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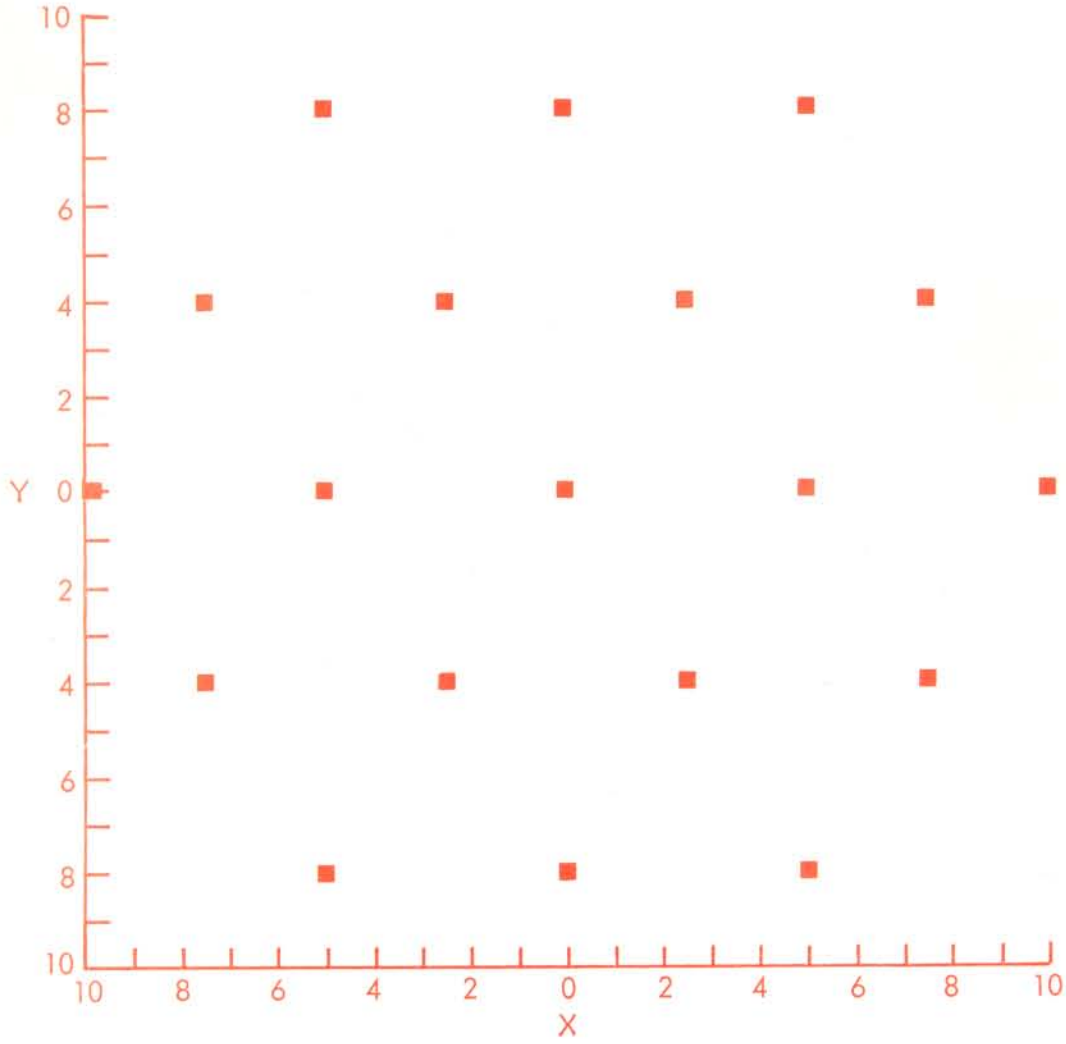
VERIFICATION OF PCB SPILL CLEANUP BY SAMPLING AND ANALYSIS



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VERIFICATION OF PCB SPILL CLEANUP BY SAMPLING AND ANALYSIS

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PREFACE

This Interim Report was prepared for the Environmental Protection Agency under EPA Contract No. 68-02-3938, Work Assignment 37. The work assignment is being directed by Mitchell D. Erickson. This report was prepared by Dr. Erickson, Bruce A. Boomer, Gary L. Kelso, and Steve E. Swanson of Midwest Research Institute (MRI). The sampling design (Section IV.A) was written by David C. Cox and Bradley D. Schultz of the Washington Consulting Group, 1625 I Street, N.W., Washington, D.C. 20006, under subcontract to Battelle Columbus Laboratories, Subcontract No. F4138(8149)435, EPA Contract No. 68-01-6721 with the Design and Development Branch, Exposure Evaluation Division. The EPA Task Managers, Daniel T. Heggem, Richard A. Levy and John H. Smith, as well as Joseph J. Breen, Joseph S.Carra, and Martin P. Halper, of the Office of Toxic Substances, provided helpful guidance and technical information.

NOTE: The second printing of this report contains additional discussion of sampling points located outside the original cleanup (contaminated) area as discussed on pages 11-16.

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January 13, 1986

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I. INTRODUCTION

The U.S. Environmental Protection Agency (EPA) under the authority of the Toxic Substances Control Act (TSCA) Section 6(e) and 40 CFR Section 761.60(d), has determined that polychlorinated biphenyl (PCB) spills must be controlled and cleaned up. The Office of Toxic Substances (OTS) has been requested to provide written guidelines for cleaning up PCB spills, with particular emphasis on the sampling design and sampling and analysis methods to be used for the cleanup of PCB spills.

This work assignment is divided into two phases. The reports of Phase I are presented in Draft Interim Report No. 1, Revision No. 1, "Cleanup of PCB Spills from Capacitors and Transformers," by Gary L. Kelso, Mitchell D. Erickson, Bruce A. Boomer, Stephen E. Swanson, David C. Cox, and Bradley D. Schultz, submitted to EPA on January 9, 1985. Phase I consists of a review and technical evaluation of the available documentation on PCB spill cleanup, contacts with EPA Regional Offices and industry experts, and preparation of preliminary guidelines for the cleanup of PCB spills. The document was aimed at providing guidance in all aspects of spill cleanup for those organizations which do not already have working PCB spill cleanup programs.

Phase II, reported in this document, reviews the available sampling and analysis methodology for assessing the extent of spill cleanup by EPA enforcement officials. This report includes some of the information from the Phase I report, incorporates comments on the Phase I report and the general issue which were received at a working conference on February 26-27, 1985, and addresses the issue from the perspective of developing legally defensible data for enforcement purposes.

This report, intended primarily for EPA enforcement personnel, outlines specific sampling and analysis methods to determine compliance with EPA policy on the cleanup of PCB spills. The sampling and analysis methods can be used to determine the residual levels of PCBs at a spill site following the completion of cleanup activities. Although the methodologies outlined in this document are applicable to PCB spills in general, specific incidents may require special efforts beyond the scope of this report. Future changes in EPA policy may affect some of the information presented in this document.

Following a summary of the report (Section II), Section III presents an overview of PCB spills and cleanup activities. The guidelines on sampling and analysis (Section IV) includes discussion of sampling design, sampling techniques, analysis, and quality assurance.

II. SUMMARY

This report presents the results of Phase II of this work assignment. Phase I consisted of a review and technical evaluation of the available documentation on PCB spill cleanup, contacts with EPA Regional Offices, and preparation of preliminary guidelines for the cleanup of PCB spills.

Phase II (this document) reviews the available sampling and analysis methodology for assessing the extent of spill cleanup by EPA enforcement officials. The report incorporates some of the information from the Phase I report and general issues received at a working conference on PCB spills.

The EPA has set reporting requirements for PCB spills and views PCB spills as improper disposal of PCBs. Cleanup activities have not been standardized since PCB spills are generally unique situations evaluated on a case-by-case basis by both the PCB owner (or his contractor) and the responsible EPA Regional Office. Components of the cleanup process may include protecting the health and safety of workers; reporting the spill; quick response/securing the site; determination of materials spilled; cleanup procedures; proper disposal of removed PCB materials; and sampling and analysis. The level of action required is dependent on the amount of spilled liquid, PCB concentration, spill area and dispersion potential, and potential human exposure.

A sampling design is proposed for use by EPA enforcement staff in detecting residual PCB contamination above a designated limit after a spill site has been cleaned. The proposed design involves sampling on a hexagonal grid which is centered on the cleanup area and extends just beyond its boundaries. Guidance is provided for centering the design on the spill site, for staking out the sampling locations, and for taking possible obstacles into account. Additional samples can be collected at the discretion of the sampling crew.

Compositing strategies, in which several samples are pooled and analyzed together, are recommended for each of the three proposed designs. Since an enforcement finding of noncompliance must be legally defensible, the sampling design emphasizes the control of the false positive rate, the probability of concluding that PCBs are present above the allowable limit when, in fact, they are not.

Sampling and analysis techniques are described for PCB-contaminated solids (soil, sediment, etc.), water, oils, surface wipes, and vegetation. A number of analytical methods are referenced; appropriate enforcement methods were selected based on reliability. Since GC/ECD is highly reliable, widely used, and is included in many standard methods, it is a primary recommended method for most samples. Secondary methods may be useful for confirmatory analyses or for special situations when the primary method is not applicable.

Quality assurance (QA) must be applied throughout the entire monitoring program. Quality control (QC) measures, including protocols, certification and performance checks, procedural QC, sample QC, and sample custody as appropriate, should be stipulated in a QA plan.

III. OVERVIEW OF PCB SPILLS AND CLEANUP ACTIVITIES

A. Introduction to PCB Spills and Cleanup

The EPA has established requirements for reporting PCB spills based on the amount of material spilled and disposal requirements for the spilled PCBs and materials contaminated by the spill. Under TSCA regulations [40 CFR 761.30(a)(1)(iii) and 40 CFR 761.60d], PCB spills are viewed as improper disposal of PCBs. Although specific PCB cleanup requirements are not established in the TSCA regulations, each regional administrator is given authority by policy to enforce adequate clean-up of PCB spills to protect human health and the environment.

1. Current Trends

Due to regional variations in PCB spill policy and the lack of a national PCB cleanup policy, PCB cleanup activities have not been standardized. Individual companies owning PCB equipment and contract cleanup companies have developed their own procedures and policies for PCB cleanup activities keyed to satisfying the requirements of the appropriate EPA Regional Office. In addition, the EPA Regional Offices typically have provided suggestions for companies unfamiliar with PCB cleanup.

PCB spills are generally viewed as unique situations to be evaluated on a case-by-case basis by both the PCB owner (or his contractor) and the EPA Regional Office. However, a general framework is often used to approach the problem. Most cleanup activities involve quick response, removal or cleaning of suspected contaminated material, and post-cleanup sampling to document adequate cleanup. Major considerations involved in the cleanup process include minimizing environmental dispersion, minimizing any present or future human exposure to PCBs, protecting the health and safety of the cleanup crew, and properly disposing contaminated materials.

In general, the involvement of EPA Regional Offices is limited to phone conversations often including a follow-up call to receive the analytical results of the post-cleanup sampling. If the EPA representative is not satisfied with the reported data, additional documentation, sampling and analysis, or cleanup (followed by further sampling and analysis) may be requested.

In cases of special concern (e.g., large spills), EPA Regional Offices may work more closely with the PCB owner or contractor in planning the cleanup, sampling and analysis activities, and on-site inspections.

2. Limitations of This Overview

The general discussion in this chapter refers to the procedures, policy, and considerations that seem to be widely used at present by PCB owners and spill cleanup contractors in meeting the requirements of the EPA Regional Offices. The activities described do not involve EPA regulations or policy except where indicated, since the EPA has not established requirements on PCB cleanup procedures.

Table 1 categorizes PCB spills into approximate levels of action for PCB spill cleanup based on concern. Potential environmental problems increase with increases in PCB concentrations, amount of spilled liquid, spill area and dispersion potential, and potential human exposure. The three spill types presented in Table 1 are based on very rough estimates. "Severity" in one key item such as human exposure could raise a spill to a Type 3 (i. e., requiring special attention). On the other hand a spill of a large volume of liquid may be considered a Type 2 spill due to a relatively low concentration of PCBs. The three categories are only approximate and are intended to demonstrate the flexibility needed in responding to PCB spills. EPA Regional Offices should provide guidance on spill cleanup activities whenever questions develop.

