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Composite and Discrete Sampling as Redundant Efforts - A Case History

Introduction

A quest to provide site characterization data that is appropriate for risk-based decision making has lead the author to using redundant sampling programs. It began with a need to investigate a former municipal and industrial waste disposal site. The Data Quality Objective (DQO) process was implemented during the investigation planning phase and highlights of this effort are discussed. The resulting investigation consisted of two separate surface soil sampling programs distinguished by discrete sampling and composite sampling. Both were used to independently estimate the mean chemical concentration of 13 subdivided areas of the site. These two representations of chemical distribution provide a unique mechanism to check the completeness of site characterization.

The completeness of site characterization was evaluated by direct comparison of the average chemical concentrations calculated using analytical results of both discrete samples and composite samples. It was observed that estimates of the average concentrations were typically greater when calculated using composite samples. A simple computer simulation is used to demonstrate that this should be expected if less than half of the investigated site exhibits contamination and the specimen collection density for composite samples is greater than that for discrete samples. Measurements of site surface soil lead and PCB concentrations are used to demonstrate this behavior.

Background

The site will remain anonymous due to pending litigation. It will be referred to simply as The Site. An intentionally distorted, however adequately representative plan view of the 50 acre site, is shown on Figure 1. A nearby area selected to represent background conditions is also portrayed. The Site was operated as a municipal and industrial dump and/or salvage yard from around 1950 until the early 1980s. Waste removal actions in the late 1980's and early 1990's resulted in the clearing of most surface debris and visible waste. Vegetation consisted primarily of native grasses; surface was soil is predominantly clay; and access to nearly all locations was unobstructed.

Historical data suggested a potential for any of a large number of chemicals to have been released at any location on the site in unknown quantities. It was assumed in developing the sampling plan that hot spots presenting unacceptable conditions could exist without visual traces. Determining the minimum number of samples required to detect a surface hot spot that may present an unacceptable human health impact was established as an investigation goal. In addition, an unacceptable hot spot would need to be characterized adequately to meet human health risk assessment needs.

Technical Approach

The DQO Process was implemented to develop a risk-based sampling plan. The resulting plan attempted to reasonably assure that, if no contamination was discovered at the site, it meant that unacceptable contamination was not present. Conceptual models of contamination and human exposure were created to aid in identifying data needs. These were designed to represent minimally acceptable site conditions. The exposure scenario consisted of a child spending one percent of an anticipated 70-yr life on the Site.

Since size and location of any contaminated area was uncertain, a circular conceptual hot spot, with the maximum chemical concentration in its center and decreasing concentration towards the edge, was considered capable of being located anywhere on the site. An example such a conceptual hot spot is illustrated on Figure 2. The expected maximum concentrations of various chemicals were estimated from data collected during an earlier waste removal operation. The size of the smallest conceptual hot spot that would cause the Site to have an average chemical concentration great enough to result in an unacceptable exposure was calculated[1]. The minimum number of samples that would reasonably assure detection of this conceptual hot spot, as well as provide reasonable representation of the hot spot in estimates of the site average concentration, were also calculated.

The minimally acceptable conditions described above were selected to exemplify the expected effectiveness of the proposed sampling effort and provide a basis to estimate data needs for risk assessment. Additional data needs were anticipated for more conservative scenarios expected to be used in the Baseline Health Risk Assessment (BHRA), and also for remedial alternative development. Consequently, a decision tree was created that expanded the sampling program when specific chemical conditions were encountered. This part of the program is beyond the scope of this article but is mentioned to illustrate the place of the presented initial sampling program within a larger surface investigation program.

The Site was divided into 13 areas of concern (AOC's) as depicted on Figure 1. The background site was divided into three areas which are also be referred to as AOC's. Site AOC's represented different surface drainage areas or locations that exhibited different dump operational characteristics such as suspected lagoons, fills, site entrance, etc. AOC's thought most likely to be contaminated were designated (high) H1, H2,...H6. AOC's thought less likely to be contaminated were designated (low) L1, L2, ... L7. Background AOC's were designated B1, B2 and B3. AOC numbers prefixed by H, L, and B will be referred to as high, low, and background respectively.

A staged sampling plan was designed that focused the investigation on the most likely contaminated AOC's. Surface soils in high and low AOC's were sampled at discrete locations on 100 ft and 200 ft square grids respectively. Figure 3 illustrates the discrete sampling effort for AOC H1. Random locations were selected for sampling in small AOC's. Approximately 120 surface samples were collected and analyzed for selected constituents of the Target Analyte List (TAL), Target Compound List (TCL), PCB's, and pesticides. The calculated sampling density was considered adequate to locate contamination if it presented an unacceptable human health

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impact for all chemicals considered important to the investigation except PCB’s. The plan, as designed, would also permit the detection of large PCB hot spots of low concentration which could present an unacceptable human health impact. However, unacceptable smaller hot spots having higher concentrations could be missed. Consequently, characterizing site surface soil PCB concentration required a greater effort.

For PCB’s, an additional staged effort was designed. The first stage is as previously described. The second stage concentrated on detecting small, high-concentration PCB hot spots using a quick, low cost, field screening method that exhibits a relatively high detection limit. Surface soil was collected for PCB screening at 25-ft centers in high AOC’s and 50-ft centers in low AOC’s. For example, the sampling effort for AOC H1 is shown on Figure 4. Soils from approximately 1700 locations throughout the Site were screened.

The sampling program described above focused on simply detecting contaminants if they presented a potential threat to human health. It was recognized that this would not be adequate characterization for risk assessment purposes. However, the many-fold increase in the number of samples that would be required to assure adequate characterization of a small consequential hot spot was overwhelming. Composite samples were introduced to the sampling plan to overcome this problem.

Risk Assessment Guidance (RAGS)[2] suggests using an estimate of an area average concentration to calculate the dose of a chemical that a human receptor is likely to receive by direct exposure to the area. The site was considered as an exposure unit for the previously described minimally acceptable exposure scenario. Consequently, the averages of this area was sought such that the average included adequate representation of the minimally acceptable hot spot. Again, risk-based statistical calculations were employed and it was decided that an adequate representation of the hot spot could be attained if approximately 16 times as many samples were collected as previously proposed for discrete sampling[1].

It was considered impractical to collect and analyze this large number of discrete samples. Instead, since an average was sought, it was decided to create a composite of these samples. This decision was based on the premise that a representative value of chemical concentration for a mechanically mixed set of samples is analogous to numerically averaged representative values of the individual samples. The term "specimen" will be used in subsequent discussion to represent individual samples that are mixed together to form a composite.

