes it, postdates the Krejci remedial investigation. Never-the-less, an application of the process is demonstrated in the context of original remedial investigation planning. The ensuing plan is compared to the actual plan implemented during the remedial investigation.

### ***Decision:***

It is desired to not erroneously declare decision units clean with respect to total PCBs if either the SCHS or a greater amount of PCBs contamination is present.

### ***Study Boundaries:***

- $A_c$ : Each decision unit represents an anticipated human health risk assessment exposure area for which an estimate of the mean concentration is desired. Hence,  $A_c$ 's are individual decision units.
- The human health risk associated with site contamination at the time of the remedial investigation, 1994, is the concern. Therefore contaminant dispersion

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and attenuation that will lower maximum concentrations in the future will not be considered during development of the remedial investigation plan.

- Total PCBs concentrations, expressed in units of mg/kg, is the contaminant of concern.
- It is assumed that the surface expression of subsurface contamination has higher maximum concentration.

### ***Inputs:***

- $C_{index}$ : A cursory risk assessment suggested total PCBs concentration equal or exceeding 20 mg/kg will present an unacceptable  $10^{-5}$  carcinogenic risk to human health [BOR 1994]. Hence  $C_{index} = 20$  mg/kg. The minimally acceptable average total PCB concentration is 20 mg/kg.
- $C_{max}$ : Records indicated that PCBs from transformers may have been released at various unknown locations as late as 1980. Soil saturated with transformer oil containing PCBs are expected to exhibit a soil concentration of about 100,000 mg/kg total PCBs. Contemporary literature suggests an approximately 6 year half-life, therefore it is reasonable to expect that the maximum concentration in 1994,  $C_{max}$ , is about 20,000 mg/kg. A considerable amount of PCBs contaminated soil had been removed from the Site during the initial removal actions by the EPA and NPS during 1987 and 1988. The soil maximum total PCBs concentration measured during that period was about 8000 mg/kg. It is expectedly less than the 20,000 because only a few soil measurements were made and consequently the true maximum was likely missed. Hence, and  $C_{max}/C_{index} = 1000$ .
- $C_{act}$ : To help avoid an erroneous declaration that the  $A_c$  average does not exceed  $C_{index}$  it is decided that remedial action will be required if  $C_{ave}$  exceeds 2.0 mg/kg. This value is the estimated concentration that would result in an acceptable  $10^{-6}$  human carcinogenic risk. Hence,  $C_{act}/C_{index} = 0.10$
- $C_{ave}$ : The average concentration for each  $A_c$  will be the numerical average of quadruplicate composite sample representations. Each composite will be comprised of  $n/4$  equal volume specimens collected from within  $A_c$ .

### ***Decision Rule:***

It will be concluded that unacceptable PCBs contamination may be present if  $C_{ave}$  exceeds  $C_{act}$ .

### ***Limit on Decision Error:***

The probability of an erroneous declaration that the mean  $A_c$  total PCBs concentration is less than  $C_{index}$ , when the SVHS or greater amounts of PCBs are present, is limited to less than 0.50.

### ***Design:***

From Table 1,  $n = 250$  for the condition that  $C_{act}/C_{index} = 0.10$  and  $C_{max}/C_{index} = 1000$ . Therefore, quadruplicate sets of 63-specimen composite samples will be created to represent each  $A_c$ . The total number of locations represented at the site will be 3024 (12 decision units x 4 samples/unit x 63 specimens/sample).

**Outcome:**

A work plan for the Remedial Investigation and Feasibility Study (RI/FS) was developed during the period 1990 through 1993 and implemented during the summers of 1994 and 1995. The approach used at that time resulted in 2520 locations being represented in sampling. Quadruplicate and sometimes octuplicate sets of composite samples were created to represent each  $A_c$ . Altogether, 72 composite samples were collected, processed and tested.  $C_{ave}$  exceeded  $C_{act}$  in eight of the twelve  $A_c$ 's. Remedial action was implemented to address PCBs contamination in the eight exceeding  $A_c$ 's.

In addition to composite samples, 85 discrete surface samples were concurrently collected from throughout the site, analyzed, and used to calculate  $A_c$  averages. Only four of these  $A_c$  averages exceeded  $C_{act}$ . The observation that half as many of the  $A_c$  averages indicated  $C_{act}$  exceedance when calculated using discrete samples indicates that discrete samples often missed consequential contamination. This conclusion is also supported by the observation that the average  $A_c$  total PCBs concentration calculated using composite samples exceeded the  $A_c$  average calculated using discrete samples in all but one  $A_c$ .