The situations described in this chapter are limited to recent PCB spills of similar magnitude to the reported spills associated with PCB oil transformers and capacitors (i.e., Type 2 in Table 1). Unusually severe spill incidents (Type 3 in Table 1) involving large volumes of PCBs, a large spill area, a high probability of significant human exposure, and/or severe environmental or transportation scenarios may require special considerations, beyond the scope of this discussion.

All spills from regulated equipment are typically subject to the detail of effort outlined in this chapter. Although cleanup of smaller spills (Type 1 in Table 1) is required if the concentration of PCBs in the spilled material is 50 ppm or greater, the spill and the cleanup activities normally are not reported to EPA.

Future changes in EPA policy may invalidate some of the discussions appearing in this chapter. For example, if EPA adopts any type of formal categorization scheme for PCB spills, some of the assumptions made in this chapter may become inappropriate.

B. Components of the Cleanup Process

1. Health and Safety

Protection of the health and safety of the clean-up crew during the PCB cleanup operation is an important concern. References discussing health and safety considerations relevant to some PCB spill incidents include NIOSH Criteria for A Recommended Standard for Exposure to Polychlorinated Biphenyls (PCBs) (1977c) and Health Hazards and Evaluation Report No. 80-85-745 (NIOSH 1980). The appropriate level of health and safety protection is dependent upon the specifics of the spill.

2. Reporting the Spill

If the regulatory limits are exceeded, the spill must be reported to Federal, State, and local authorities as applicable. Under EPA regulations [Fed. Reg. 50:13456-13475], spills over 10 lb must be reported to The National Response Center. The toll free phone number is (800) 424-8802.

Table 1. Approximate Levels of Action for PCB Spill Cleanup Based on Concern

	Categories of increasing concern		
	Type 1	Type 2	Type 3
Approximate gallons of spilled liquid	< 1	> 1	> 5
Area of spill (sq ft)	< 125	250 (avg.)	> 1,000
PCB concentration in spilled liquid (ppm)	< 500	≧ 50	Variable or high
Types of spilled liquid	Mineral oil (or variable)	Variable	Variable, Askarel
Exposure scenario	Various	Various	Special concern for high exposure situations

Notes:
- Type 1 spill is usually not reported.
- Type 2 spill is reported and discussed in this chapter.
- Type 3 spill is not discussed in this chapter and may require special EPA assistance.
- "Severity" in one key item may raise the spill to a higher risk category.

3. Quick Response/Securing the Site

Quick response is desirable to mitigate the dispersion of the spilled material and to secure the site. Federal regulations require that cleanup actions commence within 48 hr of discovery of a spill [40 CFR 761.30(a)(1) (iii)]. More rapid response is highly preferable.

A quick response allows removal or cleaning of the PCB-contaminated material before it is dispersed by wind, rain, seepage, and other natural causes or by humans or animals. In securing the site, the cleanup crew determines the spill boundaries, prevents unauthorized access to the spill site, and notifies all parties involved.

The methods used to secure the site will vary on a case-by-case basis, depending on the specific circumstances. The extent of the spill is usually determined by visual inspection with the addition of a buffer area that may include PCBs finely dispersed from splattering. Evaluating the extent of the spill involves considerable judgment, including consideration of the cause of the spill, weather conditions, and specifics of the site.

Field analysis kits may aid the crew in determining the extent of the spill in some instances. The field kits, when used properly, can serve as a screening tool. The need for quick response has limited the usefulness of the more accurate field analytical techniques such as field gas chromatography. Practical problems associated with availability of the equipment and trained staff, set-up time, and cost have limited the use of such techniques at this time.

4. Determination of Materials Spilled/Cleanup Plan

After securing the site, the response crew will either (a) immediately proceed with the cleanup operation, or (b) identify the materials spilled and formulate an appropriate cleanup plan. A suitable cleanup plan can be developed by identifying the type of PCB material (i.e., mineral oil, PCB oil, Askarel) and considering such factors as the volume spilled, area of the spill, and site characteristics.

Based on reasoning similar to Table 1, the crew leader can determine the necessary level of effort in accordance with the policy of the PCB owner and the EPA Regional Office. He can determine if additional guidance is needed, plan the sampling and analysis, and make other decisions related to the level of effort and procedures needed.

5. Cleanup Procedures

The cleanup procedure may include, but may not necessarily be limited to, the following activities:

- Removal or repair of failed/damaged PCB equipment,
- Physical removal of contaminated vegetation;

- Physical removal of contaminated soils, liquids, etc.,
- Decontamination or physical removal (as appropriate) of contaminated surfaces, and
- Decontamination or removal of all equipment potentially contaminated during the cleanup procedures.
- Encapsulation may be employed only with EPA approval.

The specific procedures used in a cleanup are selected by the PCB owner or the cleanup contractor. Key considerations include removal of PCBs from the site to achieve the standards required by the EPA region, company, or other applicable control authority; avoidance of unintentional cross contamination or dispersion of PCBs from workers' shoes, contaminated equipment, spilled cleaning solvents, rags, and other sources; and protection of workers' health.

The cleanup crew shall make every possible effort to keep the spilled PCBs out of sewers and waterways. If this has already occurred, the crew needs to contact the local authorities. Water is never used for cleaning equipment or the spill site.

A simple PCB spill cleanup may involve the removal of the leaking equipment, removal of contaminated sod and soil by shovel, cleaning pavement with an absorbant material and solvents, and decontamination or disposal of the workers' equipment (shovels, shoes, gloves, rags, plastic sheets, etc.). More complicated situations may include decontamination of cars, fences, buildings, trees and shrubs, electrical equipment, or water (in pools or bodies of water).

In some cases, adequate decontamination of surfaces (pavements, walls, etc.) may not be possible. An alternate to physical removal of the surface material is encapsulation of the contaminated area under a coating impervious to PCBs. (EPA approval would be required.)

6. Proper Disposal of Removed PCB Materials

All PCB-contaminated materials removed from the spill site, must be shipped and disposed in accordance with relevant Federal, State, and local regulations. TSCA Regulations [40 CFR 761.60] outline the requirements for the disposal of PCBs, PCB articles, and PCB containers in an incinerator, high efficiency boiler, chemical waste landfill, or an approved alternative method. Facility requirements for incineration and chemical waste landfills are presented in 40 CFR 761.70 and 40 CFR 761.75, respectively. Applicable Department of Transportation regulations are listed in 49 CFR 172.101.

7. Sampling and Analysis

Although sampling and analysis will be discussed in detail in Chapter IV, this discussion gives an overview of applicable considerations and current practice. Sampling and analysis may not always be needed (especially for the spills described as Type 1 in Table 1), but enforcement authorities or property owners may ask for proof that the spill site has been adequately

decontaminated. This can be accomplished by taking a number of samples representative of the area contaminated by the spill. Samples should represent the full extent of the spill, both horizontal and vertical, as well as the types of materials in the spill area (soil, surfaces, water, etc.).

Sampling design and technique as well as sample handling and preservation should incorporate acceptable procedures for each matrix to be sampled and concern for the adequacy and accuracy for the samples in the final analysis.

Analysis of the samples for PCB content should be performed by trained personnel using acceptable procedures with due consideration of quality assurance and quality control.

Further discussion of sampling and analysis (applicable to EPA enforcement activities) appears in Chapter IV.

8. Remedial Action

If the analysis results indicate the cleanup was not in compliance with designated cleanup levels, additional cleanup is needed. Additional sampling can pinpoint the location of remaining contaminated areas if the original sampling plan was not designed to identify contaminated sub-areas within the spill site. If additional cleanup is needed, the cleanup crew will continue as before, removing more material or cleaning surfaces more thoroughly. Remedial action will be followed by additional sampling and analysis to verify the adequacy of the cleanup.

9. Site Restoration

This is not addressed under TSCA and is a matter to be settled between the company responsible for the PCB spill and the property owner.

10. Records

Although there are no TSCA requirements for records of PCB cleanup activities except for documentation of PCBs stored or transported for disposal [40 CFR 761.80(a)], the PCB owner should keep records of the spill cleanup in case of future questions or concern. Relevant information may include dates, a description of the activities, records of shipment and disposal of PCB-contaminated materials, and a report of collected samples and results of analysis.

11. Miscellaneous Considerations

a. Expeditious and effective action are desired throughout the cleanup process to minimize the concern of the public, especially residents near the site or individuals with a special interest in the site. Likewise, speed and effectiveness in the cleanup may prevent any future concern or action related to the PCB spill.

b. Education and training of the spill response crews and responsible staff members is a constant concern. The employees need sufficient training to make proper judgements and to know when additional assistance or guidance is needed.

IV. GUIDELINES ON SAMPLING AND ANALYSIS

Reliable analytical measurements of environmental samples are an essential ingredient of sound decisions for safeguarding public health and improving the quality of the environment. Effective enforcement monitoring should follow the general operational model for conducting analytical measurements of environmental samples, including: planning, quality assurance/quality control, verification and validation, precision and accuracy, sampling, measurements, documentation, and reporting. Although many options are available when analyzing environmental samples, differing degrees of reliability, dictated by the objectives, time, and resources available, influence the protocol chosen for enforcement monitoring. The following section outlines the factors critically influencing the outcome and reliability of enforcement monitoring of PCB spill cleanup.

A. Sampling Design

This section presents a sampling scheme, for use by EPA enforcement staff, for detecting residual PCB contamination above a limit designated by EPA-OPTS after the site has been cleaned up. Two types of error traceable to sampling and analysis are possible. The first is false positive, i.e., concluding that PCBs are present at levels above the allowable limit when, in fact, they are not. The false positive rate for the present situation should be low, because an enforcement finding of noncompliance must be legally defensible; that is, a violator must not be able to claim that the sampling results could easily have been obtained by chance alone. Moreover, all sampling designs used must be documented or referenced.

The second type of error possible is a false negative, i.e., failure to detect the presence of PCB levels above the allowable limit. The false negative rate will depend on the size of the contaminated area and on the level of contamination. For large areas contaminated at levels well above the allowable limit, the false negative rate must, of course, be low to ensure that the site is brought into compliance. The false negative rate can increase as the area or level of contamination decrease.

1. Proposed Sampling Design

In practice, the contaminated area from a spill will be irregular in shape. In order to standardize sample design and layout in the field, and to protect against underestimation of the spill area by the cleanup crew, sampling within a circular area surrounding the contaminated area is proposed. Guidance on choosing the center and radius of the circle, as well as the number of sample points to be used is provided in Section 2 below.

The detection problem was modeled as follows: try to detect a circular area of uniform residual contamination whose center is randomly placed within the sampling circle. Figure 1 illustrates the model. The figure depicts a sampling circle of 10 ft centered on a utility pole (site of the spill). After cleanup, a residually contaminated circle remains. However, in choosing locations at which to sample, the sampler has no knowledge of either the location of the circle or the level of contamination. This

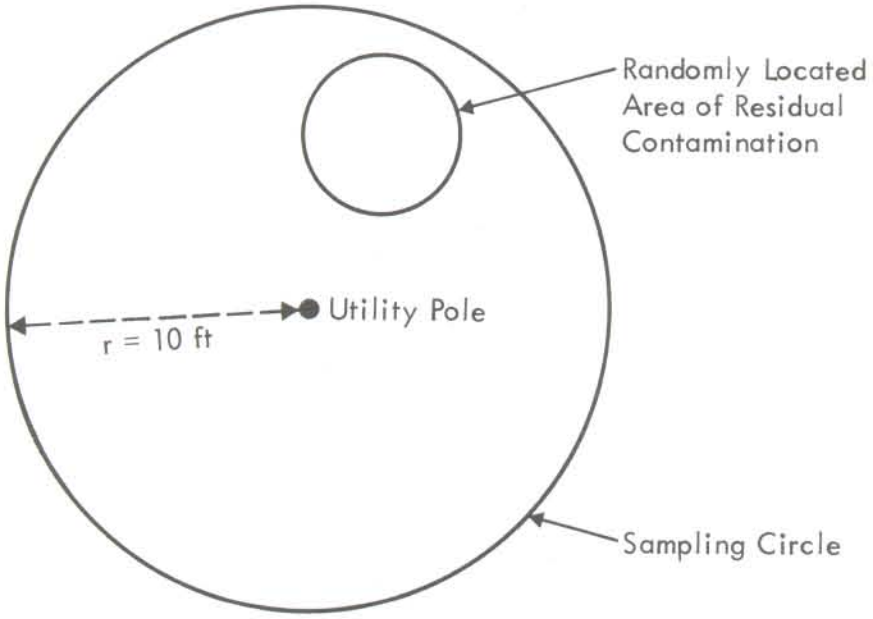


Figure 1. Randomly located area of residual contamination within the sampling circle.

lack of knowledge was modeled by treating the sampling locations as fixed and the center of the contaminated circle as a randomly located point in the circle of radius 10 ft. The implicit assumption that residual contamination is equally likely to be present anywhere within the sampling area is reasonable, at least as a first approximation (Lingle 1985). This is because more effort is likely to have been expended in cleaning up the areas which were obviously highly contaminated.