It was considered physically impractical to composite all the needed specimens in a given AOC into one sample. The volume of soil would be difficult to handle and would complicate mixing. Also, it was recognized that one sample is not adequate to set limits on an expected mean chemical concentration or permit statistical tests of hypotheses related to the mean. In order to obtain information needed to estimate the variance of the mean, and to simplify sample handling, four composite samples were created to represent each AOC. Each composite was

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comprised of four times as many specimen collection locations as were proposed for discrete sampling locations. These were collected from grid locations throughout the AOC, as illustrated for AOC H1 on Figure 5. Each symbol on this figure represents locations where a specimen was collected. All specimens represented by like symbols (e.g. all circles) were combined to form a composite sample. This resulted in quadruplicate representation of the AOC . For various reasons, including the desire to improve estimates of AOC mean concentrations, a second set of four composite samples was created for most AOC's. Hence, octuplicate representations were often created. Specimen collection locations for the second set were the midpoints of the previously used specimen collection locations. Cumulatively, the number of specimens collected for composites in most AOC's is either 16 or 32 times greater than the total number of discrete samples depending on the number of composite samples collected, i.e. 4 or 8.

Expectations

If less than half of an area is contaminated, any single randomly selected sampling location is more likely to be outside the area of contamination than within. For this reason, it is expected that the average chemical concentration, when calculated from data representing a limited number of samples, will under-represent the average concentration more frequently than over-represent it. This is demonstrated by the following computer simulation.

Assume the hot spot portrayed in Figure 2 covers 6 percent of the Site. Also assume that the maximum concentration of the hot spot is 10,000 (concentration units are irrelevant to this example). This makes the conceptual hot spot average concentration 3333. The corresponding Site average concentration would be 200. Since 6 percent of the area is contaminated, it is expected that a single sample, collected at random, has only a 6 percent chance of encountering any contamination. Consequently, if a sampling episode consisting of collecting one randomly located sample is repeated a large number of times, then contamination is expected to be encountered 6 percent of the time. A computer algorithm that emulated this scenario was executed 1000 times and resulted in a frequency distribution of concentration measurements shown on Figure 6. The high frequency of samples exhibiting concentration less than 40 supports the expectation that approximately 94 percent of the modeled samples missed the hot spot. The histogram also correctly portrays that nearly all of the hypothetically contaminated area exhibits concentrations greater than 360.

The computer simulation was repeated again, this time using 10 samples per sampling episode rather than 1, and plotting the distribution of the calculated average instead of the individual concentrations. A thousand episodes were simulated and the frequency distribution of results is shown on Figure 7. Statistical calculations suggest that 54 percent of the time the hot spot will remain undetected. This explains why most of the occurrences are represented in the 0 to 40 range of the histogram. Note that a majority of the sampling episodes result in calculated averages that are less than the modeled site average concentration of 200 mg/kg.

The scenario was repeated with sampling episodes consisting of 30, 100, and 500 samples

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per episode and the resulting histograms of all these modeling events are shown on Figure 8 along with the previous two examples. It is observed that, as the number of samples increase, the distribution of the mean approaches the normal distribution. This is a demonstration of the Central Limit Theorem of Statistics. Because of this, the frequency of underestimating the mean approaches the frequency of overestimating the mean as the number of samples increases. This can also be seen on Figure 8. The frequencies never become equal until the entire site surface is sampled. Therefore it is concluded that the estimate of the mean will more likely be low than high when less than half the site area is contaminated. The converse would be true if less than half the site is clean.

In general, at the Site, it was expected that less than half of the surface area of each AOC would exhibit chemical contamination. Consequently, based on the above discussion, it was expected that the average chemical concentrations calculated from the results of composite sampling would typically be greater than the average concentration calculated from the results of the much more limited discrete sampling. This was observed and is discussed in the following section.

Observations

The discrete and composite samples collected as described in the previous section represent redundant AOC characterization efforts. The results of both programs can be used to independently estimate mean chemical concentrations. Lead and PCB’s were two contaminants commonly found in AOC’s. These will be used to demonstrate the usefulness of the redundant programs.

The previously described expectations are demonstrated in the results the Site investigation. Tables 1 and 2 list the calculated average concentrations for lead and total PCB’s. Also provided on these tables in parentheses and brackets are, respectively, the number of samples used in the calculation of the averages, and the total number of specimens used in composite samples. Not all AOC’s exhibited measurable PCB concentrations. Accordingly, values are only presented for AOC’s in which PCBs were detected. PCB’s detection limits were typically less than 1 mg/kg. Half the detection limit was used to represent concentrations in samples with immeasurable levels of PCB’s. Lead concentrations were measurable in all samples.

As expected, averages calculated from composite samples are typically greater than those calculated from discrete samples. Sometimes this is a large difference. Large differences imply that the unbiased discrete sampling effort did not appropriately represent a contamination within the area. Occasionally only one composite sample in an AOC would encounter. This indicates that contamination is spatially noncontinuous, i.e. located in hot spots.

The PCB screening data was not used in the previous comparison, yet provides considerable insight into the distribution of PCB’s on the site. The spatial distribution of total

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PCB's was estimated by cokriging the soil screening and the laboratory data from the discrete sampling program. A typical result is portrayed graphically on Figure 9. The red areas indicate the greatest PCB concentrations and blue the least. To evaluate the appropriateness of this representation, a computer algorithm was created to simulate composite sampling of this modeled site contamination. Similarity between the computer simulated measurements and direct measurements, would bolster confidence of a good geostatistical representation of PCB distribution. The computer estimated means and variances were calculated and compared with the actual field composite test results.

When comparison revealed that the simulated average concentrations were higher than actual field composite values, it was concluded that the map generated by cokriging was portraying more surface PCB contamination than probably exists. Also, when the variance of the simulated composite samples were considerably less than the variance of real field composite test results, it was interpreted as the model indicating a more uniform distribution of contamination than truly exists.

Unlike field composite samples, the computer simulation provides estimates of chemical concentration for individual composite specimens. It was observed that occasionally only one or two simulated specimens accounted for nearly all PCB's encountered in AOC composites.