### **3.2 Example 2: Krejci Dump Site Cleanup Verification – 2005 through 2010**

**Background:**

The Krejci Dump Site Remedial Action (RA) was initiated in 2005 following several years dedicated to completing the RIFS, CERCLA litigation, and planning. The Record of Decision required, among other things, that all debris and soils containing unacceptable levels of contaminants be excavated and disposed off-site at appropriately licensed or permitted facilities. Ecological and human health risk assessments had been performed as part of the feasibility study. Risk assessments established risk-based concentration limits for each of 33 identified site contaminants of concern,  $C_{index}$ . Action levels,  $C_{act}$ , were subsequently established as remediation goals for cleanup verification.

PCBs remediation was driven by the need to protect native omnivores. The ecological risk assessment used an approximately 1000 m<sup>2</sup> area to represent the home range of a native omnivore. Hence, the site was subdivided into 186 approximately 1000 m<sup>2</sup> decision units. Ecological risk assessment established that limiting decision unit mean total PCB's concentrations to less than 0.075 mg/kg will protect individual omnivores. It was also concluded that limiting 4000 m<sup>2</sup> area mean total PCBs to 2.5 mg/kg will sufficiently protect omnivore populations.

The following design process utilizes Equation 1 to determine  $n$ . It necessarily deviates from the actual design process since Table 1 and Equation 1 were developed after this design was complete.

**Decision:**

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It is desired to not erroneously declare decision units clean with respect to total PCBs if either the SCHS or a greater amount of PCBs contamination is present. The first priority is to protect populations of omnivores and the second priority is to protect individual omnivores.

### **Study Boundaries:**

- $A_c$ : Each 1000 m<sup>2</sup> decision unit represents the approximate size of the home range for the omnivore. Hence,  $A_c$ 's are individual 1000 m<sup>2</sup> decision units. These will be called Tier 1  $A_c$ 's. Each set of four adjacent Tier 1  $A_c$ 's, approximately 4000 m<sup>2</sup>, represents the area associated with omnivore populations. Therefore each set of four adjacent Tier 1  $A_c$ 's represents a Tier 2  $A_c$ . Hence, every Tier 1  $A_c$  has four adjacent Tier 2  $A_c$ 's, each having a corner of a corner of the Tier 1  $A_c$  at its center.
- The risk associated with site contamination at the time of remediation, 2005, is the concern. Therefore contaminant dispersion and attenuation that will lower maximum concentrations in the future will not be considered during development of the cleanup verification plan.
- Total PCBs concentrations, expressed in units of mg/kg, is the contaminant of concern.
- It is assumed that subsurface contamination will decrease with depth and the maximum concentration will always be at the ground surface.

### **Inputs:**

- $C_{index}$ : Ecological risk assessment indicated that an Tier 2  $A_c$  average total PCBs concentration equal or exceeding 2.5 mg/kg would present an unacceptable risk to an omnivore population. Hence  $C_{index} = 2.5$  mg/kg.
- $C_{max}$ : As in the first example,  $C_{max}$  was calculated by presuming exponential decay. In this instance, the shortest period for decay is estimated to be 2005-1975 = 30 years. Assuming an initial soil concentration of 100,000 mg/kg and a contemporary published half-life of 5 years, the maximum concentration of PCB was calculated to be  $C_{max} = 1563$  mg/kg.
- $C_{act}$ :  $C_{act}$  is 0.075 mg/kg, the value which ecological risk assessment indicated would protect individual omnivores if not exceeded as an Tier 1  $A_c$  average.
- $C_{ave}$ : The Tier 1  $A_c$  mean total PCBs concentration will be represented by analysis of a single composite sample comprised of  $n$  specimens. Therefore Tier 1  $C_{ave}$  is the composite sample total PCBs concentration. The Tier 2  $C_{ave}$  will be the average of four adjacent Tier 1  $C_{ave}$ .