Two general types of design are possible for this detection problem: grid designs and random designs. Random designs have two disadvantages compared to grid designs for this application. First, random designs are more difficult to implement in the field, since the sampling crew must be trained to generate random locations onsite, and since the resulting pattern is irregular. Second, grid designs are more efficient for this type of problem than random designs. A grid design is certain to detect a sufficiently large contaminated area while some random designs are not. For example, the suggested design with a sample size of 19 has a 100% chance to detect a contaminated area of radius 2.8 ft within a sampling circle of radius 10 ft. By contrast, a design based on a simple random sample of 19 points has only a 79% chance of detecting such an area.

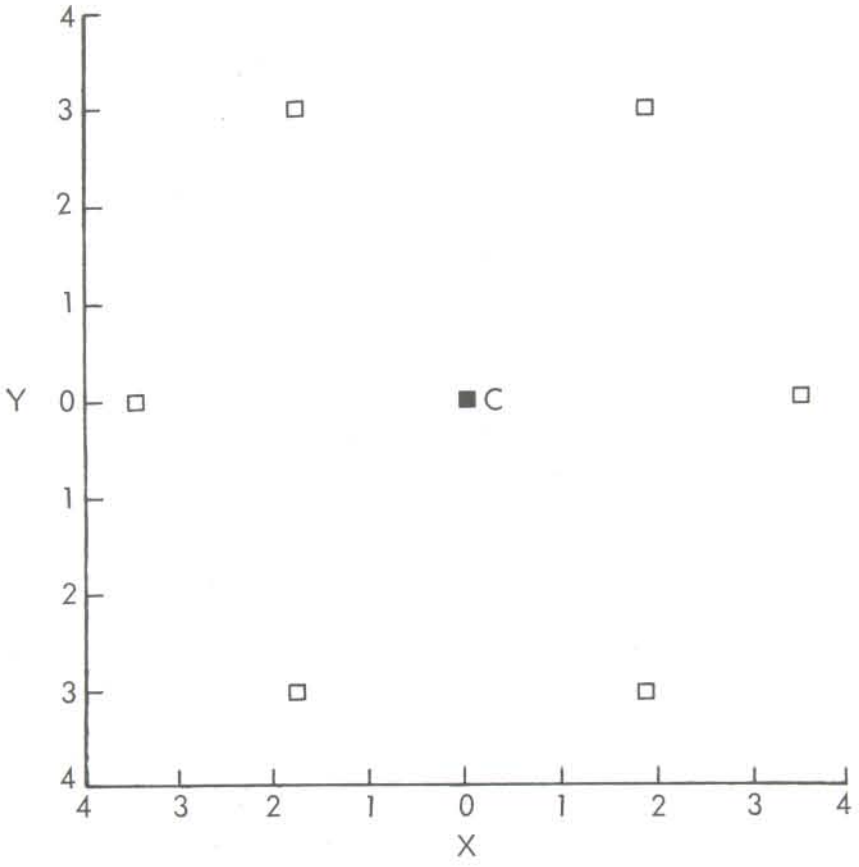
Therefore, a grid design is proposed. A hexagonal grid based on equilateral triangles has two advantages for this problem. First, such a grid minimizes the circular area certain to be detected (among all grids with the same number of points covering the same area). Second, some previous experience (Mason 1982; Matern 1960) suggests that the hexagonal grid performs well for certain soil sampling problems. The hexagonal grid may, at first sight, appear to be complicated to lay out in the field. Guidance is provided in Section 2 below and shows that the hexagonal grid is quite practical in the field and is not significantly more difficult to deploy than other types of grid.

The smallest hexagonal grid has 7 points, the next 19 points, the third 37 points as shown in Figures 2 through 4. In general, the grid has $3n^2 + 3n + 1$ points. To completely specify a hexagonal grid, the distance between adjacent points, s, must be determined. The distance s was chosen to minimize, as far as possible, the size of the residual contaminated circle which is certain to be sampled. Values of s so chosen, together with number of sampling points and radius of smallest circle certain to be sampled, are shown in Table 2. For example, the grid spacing for a circle of radius 20 ft for the 7-point design is $s = (0.87)(20) = 17.4$ ft. For a given size circle, the more points on the grid, the smaller the residual contamination area which can be detected with a given probability.

For cases in which the configuration of the contaminated area is very different from a circle (e.g., an extremely elongated ellipse), the sampling circle may be a poor approximation to the contaminated area, and a moderate-to-large percentage of the sampling points may fall outside the contaminated area. If the sampler is certain that there is no contamination outside the cleanup area, then it is permissible to disregard those sampling points falling outside the cleanup area.

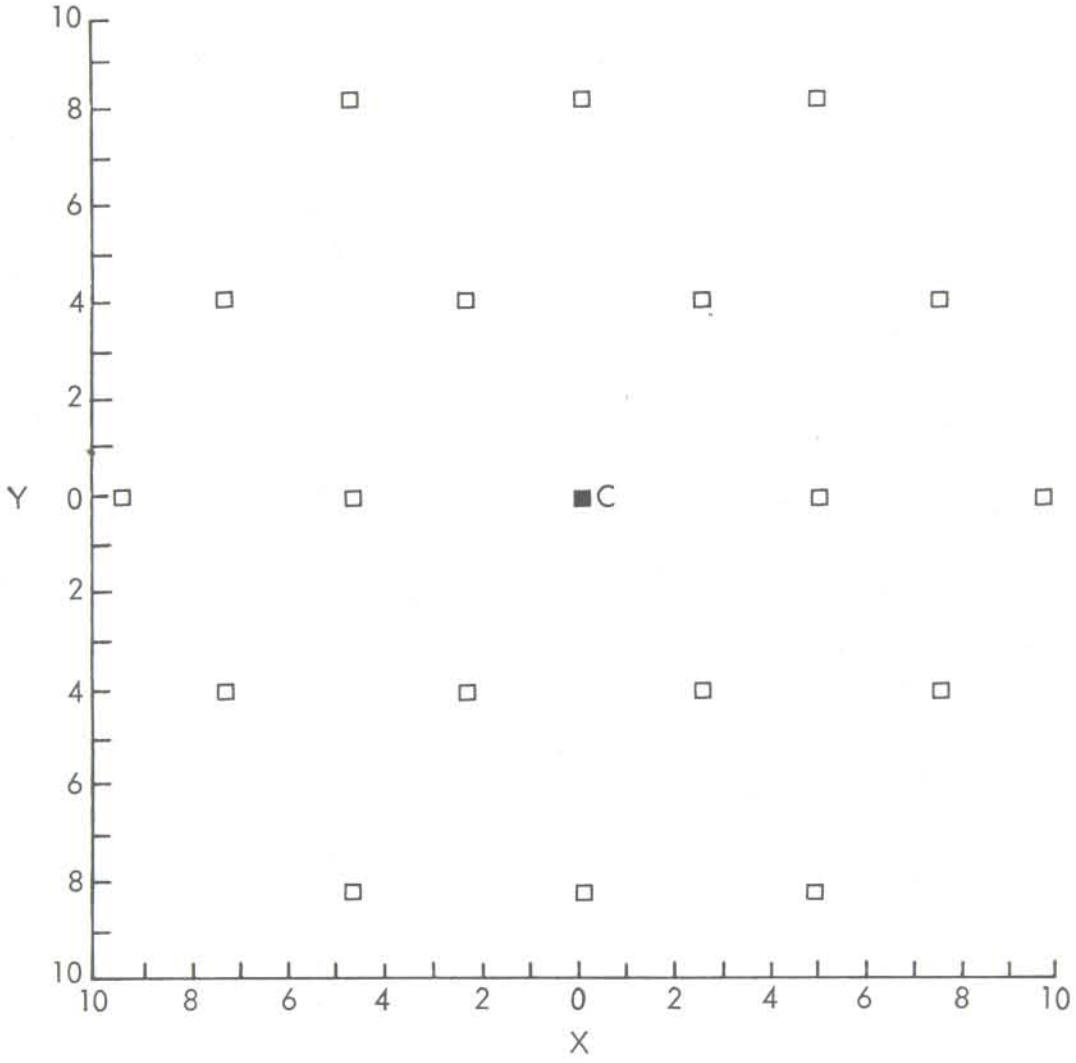
Table 2. Parameters of Hexagonal Sampling Designs for a Sampling Circle of Radius r Feet

No. of points	Distance between adjacent points, s (ft)	Radius of smallest circle certain to be sampled
7	0.87r	0.5r
19	0.48r	0.28r
37	0.3r	0.19r



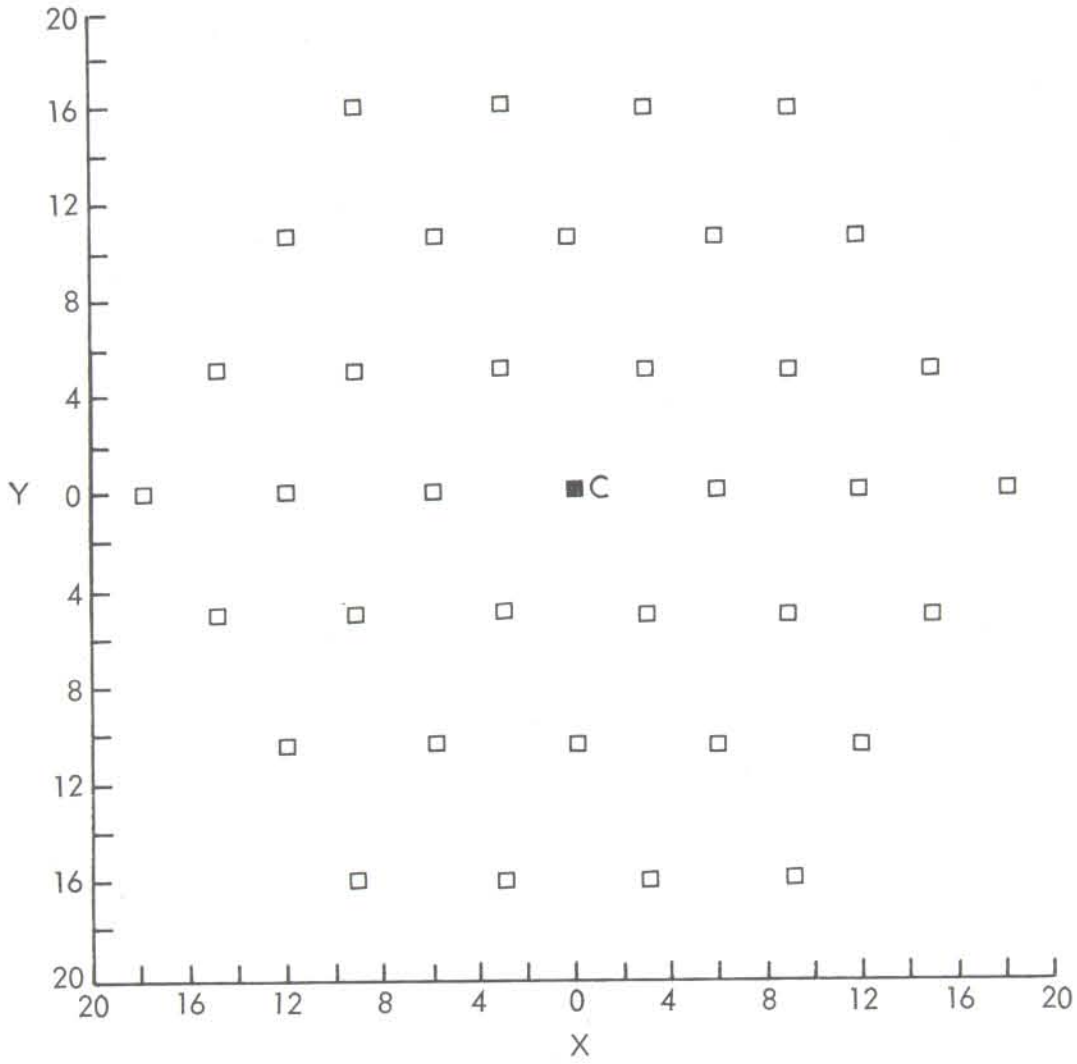
The outer boundary of the contaminated area is assumed to be 4 feet from the center (C) of the spill site.