Concerns and Controversial Aspects of Composite Sampling

There are two sources of error commonly associated with discrete sampling that are potentially more significant to composite sampling. These are the loss of volatile compounds during sample collection and processing, and heterogeneity of the mixed composite. Heterogeneity of the mixed composite can be measured and controlled, thereby making it less of a concern than the volatilization issue. The fine-grained clay soil of The Site mixed readily to a putty-like consistency with addition of small amounts of water, making it easy to homogenize. Consequently, the results of analyses on duplicates samples were typically similar. The magnitude of error associated with volatilization of chemicals is difficult to estimate or measure. Prudent controls help to minimized volatilization. These include temperature control and expedience in both specimen collection and mixing operations. New sample collection and processing techniques need to be developed to reduce these errors.

A source of error unique to composite sampling pertains to the interaction of chemicals from different locations of the site. Chemical reactions may occur when chemicals are combined. These reactions may change the concentration or form of contaminants and therefore should be considered when designing a plan which uses composite sampling.

Composite sampling has been challenged by regulators and others as a mechanism of "dilution". Compositing is a mechanical averaging process that is analogous to numerical averaging that is commonly employed to test statistical hypotheses. Therefore, they can be used to make similar decisions.

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The Site sampling plan was designed to reasonably assure that a hot spot presenting a threat to human health would be adequately represented for risk assessment purposes in AOC averages. The determination of sampling density was based on an assumed chemical distribution. No test was implemented to evaluate the adequacy of this assumption. However, this could be accomplished by collecting several composite samples each representing the same AOC, with each consecutive sample being comprised of a greater number of specimens. As discussed earlier, the composite sample concentrations should approach the true AOC mean concentration as the number of specimens in the composite is increased. If using a significantly larger number of specimens in the composite doesn’t change the measured chemical concentration value then the sampling objective was met.

The effort required to collect surface specimens required to form composite samples was small and the benefits gained by improved representation of contaminants in surface soil were significant. In contrast, the low sampling density associated with discrete samples make their use in estimating average concentrations questionable. Also, a large difference in concentration values measured in co-located discrete samples was often observed, causing concern about the ability of these samples to adequately represent concentration distributions at small scales. Based on this experience, if greater detail regarding contaminant distribution is required than can be obtained from AOC averages, the author would recommend compositing surface soil within grid blocks contained within the AOC to represent each grid area, rather than collecting single discrete samples at grid points.

The results of chemical analyses conducted on composite samples collected within an AOC represent a population of possible AOC average values. The average of measured composite sample concentrations is actually an estimate of the mean of the population of all possible AOC averages collected in this manner. The expected variance of estimates of the mean is considerably less than the variance of the site chemical distributions. Consequently, the calculated confidence interval for the expected mean utilizing composite samples is expected and observed to be much narrower than that calculated using discrete sample results. The exception to this occurs when discrete samples entirely miss site contamination that is otherwise represented in composite samples. In this instance, the variance of discrete samples concentrations is nonexistent while a value can be calculated from measured concentrations from composite samples.

The composite sampling program at The Site utilized specimen collection grids with equally spaced origins. This inherently introduces a potential for bias since the contaminant is not expected to be randomly distributed on the site. An example best illustrates this problem. Consider a 10 ft diameter hot spot of uniform concentration at an unknown location in an AOC. If two samples are collected from the AOC with the restriction that they be separated by 11 ft, then one will always be located outside the hot spot. This forces the two-sample plan to be biased towards misrepresenting the hot spot in the average. This problem is expected to be present even with greater numbers of samples collected on a grid. However, as the number increases, the

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magnitude of the misrepresentation will decrease. Randomly selecting the specimen collection locations for each composite would eliminate this error.

Summary and Conclusions

The objective of the Site surface soil sampling program was to, 1) reasonably assure that if no contamination is discovered at the site then unacceptable contamination is not present and 2) to reasonably assure that a hot spot presenting a threat to human health will be adequately represented for risk assessment purposes. Redundancy in the Site investigation provided a unique opportunity to evaluate the effectiveness of thes sampling effort. Two independent programs, one using composite samples, and the other using discrete samples, were used to characterize the distribution of chemicals. It was demonstrated that the greater sampling density associated with composite samples typically yielded higher area average concentrations than was calculated using discrete sample data. Compositing multiple specimens into a single sample reduced the analytical effort typically associated with sampling programs that utilize high discrete sampling density. It was demonstrated that composite samples can be used to evaluate the appropriateness of hypothetical contaminant distributions. Redundancy in the sample plan provided valuable insight into the effectiveness of sampling effort and promotes the continued use of composite samples in site characterization.

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2. Supplemental Guidance to RAGS: Calculating the Concentration Term, USEPA, OSWER Publication 9285.7-081. May 1992.

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Table 1. Comparison of Lead Subunit Averages from Point and Composite Samples

Subunit	**Area (ft^2/1000)**	**Average Concentration calculated from Point Samples** (mg/Kg) **with Corresponding Number of samples shown in Parentheses.**	**Average Concentration calculated from Composite Samples** (mg/Kg) **with Number of Samples in Parentheses and Total Number of Specimens in Brackets.***
H1	200	**2789** (18)	2145 (8) [640]
H2	266	1128 (27)	**1217** (8) [851]
H3	51	20 (3)	**37** (4) [82]
H4	49	122 (5)	**136** (8) [157]
H5	24	970 (4)	**6116** (8) [77]
H6	41	132 (4)	**171** (4) [66]
L1	167	415 (3)	**736** (8) [134]
L2	203	71 (5)	**83** (4) [81]
L3	245	132 (6)	**506** (4) [98]
L4	240	366 (6)	**372** (4) [96]
L5	203	194 (5)	**1463** (4) [81]
L6	198	239 (6)	**727** (8) [158]
L7	163	**857** (4)	856 (4) [65]
B1	368	42 (8)	**47** (4) [147]
B2	475	56 (10)	56 (4) [190]
B3	413	49 (9)	**59** (4) [165]

* The number of specimens is approximate.

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Table 2. Comparison of Aroclor 1254 Subunit Averages from Point and Composite Samples

Subunit	**Area (ft^2/1000)**	**Average Concentration calculated from Point Samples** (mg/Kg) **with Corresponding Number of samples shown in Parentheses.**	**Average Concentration calculated from Composite Samples** (mg/Kg) **with Number of Samples in Parentheses and Total Number of Specimens in Brackets.***
H1	200	**12.9** (18)	5.3 (8) [640]
H2	266	16.4 (22)	**27.7** (8) [851]
H3	51	0.6 (3)	**1.3** (4) [82]
H4	49	1.2 (5)	**68.6** (8) [157]
H5	24	4.7 (2)	**43.2** (8) [77]
L1	167	0.6 (4)	**17.0** (8) [134]
L2	203	0.1 (5)	**1.0** (4) [81]
L3	245	1.5 (6)	**2.7** (4) [98]
L4	240	3.0 (6)	**3.1** (4) [96]
L5	203	1.9 (5)	**2.1** (4) [81]
L6	198	0.7 (5)	**1.7** (8) [158]
L7	163	**0.8** (4)	0.7 (4) [65]

* The number of specimens is approximate.