### **Decision Rule:**

Decisions will be made for each Tier 1  $A_c$ . It will be concluded that remediation is necessary if two conditions coexist. First, the Tier 1  $C_{ave}$  equals or exceeds  $C_{act}$ . This will be called the Tier 1 decision. Second, an associated Tier 2  $C_{ave}$  equals or exceeds  $C_{act}$ . This will be called the Tier 2 decision. An exceedance will result in a minimum of 150 mm of soil being excavated from all Tier 2  $A_c$ 's associated with the failing Tier 1  $A_c$  and the sampling, analysis and decision process repeated. This process will iterate until

remediation is no longer indicated.

***Limit on Decision Error:***

It is desired to limit to less than 0.50 the probability of an erroneous declaration that an  $A_c$  mean total PCBs concentration is less than  $C_{index}$  when the SCHS or greater amounts of PCBs are present.

***Design:***

Equation 1 is used to calculate  $\underline{n}$ .

$$n = \frac{1563}{2.5} \left( 0.764 \left[ \frac{-0.102}{LN \left( \frac{.075}{2.5} \right)} \right]^{1.21} + 0.233 \right)$$

This yields,  $\underline{n} = 152$ .

Hence, 152 specimens are required per Tier 2  $A_c$ . Therefore, it was decided that each composite sample would be created by combining 40 specimens within each  $A_c$ . This results in a total of 160 specimens representing all combinations of 4 adjacent  $A_c$ 's.

This design and decision process provides a 50 percent or better chance that action will be taken to protect omnivore populations if an SCHS is present in the Tier 2  $A_c$ . The decision to excavate soil throughout each Tier 2  $A_c$  when an exceedance occurs in a Tier 1  $A_c$  ensures that all potentially discontinuous SCHS contamination is addressed.

If the decision rule were reestablished with expressed intent to protect individual omnivores,  $C_{index}$  must be 0.75 mg/kg,  $C_{act}$  selected to be less than  $C_{index}$ , and  $\underline{n}$  determined for each Tier 1  $A_c$ . Then remedial action would be required this new if  $C_{ave}$  exceeds  $C_{act}$  in a Tier 1  $A_c$ . The determination of  $\underline{n}$  is left as an exercise for the reader.

**Outcome:** The plan implemented at the Krejci Dump Site for Cleanup Verification resulted in 40 specimen composite samples being created to represent each Tier 1  $A_c$ . Any Tier 1 AC exceeding 0.75 mg/kg total PCBs was excavated a minimum of 150 mm. This process of sampling, decision making and remediation was repeated until remediation was no longer indicated. Remediation began in 2005 and was completed in 2012.

### 3.3 Example 3: Power Substation

**Problem:** The site of a former power substation is to be developed into ¼-acre residential lots. The substation operated between 1955 and 1975 and transformer oil containing PCB's may have been released during this period. The most recent release would have been at least 40 years ago.

**Decision:** It is desired to not erroneously declare any residential-size lot clean if PCB's are present in sufficient quantity to present an unacceptable risk to human health.

**Study Boundaries:** For the purpose of site characterization, the site is subdivided into approximately ¼-acre areas to mimic future residential lots. Due to the low mobility of PCBs, the highest concentrations would expectedly be in near surface soils. Therefore the upper six inches of soil in each ¼- acre subarea represents  $A_c$ .

**Inputs:**

- $C_{index}$ : The minimally acceptable average total PCB concentration is 2.0 mg/kg and represents a  $10^{-5}$  human health risk.
- $C_{max}$ : A reasonable maximum total PCBs concentration is estimated to be 390 mg/kg. This is determined by assuming exponential decay over a 40 year period, using a half-life of 5 years obtained from literature, and estimating soil concentration at the time of release to be 100,000 mg/kg.  $C_{max}/C_{index} = 195$ .

**Decision Rule:** It will be concluded that unacceptable PCBs contamination may be present if the average total PCBs concentration,  $C_{ave}$  exceeds  $C_{act} = 0.2$  mg/kg. A residential-size lot having this average concentration is estimated to present a  $10^{-6}$  carcinogenic risk.  $C_{act}/C_{index} = 0.10$ .

**Limit on Decision Error:** The probability of erroneously declaring a residential-size lot clean when the SCHS is present must be less than 50 percent.