Figure 2. Location of sampling points in a 7-point grid.



The outer boundary of the contaminated area is assumed to be 10 feet from the center (C) of the spill site.

Figure 3. Location of sampling points in a 19-point grid.



The outer boundary of the contaminated area is assumed to be 20 feet from the center (C) of the spill site.

Figure 4. Location of sampling points in a 37-point grid.

It is still good practice to collect samples from these outlying points even if they are not ever analyzed because the cost of returning to the site to perform sampling activity again is much greater than the cost of incremental sampling performed while still onsite. If sampling points outside the contaminated area are ignored, and if it is a certainty that there is no contamination outside this area, the absolute detection capability of the sampling scheme is unaffected. For example, the chance of detecting a 5 sq ft area of contamination within the restricted sampling area is the same as it would be if the contaminated area comprised the entire sampling circle.

The first three hexagonal designs are shown in Figures 2 to 4, for a sampling circle radius of r = 10 ft. The choice of sample size depends on the cost of analyzing each sample and the reliability of detection desired for various residually contaminated areas. Subsection 2 below provides some suggested sample sizes for different spill areas, based on the distribution of spill areas provided by the Utility Solid Waste Activities Group (USWAG 1984; Lingle 1985).

2. Sample Size and Design Layout in the Field

a. Sample Size

The distribution of cleanup areas for PCB capacitor spill sites, based on data collected by USWAG (1984; Lingle 1985) is shown in Table 3. The smallest spill recorded in the USWAG database is 5 ft^2, the largest 1,700 ft^2. The median cleanup area is 100 ft, the mean 249 ft^2; the wide discrepancy between the mean and the median reflects the presence of a small percentage of relatively large spills in the database.

Recommended sample sizes are given in Table 4. Several considerations were involved in arriving at these recommendations. First, the maximum number of samples recommended for the largest spills is 37, in recognition of practical constraints on the number of samples that can be taken. Even so, it is important to note that not all samples collected will need to be analyzed. The calculations in Section 5 below show that, even for the 37 sample case, no more than 8 analyses will usually be required to reach a decision. Since the cost of chemical analyses is a substantial component of sampling and analysis costs, even the 37-sample case should not, therefore, be prohibitively expensive. Second, the typical spill will require 19 samples. Small spills, with sampling radius no greater than 4 ft, will have 7 samples, while the largest spills, with sampling radius 11.3 ft and up, will require 37 samples. It should be noted that only capacitor spills are represented in Table 3. Transformer spills, however, would be expected to be generally smaller than capacitor spills because energetic releases are less likely from transformers. Thus, one would expect the smaller sample sizes to be relatively more likely for transformer spills than capacitor spills.

Table 3. Distribution of PCB Capacitor Spill Cleanup Areas Based on 80 Cases

Cleanup area (ft^2)	Percent of cases
≤ 50	32.5
51-100	18.8
101-200	15.0
201-300	12.5
301-400	3.8
401-700	7.5
701-1,300	8.8
≥ 1,300	1.3

Source: Lingle 1985.

Table 4. Recommended Sample Sizes

Sampling area (ft^2)	Radius of sampling circle (ft)	Percent of PCB capacitor spills	Sample size
≤ 50	≤ 4	32.5	7
51-400	4-11.3	50.0	19
> 400	> 11.3	17.5	37

The final consideration in recommending sample sizes was to achieve roughly comparable detection capability for different size spills. The radius of the smallest contaminated circle certain to be sampled at least once by the sampling scheme is used for comparative purposes (see Table 2). Table 5 presents some calculations of this quantity. The absolute detection capability of the sampling scheme is seen to be relatively constant for different spill sizes. This means that a given area of residual contamination is about as likely to be detected in any sized spill.

Table 5. Detection Capability of the Recommended Sampling Schemes

Sampling area (ft^2)	Radius (ft)	Sample size	Radius of smallest circle to be sampled (ft)
50	4.0	7	2.0
150	6.9	19	1.9
400	11.3	19	3.2
875	16.7	37	3.2

b. Design Layout in the Field

Figure 5 presents a typical illustration of design layout in the field. The first step is to determine the boundaries of the original cleanup area (from records of the cleanup). Next, find the center and radius of the sampling circle which is to be drawn surrounding the cleanup area. The following approach is recommended:

(a) Draw the longest dimension, L_1, of the spill area.

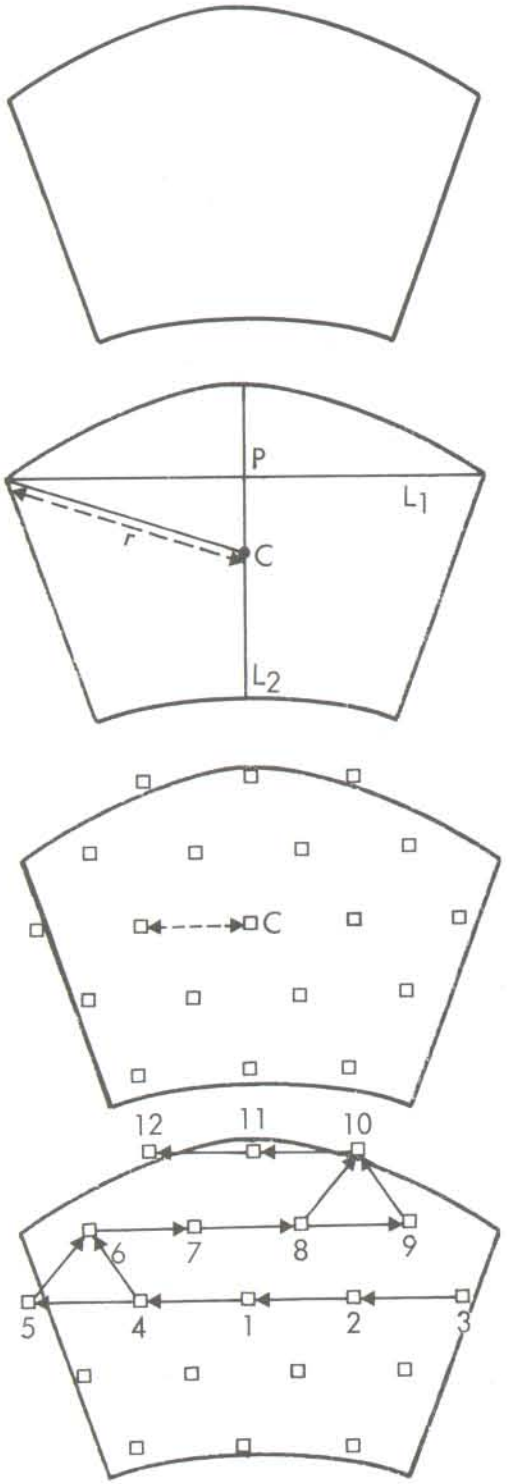
(b) Determine the midpoint, P, of L_1.

(c) Draw a second dimension, L_2, through P perpendicular to L_1.

(d) The midpoint, C, of L_2 is the required center.

(e) The distance from C to the extremes of L_1 is the required radius, r.

Figure 5 shows an example of the procedure; Figure 6 demonstrates how the center is determined for several spill shapes. Even if the center determined is slightly off, the sampling design will not be adversely affected.



(a) Original cleanup area

(b) Locating the center of the sampling circle

(c) Centering the hexagonal grid

(d) Staking out the grid points

Figure 5

Once the sampling radius, r, has been found, the sample size can be selected based on Table 4.

Example: Suppose r = 5 ft. From Table 4, a sample size of 19 should be used.

Having selected the sample size, the grid spacing can be calculated from Table 2.

Example (continued): For a 19-point design with radius r = 5, the grid spacing is s = 0.48r = (0.48)(5) = 2.4 ft.

The procedure for laying out a 19 point design is as follows. The first sampling location is the center C of the sampling circle, as shown in Figure 5. Next, draw a diameter through C and stake out locations 2 through 5 on it as shown; adjacent locations are a distance s apart. The orientation of the diameter (for example east-west) used is not important; it may be chosen at random or for the convenience of the samplers. The next 4 locations, Nos. 6-9, are laid out parallel to the first row, again a distance s apart. The only difficulty is in locating the starting point, No. 6, for this row. To accomplish this the sampler needs two pieces of rope (or surveyor's chain, or equivalent measuring device) of length s. Attach one piece of rope to the stake at each location 4 and 5. Draw the ropes taut horizontally until they touch at location 6. Once the second row is laid out, the third and final row of 3 locations in the top half of the design is found similarly, starting with number 10. In the same way, the bottom half of the design is staked out. The 7-point or 37-point designs are laid out in an analogous fashion.

Once the sampling locations are staked out the actual samples can be collected. In the example in Figure 5, three of the sampling locations fall outside the original cleanup area. Samples should be taken at these points, to detect contamination beyond the original cleanup boundaries. This verifies that the original spill boundaries were accurately assessed. However, if the sampler is certain that there is no contamination outside the original cleanup area, then it is permissible to disregard those sampling points falling outside the cleanup area. It is still good practice, however, to collect such samples even if they are not ever analyzed because the cost of returning to the site to sample again is much greater than the cost of incremental sampling performed while still onsite. As indicated on page 16, ignoring the sampling points outside the original cleanup area does not affect the absolute detection capability of the sample scheme.

In practice, various obstacles may be encountered in laying out the sampling grid. Many "obstacles" can be handled by taking a different type of sample, e.g., if a fire hydrant is located at a point in a sampling grid otherwise consisting of soil samples, then a wipe sample should be taken at the hydrant, rather than taking a sample of nearby soil. The obstacle most likely to be encountered is a vertical surface such as a wall. To determine the sampling location on such a surface, draw taut the ropes (chains) of length s attached to two nearby stakes and find the point on the vertical surface where their common ends touch. See Figure 7 for an illustration of