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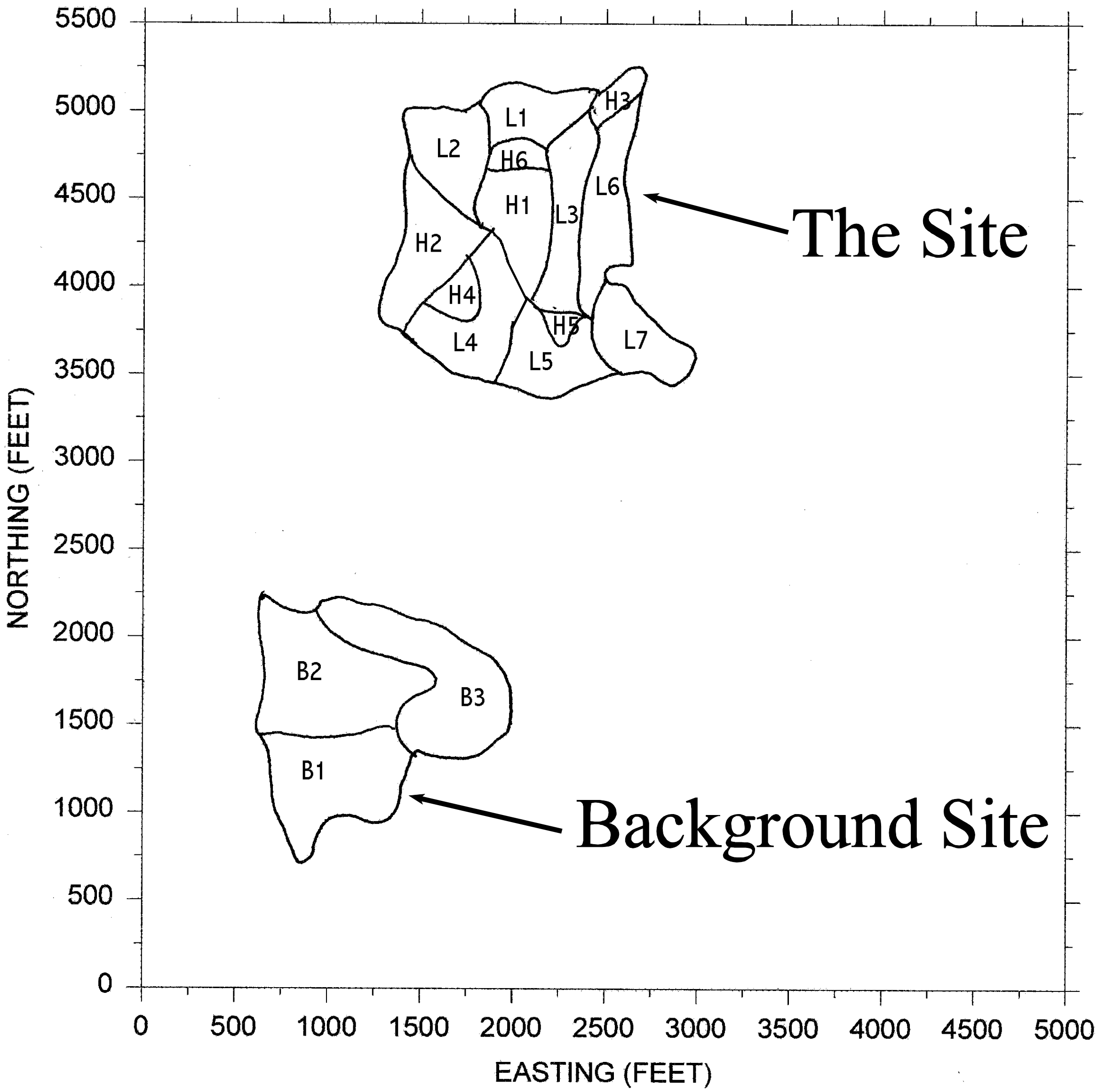