**Design:** The approximate minimum number of specimens per sample,  $\underline{n} = 49$ , is calculated using equation 1.

$$n = \frac{390}{2.0} \left( 0.764 \left[ \frac{-0.102}{LN \left( \frac{0.2}{2.0} \right)} \right]^{1.21} + 0.233 \right)$$

Four 4 x 4 grids will be used to simplify specimen collection. Each ¼-acre subarea will be represented by quadruplicate composite samples comprised of specimens collected at the nodes of four independent 4 x 4 grids. Hence each composite samples will be created by combining 16 equal mass soil specimens. The total number of locations represented in each residential-size lot is 94, acceptably more than the 49 needed. Each grid will have a random origin and orientation. Each specimen will represent the upper six inches of soil.



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$C_{ave}$  for each 1/4-acre subarea will be calculated and compared to  $C_{act}$  and the decision rule applied.

**Discussion:**  $C_{index}$  is the user controlled variable having the greatest impact on the required  $\underline{n}$ . For example, the same analysis using  $C_{index} = 10$  mg/kg results in  $\underline{n} = 10$ ; if  $C_{index} = .25$  mg/kg,  $\underline{n} = 826$ .

The 4 x 4 grid is chosen because it is simple to establish in the field and in quadruplicate results in more than the minimum  $\underline{n}$ . The use of quadruplicate representations helps to minimized laboratory measurement uncertainties associated with imprecision.

Each composite sample will be field spiked with sufficient potassium nitrate,  $KNO_3$ , to cause the average composite concentration to be 50 mg/kg. It has been predetermined that that measurements of nitrate + nitrite as N for this  $NO_3^-$  spike concentration is about 20 times greater than that of similar measurements on native site soil. The liquid volume of  $KNO_3$  solution introduced to the sample as the spike will be approximately equal to the estimated volume of pore space in one in situ specimen volume. The intent is to mimic a contaminated specimen so that recovery and RPD will reflect the effectiveness of the homogenization process at the appropriate scale.

Prior to the start of sampling, a pilot study will be performed using site soil to evaluate the homogenization effectiveness of the proposed sample processing procedure. The procedure will be adjusted during this study to reasonably ensure that recovery of  $NO_3^-$  (nitrogen as nitrate analysis) will routinely exceed 80 percent and the RPD of duplicates will routinely be less than 30 percent.

Recovery and RPD will be determined for independent duplicate aliquots obtained from each composite sample. Action will be taken to change the sample processing procedure if recovery is ever found to be less than 80 percent or RPD is ever greater than 30 percent.

## **4. DISCUSSION AND CONCLUSION**

Contamination in an abundance that is sufficient to cause the average concentration of a soil mass or a surface area to exceed a remediation goal or regulatory standard is herein termed consequential contamination. The most common approach to sample plan design inherently assumes that the absence of discovered contamination is sufficient evidence to conclude the absence of consequential contamination. This assumption is indefensible if it can be reasoned that consequential contamination might exist between sampling locations. Small areas of discontinuous contamination, e.g. hot spots, would reasonably be expected at uncontrolled dump sites, when defining the spatial limits of contamination at any site, and when determining the effectiveness of a cleanup that relies on excavation and removal of contaminated soil. In these instances, it is prudent that both soil characterization and rules for decision making minimally ensure a greater than 50 percent

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chance of responding to the reasonably conceivable smallest hot spot of consequential contamination. An approach to create, evaluate and defend sample plan designs for these and similar situations is described and examples presented.

The method may be used to determine minimum sampling requirements for either composite sampling or discrete sampling. When composite samples are used, extreme care must be taken to ensure that sample processing results in every potential test aliquot representing the mean composition of the sample. Quality control should include a field spike that is introduced prior to sample processing and that mimics a single contaminated soil specimen. Inadequate composite processing is indicated by any failure to achieve 80 percent recovery, or any field spike RPD calculation indicating an exceedance of 30 percent.

The number of locations that must be represented,  $\underline{n}$ , increases with increasing  $C_{act}$  and decreasing  $C_{index}$ .  $C_{index}$  is the user controlled variable having the greatest impact on the required  $\underline{n}$ .  $C_{act}$  may be increased as needed to reduce the likelihood of an erroneous declaration that consequential contamination may be present.

PCBs are the only contaminant discussed in the examples presented herein. However, the method is applicable to any contaminant. Also, only sites of uncontrolled chemical releases are presented in examples. However, the method is applicable for other situations. It has been used to aid in the design of pilot studies, site assessments, radiological screening, compost evaluations, and truckload waste disposal compliance. The method may also have application in the food sampling industry where bacterial or chemical contamination expectedly occurs in hot spots.

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