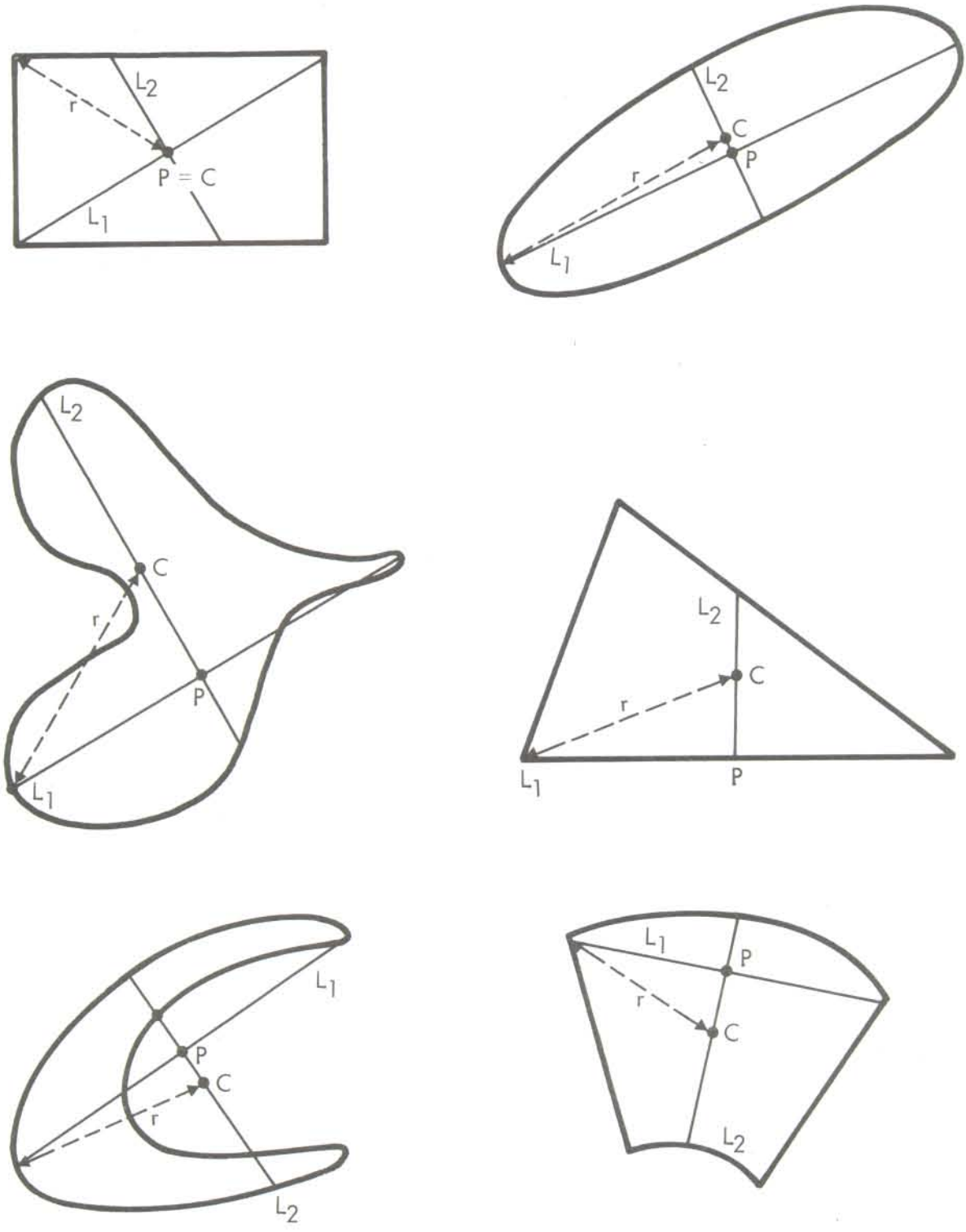


Figure 6. Locating the center and sampling circle radius of an irregularly shaped spill area.

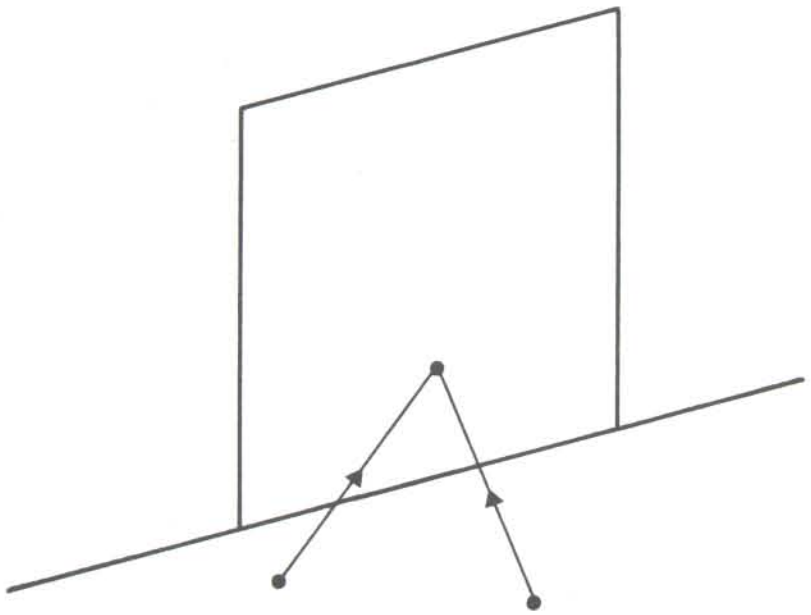


Figure 7. Location of a sampling point on a vertical surface.

the procedure. If more samples from the vertical surface are called for, the same principle may be applied, always using the last two points located to find the next one.

3. Judgemental Sampling

The inspector or sampling crew may use best judgement to collect samples wherever residual PCB contamination is suspected. These samples are in addition to those collected from the sampling grid. Examples of extra sampling points include suspicious stains outside the designated spill area, cracks or crevices, and any other area where the inspector suspects inadequate cleanup.

4. Compositing Strategy for Analysis of Samples

Once the samples have been collected at a site, the goal of the analysis effort is to determine whether at least one sample has a PCB concentration above the allowable limit. This sampling plan assumes the entire spill area will be recleaned if a single sample contaminated above the limit is found. Thus, it is not important to determine precisely which samples are contaminated or even exactly how many. This means that the cost of analysis can be substantially reduced by employing compositing strategies, in which groups of samples are thoroughly mixed and evaluated in a single analysis. If the PCB level in the composite is sufficiently high, one can conclude that a contaminated sample is present; if the level is low enough, all individual samples are clean. For intermediate levels, the samples from which the composite was constructed must be analyzed individually to make a determination. Thus, the number of analyses needed is greatly reduced in the presence of very high levels of contamination in a few samples or in the presence of very low levels in most samples.

For purposes of this discussion, assume that the maximum allowable PCB concentration in a single soil sample is 10 ppm. The calculations can easily be adapted for a different level or for different types of samples. Based on review of the available precision and accuracy data (Erickson 1985), method performance of 80% accuracy and 30% relative standard deviation should be attainable for soil concentrations above 1 ppm.

To protect against false positive findings due to analytical error, the measured PCB level in a single sample must exceed some cutoff greater than 10 ppm for a finding of contamination. Assume that a 0.5% false positive rate for a single sample is desired. As will be shown later, this single sample false positive rate controls the overall false positive rate of the sampling schemes to acceptable levels. Then, using standard statistical techniques, the cutoff level for a single sample is

$$(0.8)(10) + (2.576)(0.3)(0.8)(10) = 14.2 \text{ ppm},$$

where 0.8(80%) represents the accuracy of the analytical method, 10 ppm is the allowable limit for a single sample, 2.576 is a coefficient from the standard normal distribution, and 0.3(30%) is the relative standard deviation of the analytical method. Thus, if the measured level in a single sample is

14.2 ppm or greater, one can be 99.5% sure that the true level is 10 ppm or greater.

Now suppose that a composite of, say, 7 samples is analyzed. The true PCB level in the composite (assuming perfect mixing) is simply the average of the 7 levels of the individual samples. Let X ppm be the measured PCB level in the composite. If $X \leq (14.2/7) = 2.0$, then all 7 individual samples are rated clean. If $X > 14.2$, then at least one individual sample must be above the 10 ppm limit. If $2.0 < X \leq 14.2$, no conclusion is possible based on analysis of the composite and the 7 samples must be analyzed individually to reach a decision. These results may be generalized to a composite of any arbitrary number of samples, subject to the limitations noted below.

The applicability of compositing is potentially limited by the size of the individual specimens and by the performance of the analytical method at low PCB levels. First, the individual specimens must be large enough so that the composite can be formed while leaving enough material for individual analyses if needed. For verification of PCB spill cleanup, adequacy of specimen sizes should not be a problem. The second limiting factor is the analytical method. Down to about 1 ppm, the performance of the stipulated analytical methods should not degrade markedly. Therefore, since the assumed permissible level is 10 ppm, no more than about 10 specimens should be composited at a time.

In compositing specimens, the location of the sampling points to be grouped should be taken into account. If a substantial residual area of contamination is present, then contaminated samples will be found close together. Thus, contiguous specimens should be composited, if feasible, in order to maximize the potential reduction in the number of analyses produced by the compositing strategy. Rather than describe a (very complicated) algorithm for choosing specimens to composite, we have graphically indicated some possible compositing strategies in Figures 8 Through 11. Based on the error probability calculations presented in Section 4 below, we recommend the compositing strategies indicated in Table 6. The recommended strategy for the 7-point design requires no explanation. The strategies for the 19- and 37-point cases are shown in Figures 9 and 11, respectively. The strategies shown in Figures 8 and 10 are used in Section 5 for comparison purposes. For details on the reduction in number of analyses expected to result (as compared to individual analyses), see the next Section, 5.

5. Calculations of Average Number of Analyses, and Error Probabilities

Estimates of expected number of analyses and probabilities of false positives (incorrectly deciding the site is contaminated above the limit), and false negatives (failure to detect residual contamination) were obtained for various scenarios. The calculations were performed by Monte Carlo simulation using 5,000 trials for each combination of sample size, compositing strategy, level, and extent of residual contamination. The computations were based on the following assumptions:

A 2 GROUP COMPOSITING PLAN FOR 7 SAMPLE POINTS

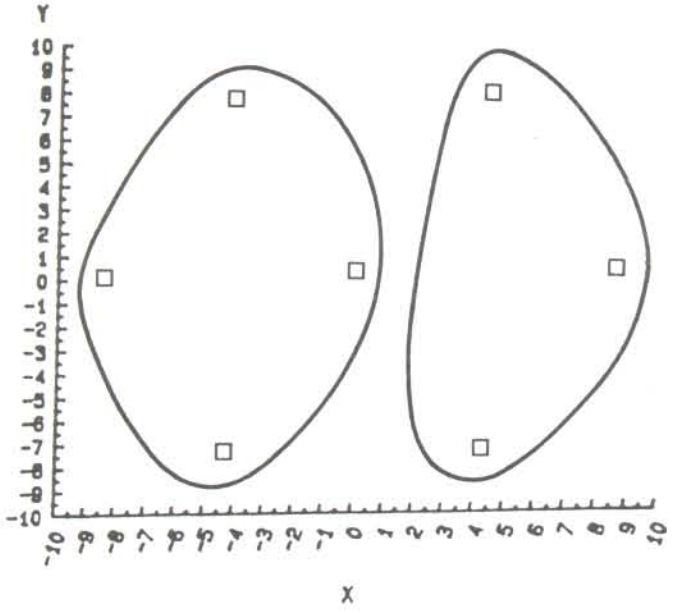


Figure 8

A 2 GROUP COMPOSITING PLAN FOR 19 SAMPLE POINTS

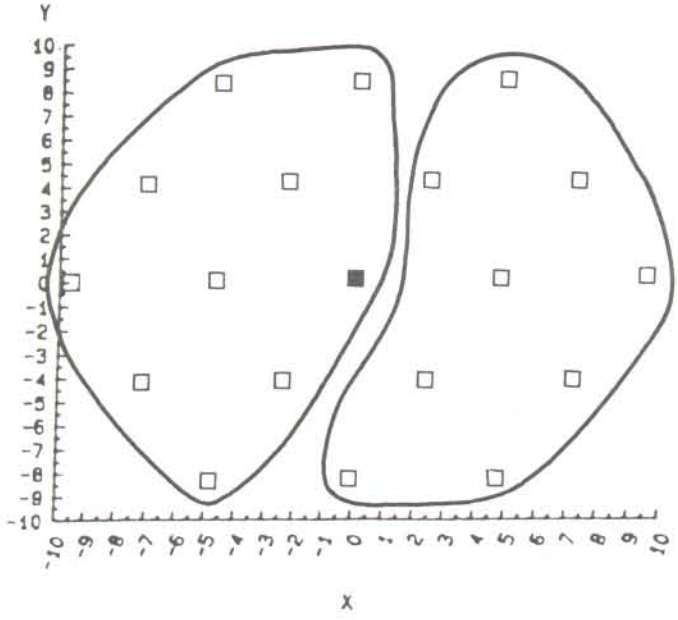


Figure 9

A 6 GROUP COMPOSITING PLAN FOR 19 SAMPLE POINTS

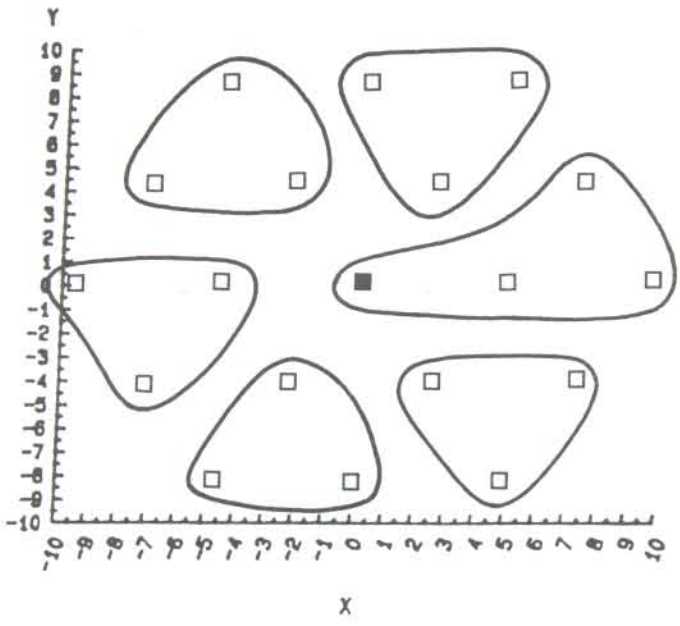


Figure 10. Location of sample points in a 19 sample point plan, with detail of a 2 group compositing design.