Figure 1. Representations of The Site and its associated Background Site

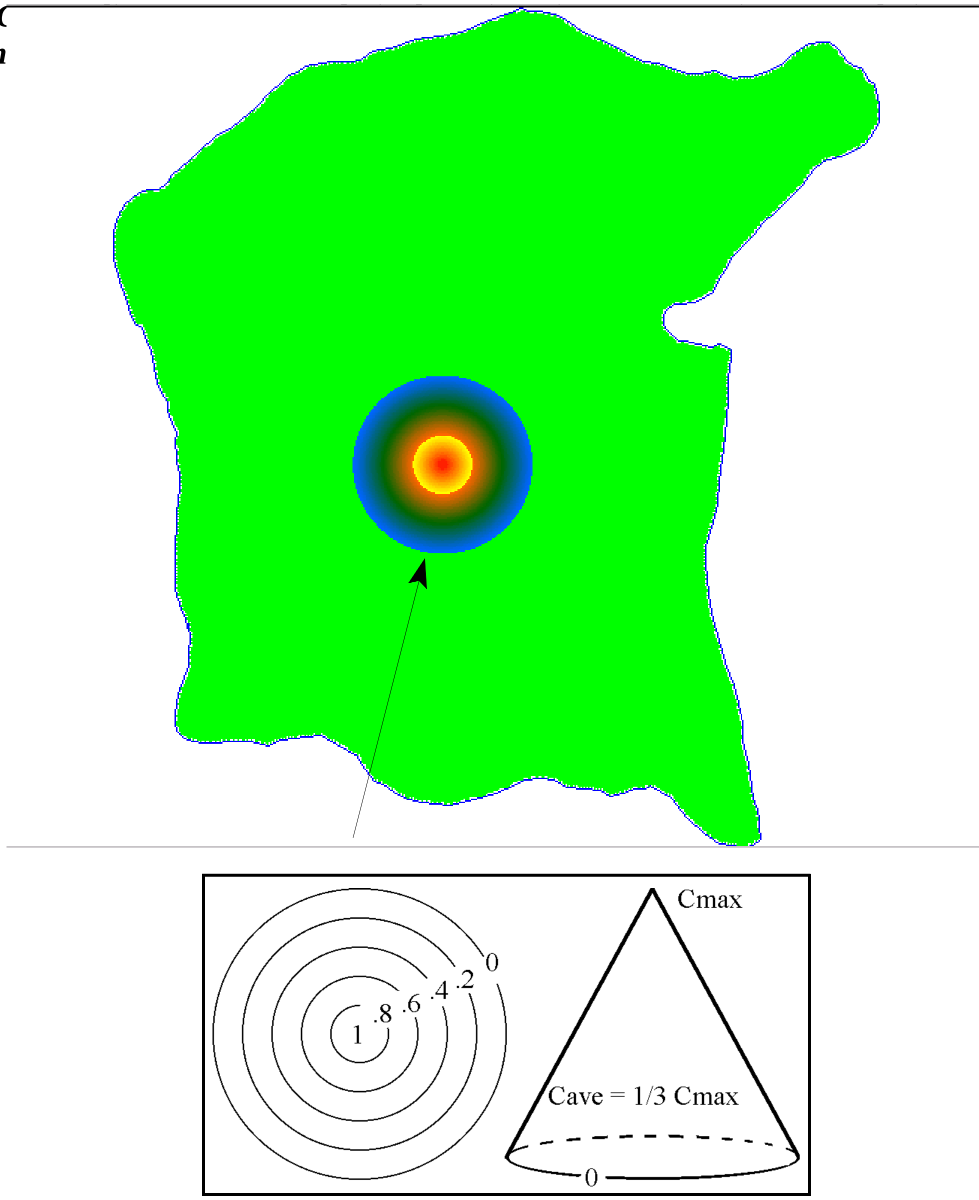

Figure 2. Conceptual Hot Spot Model Superimposed on Representation of the Site. Contours of Concentration Normalized with respect to C_{max}.

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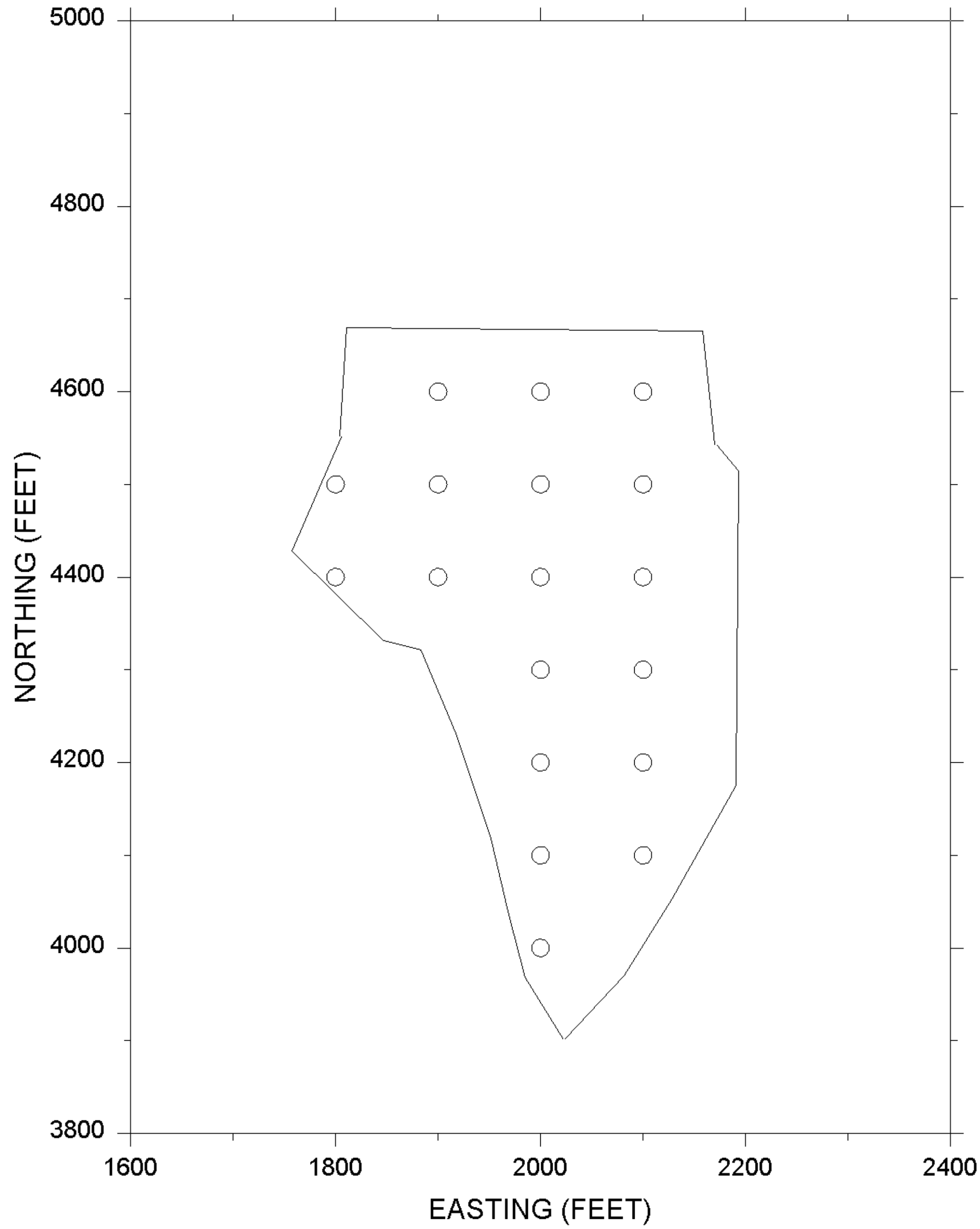

Figure 3. Discrete Surface Soil Sampling Locations in AOC H1.

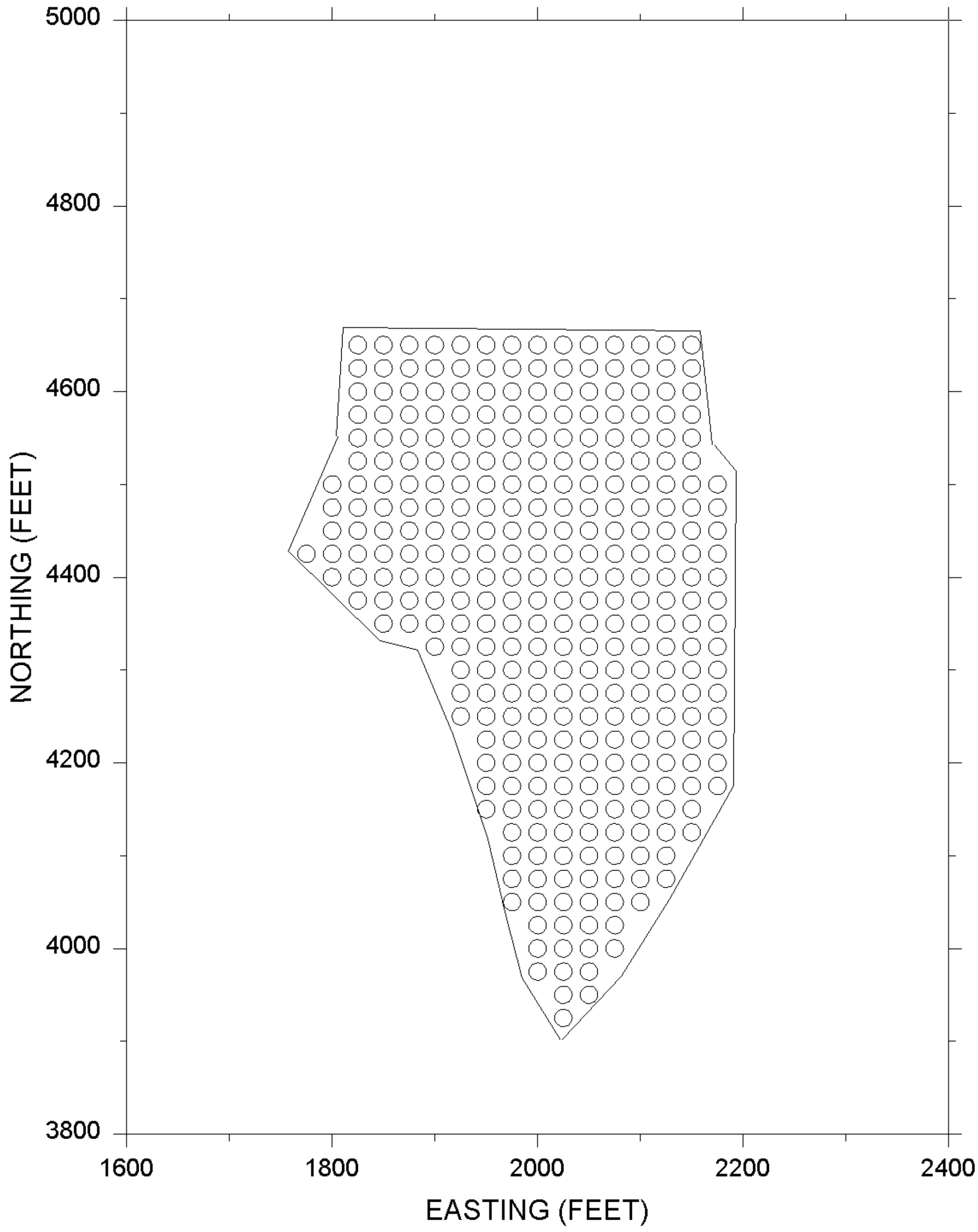

Figure 4. PCB screening locations in AOC H1.

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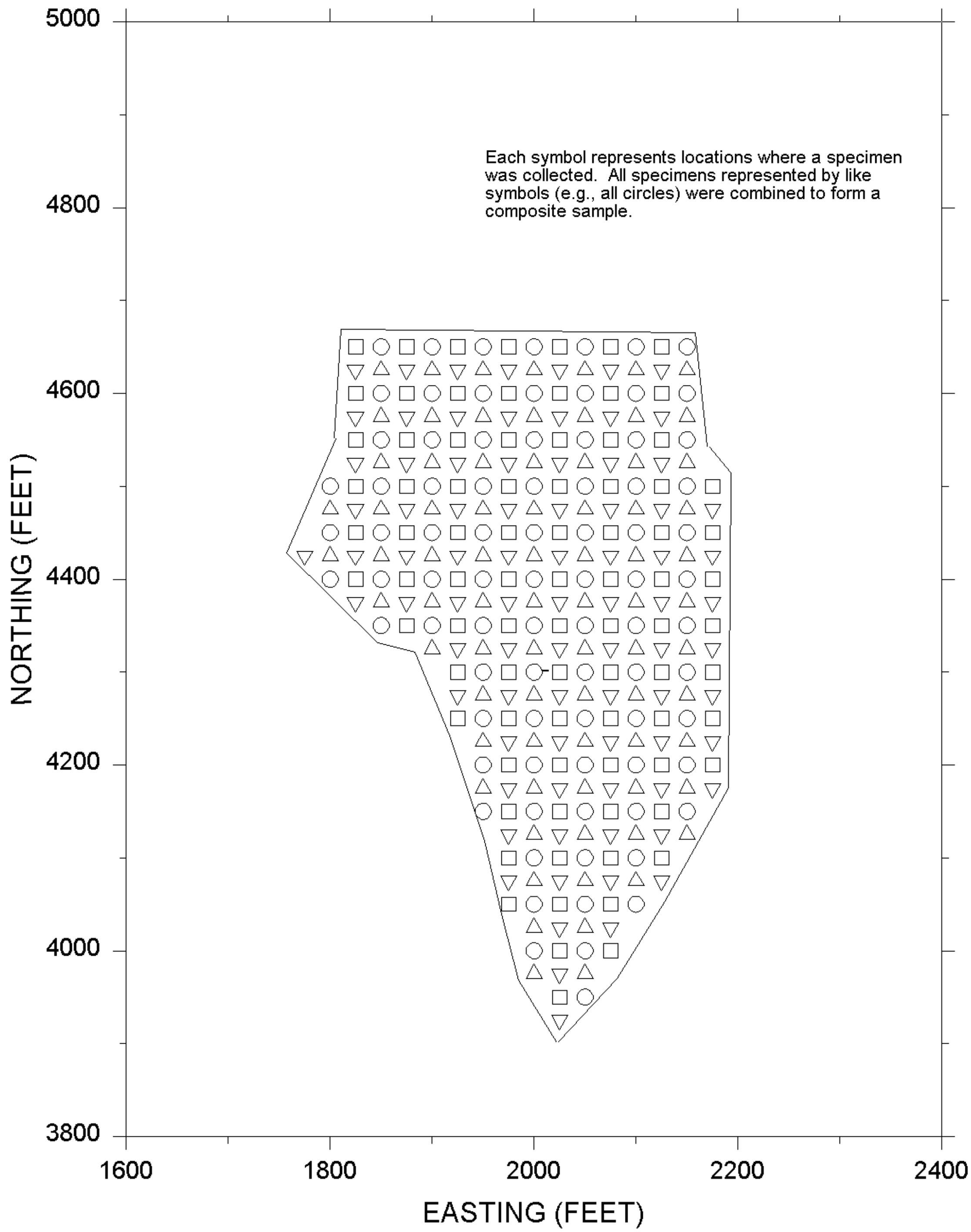

Figure 5. Composite Samples Specimen Collection Locations in AOC H1.