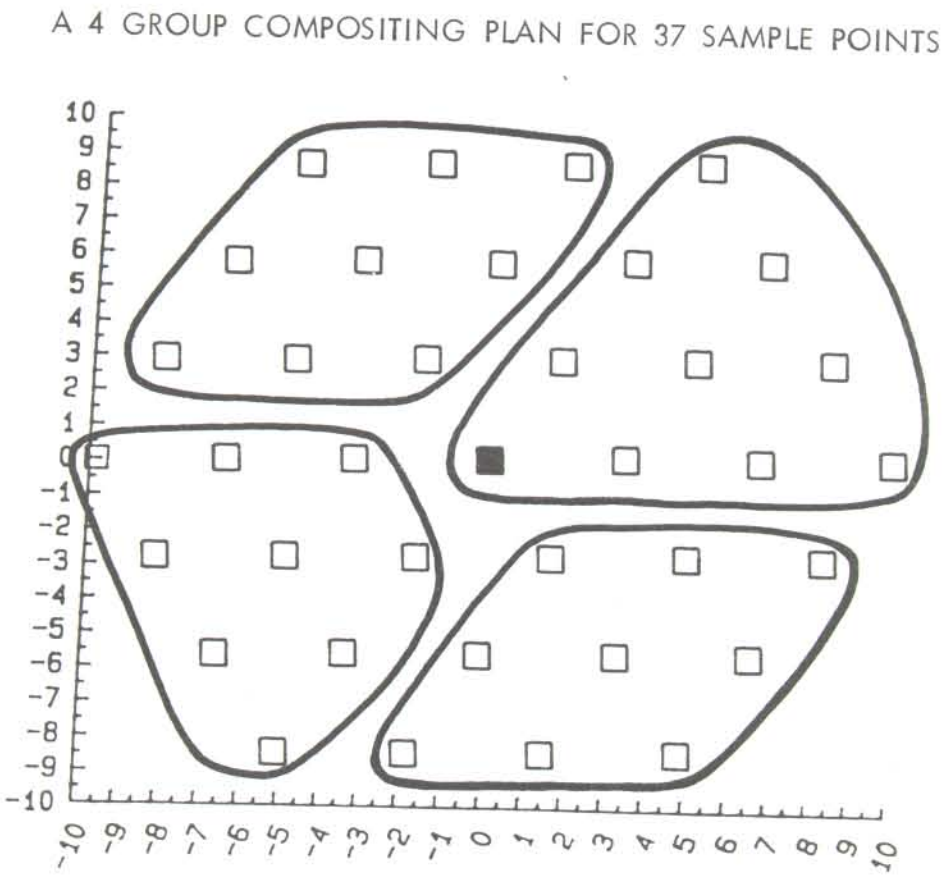


Figure 11. Location of sample points in 37 sample point plan, with detail of a 4 group compositing design.

Table 6. Recommended Compositing Strategies

No. of samples collected	Compositing strategy
7	One group of 7
19	One group of 10, one of 9
37	Three groups of 9, one of 10

a. Only soil samples are involved. In practice other types of samples will often be obtained and analyzed. Although the results of this section are not directly applicable to such cases, they do indicate in general terms the type of accuracy obtainable and the potential cost savings from compositing.

b. If the true PCB level in a sample is C, then the measured value is a normally distributed random variable with mean 0.8C and standard deviation (0.3)(0.8C) = 0.24C. Thus, it is assumed that the analytical method is 80% accurate, with 30% relative standard deviation.

c. The maximum allowable level in a single sample is 10 ppm. However, the measured level for a single sample must exceed 14.2 ppm for a finding of noncompliance. As previously discussed, this corresponds to a single-sample false positive rate of 0.5%.

d. The residual contamination present is modeled as a randomly placed circle of variable radius and contamination level. The PCB level is assumed to be uniform within the randomly-placed circle and zero outside it.

e. Analysis of samples is terminated as soon as a positive result is obtained on a single analysis. If a composite does not give a definitive result (positive or negative), the individual specimens from which the composite was formed are analyzed in sequence before any other composite.

f. The compositing strategies used are shown in Figures 8 and 11.

The results of the computations are shown in Tables 7 through 20. Tables 7 through 12 show the performance of the compositing strategies recommended in Section 3. For each strategy, there is a pair of tables. The first table shows the probability of reporting a violation of a 10 ppm cleanup standard, for different levels of residual contamination and percent of cleanup area contaminated. When the contamination level is 10 ppm or less, the number in the table is the probability of a false positive, i.e., a false finding of noncompliance. These probabilities are all very low, as they should be. When the level is above 10 ppm, the number in the table is the probability that a violation will be detected by the sampling design. For levels close to 10 ppm, and for small percentages of cleanup area residually contaminated, the detection probability is low. When the level is high and the percent of area contaminated is large, however, detection probability approaches 100%. For small areas with high contamination, detection capability is modest. This is because there is only a small chance that the contaminated area will be sampled. Similarly, detection capability is also modest for large areas contaminated near the 10 ppm limit. The reason for this is that, even though a number of contaminated samples will be found in such cases, the analytical method is not likely to give positive identification of levels near the 10 ppm cutoff. This is the price paid for reducing the single-sample false positive rate to 0.5%.

The second table for each compositing strategy shows the expected (average) number of analyses needed to reach a decision. For a fixed percent of area contaminated, the smallest number of analyses is needed if the level of contamination is very high or very low. For intermediate levels, more analyses are needed. The largest number of analyses are required with a large area contaminated at close to 10 ppm. In such a situation, the levels of the composite(s) will mostly lie in the intermediate range for which no conclusion is possible based on analysis of the composite. Thus, individual analyses will almost always be required, so that the advantage of compositing is lost.

Tables 13 through 20 compare the recommended compositing strategies for the 7-point and 19-point designs to alternative compositing strategies for these designs, for 4 different contaminated percentages (1%, 9%, 25%, and 49%). The comparison is based on the expected number of analyses required. Overall detection capabilities are comparable for the different strategies. The tables show that the recommended strategies are best, except for larger areas contaminated close to the 10 ppm level.

Table 7. Probability of Declaring a Violation of a 10 ppm Cleanup Standard, for the 7 Point, 1 Composite Design[a]

Level of residual PCB contamination (ppm)		Percent of cleanup area with residual PCB contamination					
		1	4	9	16	25	49
Compliant	8	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
	10	< 0.001	< 0.001	< 0.001	< 0.001	0.002	0.007
Noncompliant	11	< 0.001	< 0.001	< 0.001	< 0.001	0.009	0.032
	12	< 0.001	0.001	0.001	0.002	0.017	0.092
	13	0.001	0.005	0.005	0.009	0.045	0.184
	14	0.003	0.010	0.019	0.028	0.085	0.298
	15	0.006	0.016	0.039	0.065	0.134	0.396
	16	0.009	0.029	0.064	0.102	0.202	0.517
	18	0.019	0.074	0.137	0.218	0.344	0.655
	20	0.030	0.110	0.199	0.335	0.479	0.787
	25	0.048	0.186	0.342	0.554	0.736	0.905
	50	0.070	0.245	0.487	0.767	0.977	0.989
	75	0.071	0.245	0.496	0.787	0.992	0.995
	100	0.068	0.255	0.499	0.800	0.995	0.997
	150	0.070	0.246	0.481	0.796	0.998	0.999
	200	0.073	0.254	0.489	0.806	> 0.999	> 0.999
	300	0.069	0.257	0.494	0.792	> 0.999	> 0.999
	500	0.070	0.242	0.492	0.811	> 0.999	> 0.999

[a]Seven samples analyzed first as a composite, then individually if necessary to reach a decision.

Table 8. Expected Number of Analyses to Decide Compliance or Violation, for a 10 ppm Cleanup Standard, for the 7-Point, 1-Composite Design[a]

Level of residual PCB contamination (ppm)		Percent of cleanup area with residual PCB contamination					
		1	4	9	16	25	49
Compliant	4	1.00	1.00	1.00	1.00	1.00	1.11
	6	1.00	1.00	1.00	1.00	1.06	2.31
	8	1.00	1.00	1.00	1.00	1.44	3.96
	10	1.00	1.01	1.02	1.03	1.75	4.96
Noncompliant	11	1.01	1.04	1.05	1.11	2.01	5.31
	12	1.04	1.08	1.17	1.32	2.21	5.39
	13	1.04	1.18	1.40	1.59	2.56	5.35
	14	1.10	1.32	1.63	2.02	2.86	5.18
	15	1.13	1.45	1.85	2.35	3.22	4.90
	16	1.15	1.52	2.03	2.67	3.50	4.71
	18	1.19	1.69	2.41	3.18	3.95	4.36
	20	1.24	1.85	2.57	3.59	4.19	4.04
	25	1.26	1.98	2.85	3.84	4.47	3.61
	50	1.28	1.96	2.93	3.99	4.45	2.96
	75	1.28	1.94	2.93	3.98	4.23	2.26
	100	1.21	1.79	2.53	3.45	3.54	1.87
	150	1.09	1.28	1.52	1.86	1.89	1.30
	200	1.03	1.11	1.15	1.34	1.33	1.13
	300	1.01	1.01	1.04	1.09	1.06	1.03
	500	1.00	1.00	1.01	1.02	1.02	1.01

[a]Seven samples analyzed first as a composite, then individually if necessary to reach a decision.

Table 9. Probability of Declaring a Violation of a 10 ppm Cleanup Standard, for the 19 Point, 2 Composite Design[a]

Level of residual PCB contamination (ppm)		Percent of cleanup area with residual PCB contamination					
		1	4	9	16	25	49
Compliant	8	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
	10	< 0.001	< 0.001	0.002	0.007	0.015	0.028
Noncompliant	11	< 0.001	< 0.001	0.007	0.034	0.058	0.017
	12	0.001	0.002	0.029	0.084	0.153	0.281
	13	0.003	0.007	0.062	0.179	0.304	0.497
	14	0.005	0.021	0.114	0.304	0.455	0.693
	15	0.012	0.052	0.178	0.407	0.606	0.832
	16	0.025	0.083	0.264	0.518	0.744	0.908
	18	0.046	0.167	0.421	0.698	0.883	0.978
	20	0.077	0.263	0.556	0.812	0.945	0.993
	25	0.125	0.461	0.784	0.923	0.990	0.999
	50	0.161	0.631	0.978	0.992	0.999	> 0.999
	75	0.171	0.651	0.993	0.997	> 0.999	> 0.999
	100	0.168	0.642	0.994	0.999	> 0.999	> 0.999
	150	0.166	0.657	0.998	0.999	> 0.999	> 0.999
	200	0.175	0.648	0.999	0.999	> 0.999	> 0.999
	300	0.168	0.654	0.999	> 0.999	> 0.999	> 0.999
	500	0.180	0.661	0.999	> 0.999	> 0.999	> 0.999

[a]Nineteen samples analyzed first as two composites, then individually if necessary to reach a decision.