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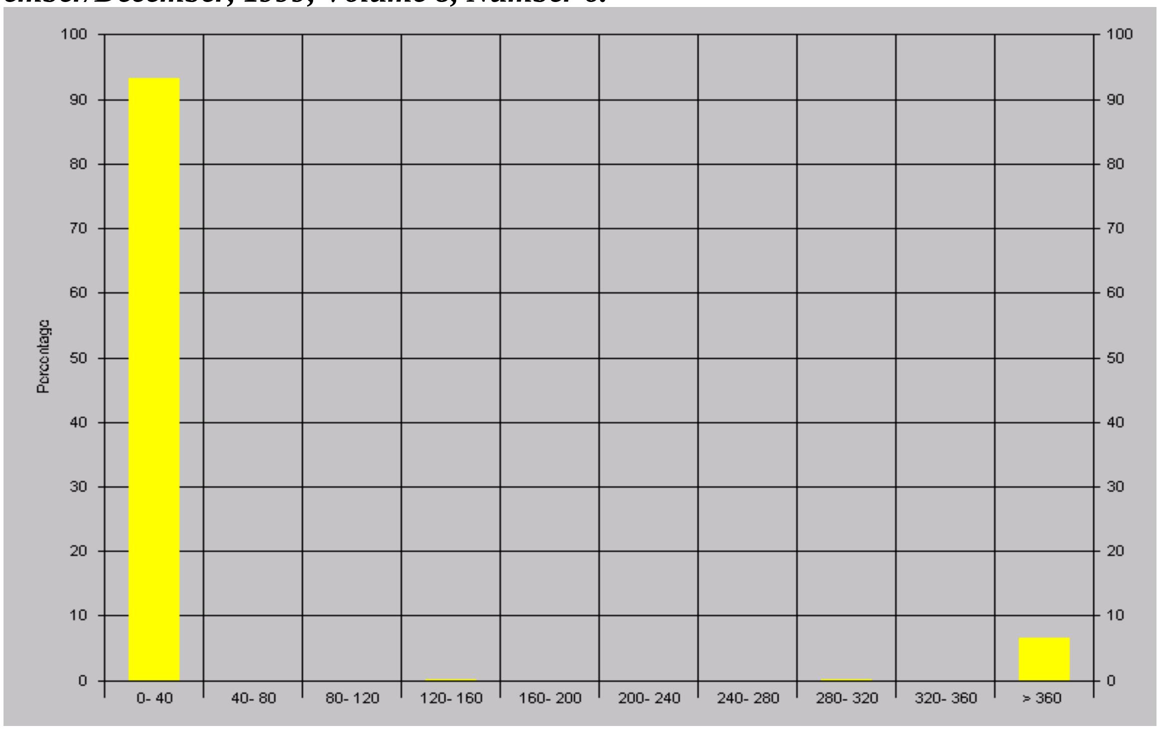

Figure 6. .Percentage distribution of measured concentrations from 1000 sampling episode consisting of 1 sample per episode.

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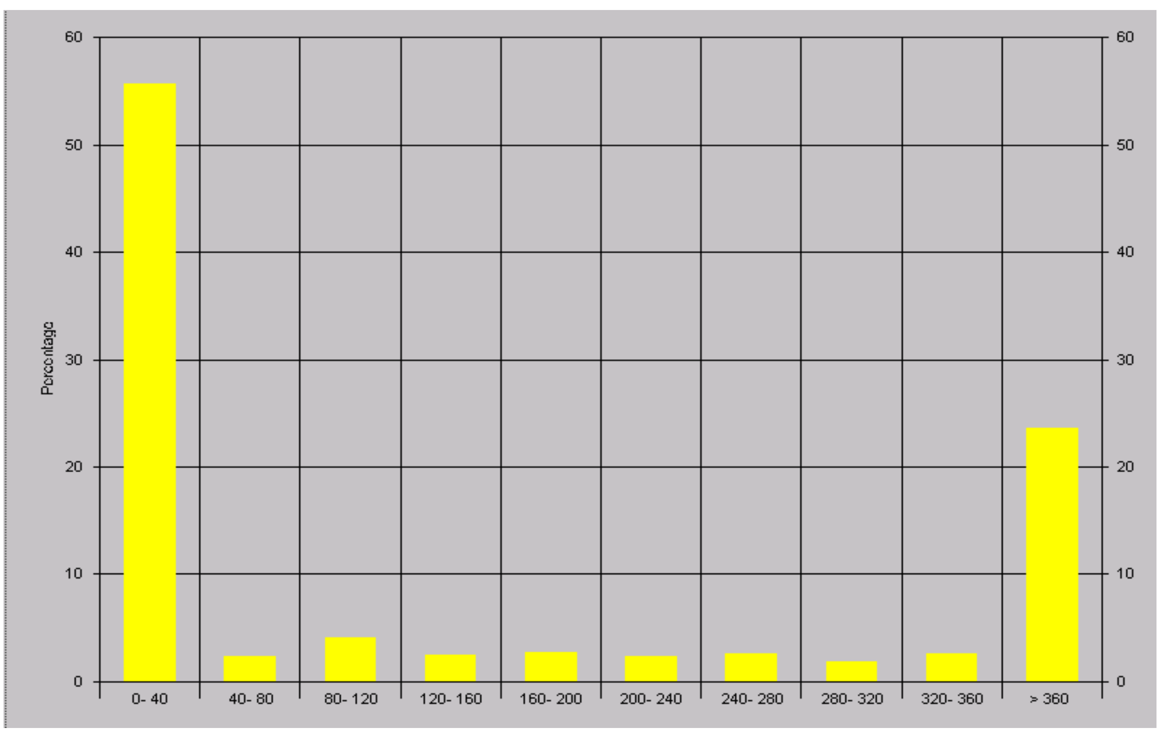

Figure 7. .Percentage distribution of measured average concentrations from 1000 sampling episodes consisting of 10 samples per episode.