Table 10. Expected Number of Analyses to Decide Compliance or Violation, for a 10 ppm Cleanup Standard, for the 19-Point, 2-Composite Design[a]

Level of residual PCB contamination (ppm)		Percent of cleanup area with residual PCB contamination					
		1	4	9	16	25	49
Compliant	4	2.00	2.00	2.00	2.18	3.30	7.49
	6	2.00	2.00	2.00	3.79	6.70	11.22
	8	2.00	2.00	3.01	6.15	9.20	13.18
	10	2.01	2.03	3.72	7.46	10.55	14.02
Noncompliant	11	2.03	2.14	4.07	7.90	10.74	13.81
	12	2.10	2.32	4.57	8.08	10.67	12.78
	13	2.21	2.74	4.84	7.94	9.95	11.00
	14	2.25	3.02	5.16	7.90	9.31	9.27
	15	2.37	3.40	5.50	7.65	8.42	7.80
	16	2.49	3.84	5.89	7.30	7.59	6.63
	18	2.60	4.36	6.11	6.57	6.29	5.02
	20	2.68	4.65	6.26	6.18	5.48	4.25
	25	2.82	5.02	6.20	5.45	4.57	3.36
	50	2.80	5.03	5.96	4.70	3.48	2.28
	75	2.80	5.05	5.69	3.68	2.63	1.84
	100	2.77	4.95	5.37	3.46	2.26	1.69
	150	2.53	3.94	3.99	2.59	1.80	1.46
	200	2.21	2.67	2.61	1.91	1.55	1.33
	300	1.99	1.89	1.70	1.50	1.34	1.19
	500	1.92	1.69	1.48	1.39	1.30	1.16

[a]Nineteen samples analyzed first as two composites, then individually if necessary to reach a decision.

Table 11. Probability of Declaring a Violation of a 10 ppm Cleanup Standard, for the 37 Point, 4 Composite Design[a]

Level of residual PCB contamination (ppm)		Percent of cleanup area with residual PCB contamination					
		1	4	9	16	25	49
Compliant	8	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
	10	< 0.001	0.002	0.010	0.022	0.031	0.060
Noncompliant	11	0.001	0.008	0.041	0.084	0.124	0.225
	12	0.001	0.024	0.103	0.217	0.305	0.488
	13	0.005	0.053	0.224	0.388	0.536	0.751
	14	0.012	0.094	0.360	0.575	0.726	0.908
	15	0.023	0.159	0.501	0.740	0.859	0.950
	16	0.039	0.242	0.621	0.831	0.936	0.991
	18	0.091	0.390	0.785	0.940	0.985	> 0.999
	20	0.147	0.542	0.884	0.981	0.996	> 0.999
	25	0.249	0.771	0.958	0.995	0.999	> 0.999
	50	0.340	0.976	0.997	0.999	0.999	> 0.999
	75	0.343	0.991	0.999	0.999	> 0.999	> 0.999
	100	0.353	0.993	0.999	> 0.999	> 0.999	> 0.999
	150	0.339	0.997	> 0.999	> 0.999	> 0.999	> 0.999
	200	0.357	0.996	> 0.999	> 0.999	> 0.999	> 0.999
	300	0.344	0.997	> 0.999	> 0.999	> 0.999	> 0.999
	500	0.348	0.999	> 0.999	> 0.999	> 0.999	> 0.999

[a]Thirty-seven samples analyzed first as four composites, then individually if necessary to reach a decision.

Table 12. Expected Number of Analyses to Decide Compliance or Violation, for a 10 ppm Cleanup Standard, for the 37-Point, 4-Composite Design[a]

Level of residual PCB contamination	(ppm)	Percent of cleanup area with residual PCB contamination					
		1	4	9	16	25	49
Compliant	4	4.00	4.01	4.41	6.72	9.85	15.69
	6	4.00	4.15	6.66	10.22	13.48	19.36
	8	4.00	4.77	9.01	12.76	15.98	22.08
	10	4.02	5.36	10.56	14.29	17.18	23.04
Noncompliant	11	4.07	5.69	10.87	14.29	16.93	21.28
	12	4.18	5.97	10.94	13.74	15.68	17.84
	13	4.35	6.28	10.56	12.74	13.44	13.54
	14	4.57	6.78	10.21	11.21	11.13	10.10
	15	4.73	7.04	9.60	9.71	9.33	7.78
	16	4.90	7.33	9.08	8.77	7.83	6.12
	18	5.09	7.59	8.02	7.05	6.16	4.71
	20	5.26	7.74	7.28	6.26	5.30	3.96
	25	5.34	7.55	6.53	5.28	4.37	3.08
	50	5.27	7.14	5.39	3.78	3.06	2.16
	75	5.23	6.84	4.31	3.04	2.55	1.90
	100	5.22	6.43	3.73	2.64	2.32	1.73
	150	4.55	4.89	3.02	2.37	2.07	1.57
	200	3.95	3.57	2.53	2.15	1.90	1.52
	300	3.59	2.67	2.28	2.04	1.81	1.44
	500	3.49	2.48	2.22	1.99	1.79	1.44

[a]Thirty-seven samples analyzed first as four composites, then individually if necessary to reach a decision.

Table 13. Comparison of Expected Number of Analyses for Different Compositing Strategies for the 7-Point Design, When an Area 1% of the Size of the Cleanup Site Remains Contaminated

Level of residual PCB contamination (ppm)		1 Composite	2 Composites	Individually
Compliant	4	1.00	2.00	7.00
	8	1.00	2.00	7.00
	10	1.00	2.00	7.00
Noncompliant	12	1.04	2.02	6.98
	14	1.10	2.05	6.96
	16	1.15	2.07	6.92
	20	1.24	2.10	6.88
	25	1.26	2.11	6.84
	50	1.28	2.09	6.80
	100	1.21	1.98	6.78
	200	1.03	1.96	6.80
	500	1.00	1.96	6.81

Table 14. Comparison of Expected Number of Analyses for Different Compositing Strategies for the 7-Point Design, When an Area 9% of the Size of the Cleanup Site Remains Contaminated

Level of residual PCB contamination (ppm)		1 Composite	2 Composites	Individually
Compliant	4	1.00	2.00	7.00
	8	1.00	2.00	7.00
	10	1.02	2.01	6.99
Noncompliant	12	1.17	2.09	6.91
	14	1.63	2.32	6.69
	16	2.03	2.50	6.49
	20	2.57	2.77	6.06
	25	2.85	2.79	5.65
	50	2.93	2.60	5.45
	100	2.53	1.85	5.46
	200	1.15	1.72	5.45
	500	1.01	1.17	5.45

Table 15. Comparison of Expected Number of Analyses for Different Compositing Strategies for the 7-Point Design, When an Area 25% of the Size of the Cleanup Site Remains Contaminated

Level of residual PCB contamination (ppm)		1 Composite	2 Composites	Individually
Compliant	4	1.00	2.00	7.00
	8	1.44	2.13	7.00
	10	1.71	2.24	6.98
Noncompliant	12	2.21	2.44	6.81
	14	2.86	2.84	6.29
	16	3.50	3.23	5.64
	20	4.19	3.54	4.68
	25	4.47	3.56	4.12
	50	4.45	2.97	3.58
	100	3.54	1.61	3.51
	200	1.33	1.38	3.50
	500	1.02	1.37	3.50

Table 16. Comparison of Expected Number of Analyses for Different Compositing Strategies for the 7-Point Design, When an Area 49% of the Size of the Cleanup Site Remains Contaminated

Level of residual PCB contamination (ppm)		1 Composite	2 Composites	Individually
Compliant	4	1.11	2.02	7.00
	8	3.96	2.99	7.00
	10	4.96	3.50	6.96
Noncompliant	12	5.39	3.81	6.61
	14	5.18	3.94	5.79
	16	4.71	3.86	4.82
	20	4.04	3.49	3.53
	25	3.61	3.03	2.87
	50	2.96	2.22	2.40
	100	1.87	1.36	2.40
	200	1.13	1.23	2.39
	500	1.01	1.20	2.39

Table 17. Comparison of Expected Number of Analyses for Different Compositing Strategies for the 19-Point Design, When an Area 1% of the Size of the Cleanup Site Remains Contaminated

Level of residual PCB contamination (ppm)		2 Composites	6 Composites	Individually
Compliant	4	2.00	6.00	19.00
	8	2.00	6.00	19.00
	10	2.01	6.00	19.00
Noncompliant	12	2.10	6.03	18.93
	14	2.25	6.07	18.74
	16	2.49	6.11	18.46
	20	2.68	6.07	18.06
	25	2.82	6.01	17.75
	50	2.80	5.80	17.49
	100	2.77	5.56	17.46
	200	2.21	5.53	17.46
	500	1.92	5.57	17.46

Table 18. Comparison of Expected Number of Analyses for Different Compositing Strategies for the 19-Point Design, When an Area 9% of the Size of the Cleanup Site Remains Contaminated

Level of residual PCB contamination (ppm)		2 Composites	6 Composites	Individually
Compliant	4	2.00	6.00	19.00
	8	3.01	6.19	19.00
	10	3.72	6.32	18.96
Noncompliant	12	4.57	6.54	18.40
	14	5.16	6.74	16.90
	16	5.89	6.83	14.86
	20	6.26	6.33	11.89
	25	6.20	5.74	10.22
	50	5.96	4.45	8.94
	100	5.37	3.34	8.64
	200	2.61	3.17	8.63
	500	1.48	3.17	8.62

Table 19. Comparison of Expected Number of Analyses for Different Compositing Strategies for the 19-Point Design, When an Area 25% of the Size of the Cleanup Site Remains Contaminated

Level of residual PCB contamination (ppm)		2 Composites	6 Composites	Individually
Compliant	4	3.30	6.07	19.00
	8	9.20	7.73	19.00
	10	10.55	8.44	18.83
Noncompliant	12	10.67	8.47	17.31
	14	9.31	7.67	13.72
	16	7.59	6.57	10.58
	20	5.48	5.09	6.25
	25	4.57	4.24	4.35
	50	3.48	3.22	3.34
	100	2.26	2.51	3.29
	200	1.55	2.41	3.26
	500	1.30	2.43	3.23

Table 20. Comparison of Expected Number of Analyses for Different Compositing Strategies for the 19-Point Design, When an Area 49% of the Size of the Cleanup Site Remains Contaminated

Level of residual PCB contamination (ppm)		2 Composites	6 Composites	Individually
Compliant	4	7.49	6.28	19.00
	8	13.18	9.85	19.00
	10	14.02	10.84	18.73
Noncompliant	12	12.78	10.10	16.15
	14	9.27	7.78	11.34
	16	6.63	5.87	7.14
	20	4.25	3.92	3.74
	25	3.36	3.23	2.61
	50	2.28	2.46	2.10
	100	1.69	1.85	2.06
	200	1.33	1.79	2.04
	500	1.16	1.78	2.02

The major conclusions that can be drawn from these results are as follows. First, the proposed cutoff on the measured PCB level for a finding of noncompliance for a single sample, 14.2 ppm, is successful in controlling the overall false positive rate of the sampling scheme. For example, when an area half the size of the entire site remains contaminated just at the allowable limit of 10 ppm, the false positive rate is 1% for the 7-point design, 3% for the 19-point design, and 6% for the 37-point design. Note, that the overall false-positive rate is highest for contamination just at the allowable limit. Second, the detection capabilities of the design appear satisfactory, bearing in mind the difficulty of detecting randomly-located contamination by any sampling scheme without exhaustive sampling. As an example, the proposed 19-point design can detect 50 ppm contamination present in 9% of the cleanup area with 98% probability. Similarly, the 19-point design can detect 20 ppm contamination present in 25% of the area with 95% probability. Third, the proposed compositing strategies are quite effective in reducing the number of analyses needed to reach a decision in all cases except those involving large areas contaminated near the cutoff of 10 ppm. For example, for contaminated levels of 25 ppm or greater, the expected number of analyses to reach a decision never exceeds 5 for the 7-point design, or 7 for the 19-point design, or 8 for the 37-point design. Larger number of analyses are needed in cases of contamination close to the allowable limit of 10 ppm, up to 23 for the 37-point design when 49% of the area is contaminated at 10 ppm.

B. Sampling Techniques

The types of media to be sampled will include soil, water, vegetation and solid surfaces (concrete, asphalt, wood, etc.). General sampling methods are described below. Additional sampling guidance documents are available (Mason 1982, USWAG 1984).