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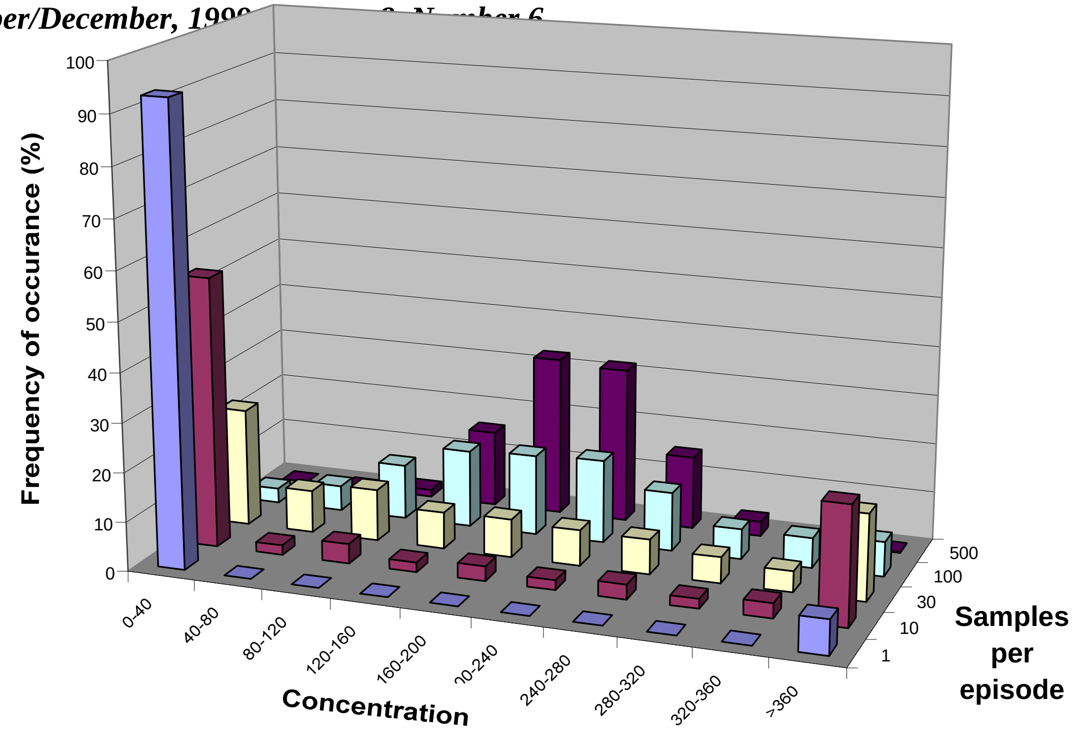

Figure 8. Percentage distribution of measured average concentration s from 1000 sampling episodes consisting of 100 samples per episode.

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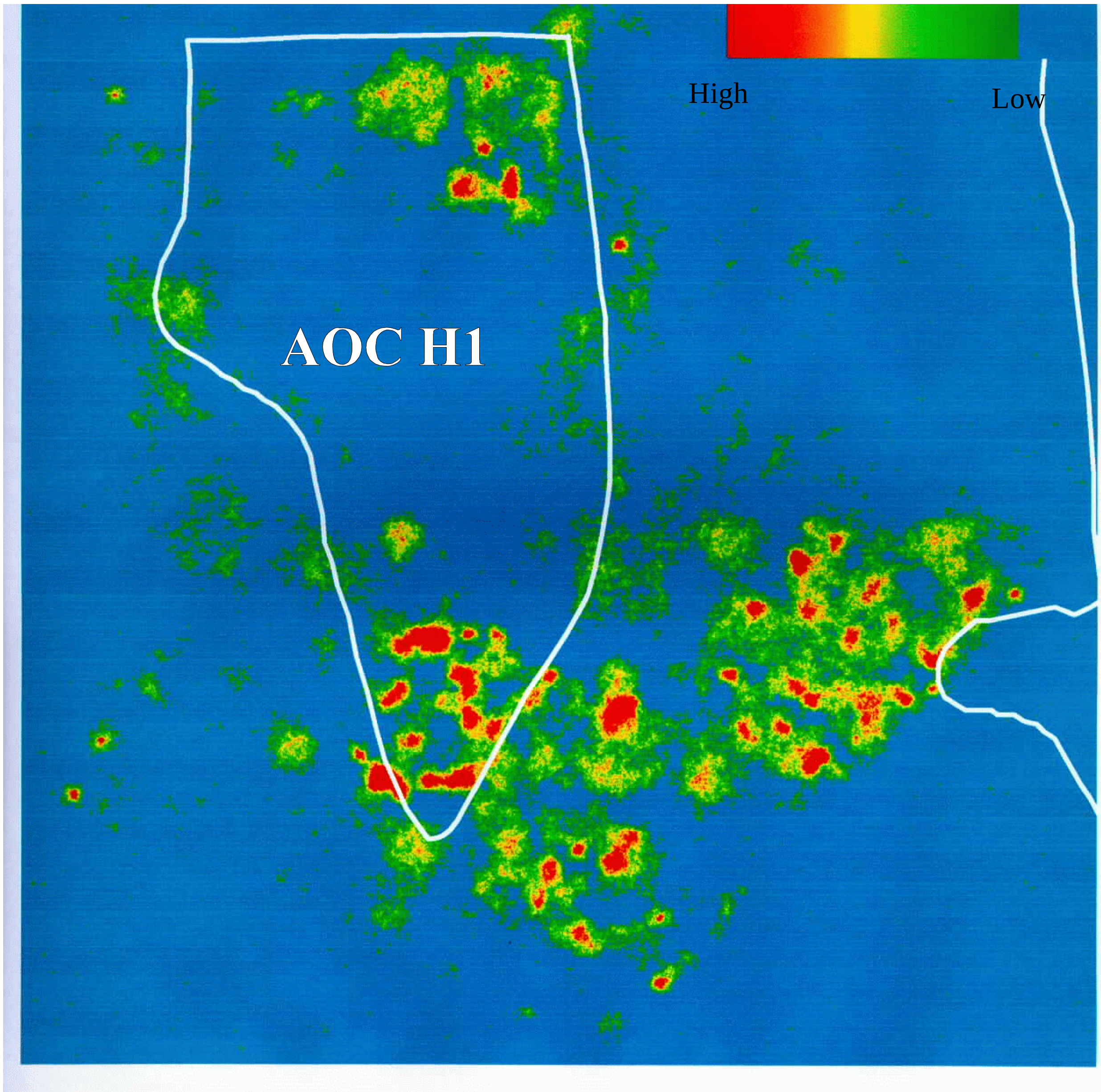

Figure 9. Hypothetical Distribution of PCBs.

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