1. Solids Sampling

When soil, sand, or sediment samples are to be taken, a surface scrape samples should be collected. Using a 10 cm x 10 cm (100 cm^2) template to mark the area to be sampled, the surface should be scraped to a depth of 1 cm with a stainless steel trowel or similar implement. This should yield at least 100 g soil. If more sample is required, expand the area but do not sample deeper. Use a disposable template or thoroughly clean the template between samples to prevent contamination of subsequent samples. The sample should be scraped directly into a precleaned glass bottle. If it is free-flowing, the sample should be thoroughly homogenized by tumbling. If not, successive subdivision in a stainless steel bowl should be used to create a representative subsample.

In some cases, such as sod, scrape samples may not be appropriate. For these cases, core samples, not more than 5 cm deep, should be taken using a soil coring device. These core samples should be well-homogenized in a stainless steel bowl by successive subdivision. A portion of each sample should then be removed, weighed and analyzed.

Samples should be stored in the dark at 4°C in precleaned glass bottles. If samples are to be analyzed quickly, the storage requirements may be relaxed as long as sample integrity is maintained. Before collection of

verification samples, this equipment must be used to generate a field blank as described in Section IV.E.

2. Water Sampling

a. Surface Sampling

If PCBs dissolved in a hydrocarbon oil were spilled, they will most likely be dispersed on the surface. Therefore, a surface water collection technique should be used. Surface water samples should be collected by grab techniques. Where appropriate, the precleaned glass sample bottle may be dipped directly into the body of water at the designated sample collection point. A sample is collected from the water surface by gently lowering a precleaned sample bottle horizontally into the water until water begins to run into it. The bottle is then slowly turned upright keeping the lip just under the surface so that the entire sample is collected from the surface.

b. Subsurface Sampling

If the PCBs were in an Askarel or other heavier-than-water matrix, the PCBs will sink. In these cases water near the bottom should be collected. To collect subsurface water, the bottle should be lowered to the specified depth with the cap on. The cap is then removed, the bottle allowed to fill, and the bottle brought to the surface.

c. Other Sampling Approaches

When the above approaches are not feasible, other dippers, tubes, siphons, pumps, etc., may be used to transfer the water to the sample bottle. The sampling system should be of stainless steel, Teflon, or other inert, impervious, and noncontaminating material. Before collection of samples, this equipment must be used to generate a field blank as described in Section IV.E.

d. Sample Preservation

The bottle is then lifted out of the water, capped with a PTFE- or foil-lined lid, identified with a sample number, and stored at approximately 4°C (USEPA 1984a) until analysis to retard bacterial growth. If samples are to be analyzed quickly, the storage requirements may be relaxed as long as sample integrity is maintained.

3. Surface Sampling

a. Wipe Samples

If the surface to be sampled is smooth and impervious (e.g., rain gutters, aluminum house siding), a wipe sample should indicate whether the cleanup has sufficiently removed the PCBs. These surfaces should be sampled by first applying an appropriate solvent (e.g., hexane) to a piece of 11 cm filter paper (e.g., Whatman 40 ashless, Whatman "50" smear tabs, or equivalent) or gauze pad. This moistened filter paper or gauze pad is held with a pair of stainless steel forceps and used to thoroughly swab a 100-cm^2 area as measured by a sampling template.

Care must be taken to assure proper use of a sampling template. Different templates may be used for the variously shaped areas which must be sampled. A 100 cm^2 area may be a 10 cm x 10 cm square, a rectangle (e.g., 1 cm x 100 cm or 5 cm x 20 cm), or any other shape. The use of a template assists the sampler in the collection of a 100 cm^2 sample and in the selection of representative sampling sites. When a template is used it must be thoroughly cleaned between samples to prevent contamination of subsequent samples by the template.

The wipe samples should be stored in precleaned glass jars at 4°C. Before collection of verification samples, the selected filter paper or gauze pad and solvent should be used to generate a field blank as described in Section IV.E.

b. Sampling Porous Surfaces

Wipe sampling is inappropriate for surfaces which are porous and would absorb PCBs. These include wood and asphalt. Where possible, a discrete object (e.g., a paving brick) may be removed. Otherwise, chisels, drills, saws, etc., may be used to remove a sufficient sample for analysis. Samples less than 1 cm deep on the surface most likely to be contaminated with PCBs should be collected.

4. Vegetation Sampling

The sample design or visual inspection may indicate that samples of vegetation (such as leaves, bushes, and flowers) are required. In this case, samples may be taken with pruning shears, a saw, or other suitable tool and placed in a precleaned glass bottle.

C. Analytical Techniques

A number of analytical techniques have been used for analysis of PCBs in the types of samples which may be associated with PCB spills. Some of the candidate analytical methods are listed in Table 21. The analysis method(s) most appropriate for a given spill will depend upon a number of factors. These include sensitivity required, precision and accuracy required, potential interferents, ultimate use of the data, experience of the analyst, availability of laboratory equipment, and number of samples to be analyzed.

As shown in Table 21, many analytical methods are available. The general analytical techniques are discussed and then compared below.

1. Gas Chromatography (GC)

As can be seen in Table 21, analysis of PCBs by gas chromatography is frequently the method of choice. PCBs are chromatographed using either packed or capillary columns and may be detected using either specific detectors or mass spectrometry. A comprehensive method for analysis of PCBs in transformer fluid and waste oils was developed by Bellar and Lichtenberg (1982). This method describes six different cleanup techniques, recommends three GC detectors, and suggests procedures for GC calibration and for measurement of precision and accuracy. This method also discusses several calculation methods.

Table 21. Standard Procedures of Analysis for PCDs

Procedure designation	Matrix	Extraction	Cleanup[c]	Determination method	Qualitative assessment	Quantitation method	LOD	QC discussed	Reference
D3534-80	Water	Hexane/CH_2Cl_2	(Florisil) (Silica Gel)	PGC/ECD[d]	No	Total area or Webb-McCall	0.1 µg/L	No	ASTM, 1981a
608	Water	CH_2Cl_2	(Florisil) (S removal)	PGC/ECD	No	Area	0.04-0.15 µg/L	Yes	EPA, 1984a; Longbottom and Lichtenberg, 1982
625	Water	CH_2Cl_2	None	PGC/EIMS (CGC)	Yes	Area	30-36 µg/L	Yes	EPA, 1984b; Longbottom and Lichtenberg, 1982
304h	Water	Hexane/ CH_2Cl_2 (85/15)	Florisil/ silica gel (CH_3CN) (S removal)	PGC/ECD or HECD	Yes	Summed areas or Webb-McCall	NS	Yes	EPA, 1978
EPA (by-products)	Water	Several	Several	HRGC/EIMS	Yes	Ind. peaks	NS	Yes	Erickson et al., 1982, 1983d; EPA, 1984c
ANSI	Water	Hexane	(H_2SO_4) (Saponification) Alumina	PGC/ECD	No	Single peak or summed peaks	2 ppm	Yes	ANSI, 1974
Monsanto	Water	Hexane	Alumina	PGC/ECD	No	Individual or total peak heights	2 ppb	No	Moein, 1976
UK-DOE	Water	Hexane	Silica gel	PGC/ECD	No	NS	106 ng/L	No	UK-DOE, 1979; Devenish and Harling-Bowen, 1980
D3304-74	Air Water Soil, sediment	DI Hexane H_2O/CH_3CN	(H_2SO_4) (Saponification) (Alumina)	PGC/ECD	No	Total area	NS	Yes	ASTM, 1981b
EPA (homolog)	Solids and liquids	Several	Several	HRGC/EIMS	Yes	Ind. peaks	NS	Yes	Erickson et al., 1985a
EPA 625-S	Sludge	CH_2Cl_2	Florisil, Silica gel, or GPC	HRGC/EIMS or PGC/EIMS	Yes	Area	NS	Yes	Haile and Lopez-Avila, 1984

Table 21 (Continued)

Procedure designation	Matrix	Extraction	Cleanup[c]	Determination method	Qualitative assessment	Quantitation method	LOD	QC discussed	Reference
EPA (Halocarbon)	Sludge	Hexane/ CH_2Cl_2/ acetone (83/15/2)	GPC S removal	PGC/ECD	Yes	Peak area or peak height	NS	Yes	Rodriguez et al., 1980
Priority Pollutant	Sludge	CH_2Cl_2 (base/ neutral and acid fractions)	GPC	PGC/EIMS	Yes	NS	NS	Yes	EPA, 1979c
B100	Sludge	CH_2Cl_2 (3 fractions)	GPC Silica gel	HRGC/EIMS or PGC/EIMS	Yes	NS	NS	Yes	Ballinger, 1978
8080	Solid waste	CH_2Cl_2	(Florisil)	PGC/ECD	No	Area	1 µg/g	Yes	EPA, 1982e
8250	Solid waste	CH_2Cl_2	None	PGC/EIMS	No	NS	1 µg/g	Yes	EPA, 1982e
8270	Solid waste	$CHCl_2$	None	CGC/EIMS	No	NS	1 µg/g	Yes	EPA, 1982e
EPA (spills)	Unspecified	Hexane/ acetone	(CH_3CN) (Florisil) (Silica gel) (Mercury)	PGC/ECD	No	Total area or Webb-McCall	NS	No	Beard and Schaum, 1978
EPA	Soil and Sediment	Acetone/ Hexane	Florisil Silica gel (S removal)	PGC/ECD	No	Computer	NS	Yes	EPA, 1982d
Monsanto	Sediment	CH_3CN	Saponification H_2SO_4 Alumina	PGC/ECD	No	Individual or total peak heights	2 ppb	No	Moein, 1976
ANSI	Sediment, soil	CH_3CN	Saponification H_2SO_4 Alumina	PGC/ECD	No	Single peak or summed peaks	2 ppm	Yes	ANSI, 1974
EPA (by-products)	Air collected on Florisil or XAD-2	Hexane	(H_2SO_4) (Florisil)	HRGC/EIMS	Yes	Ind. peaks	NS	Yes	Erickson et al., 1982, 1983d; Erickson, 1984b
EPA (ambient air)	Air near hazardous waste sites collected on PUF	Hexane/ ether	Alumina	PGC/ECD	No	Total area or peak height	10-50 ng/m^3	No	Lewis, 1982

Table 21 (Continued)

Procedure designation	Matrix	Extraction	Cleanup[c]	Determination method	Qualitative assessment	Quantitation method	LOD	QC discussed	Reference
EPA (stack)	Incinerator emissions and ambient air collected on Florisil	Hexane	(H_2SO_4)	Perchlorination PGC/ECD	No	Area	10 ng	No	Haile and Baladi, 1977; Beard and Schaum, 1978
EPA	Combustion sources collected on Florisil	Pentane or CH_2Cl_2	(Florisil/ silica gel)	PGC/MS	Yes	Area/homolog	0.1 ng/inj	No	Levins et al., 1979
EPA (incinerators)	Stack gas	Pentane/ methanol		PGC/MS	Yes	Single peak	NS	Yes	Beard and Schaum, 1978
ANSI	Air (toluene impinger)	-	(H_2SO_4) (Saponification) (Alumina)	PGC/ECD	No	Single peak	2 ppb	Yes	ANSI, 1974
NIOSH (P&CAM 244)	Air collected on Florisil	Hexane	None	PGC/ECD	No	Peak height or area from standard curve or Webb-McCall	0.01 mg/m³	No	NIOSH, 1977a
NIOSH (P&CAM 253)	Air collected on Florisil	Hexane	None	PGC/ECD Perchlorination	No	Peak height or area from standard curve	0.01 mg/m³	No	NIOSH, 1977b,c
EPA (gas)	Natural gas sampled with Florisil	Hexane	H_2SO_4	PGC/ECD		Total area, peak height or Webb-McCall (Perchlorination)	0.1-2 µg/m³	No	Harris et al., 1981
EPA [5,A,(3)]	Blood	Hexane	(Florisil)	PGC/ECD	No	NS	NS	No	Watts, 1980
EPA [5,A,(1)]	Adipose	Pet. ether/ CH_3CN	Florisil	PGC/ECD	No	NS	NS	Yes	Watts, 1980
EPA (9,D)	Adipose	Pet. ether/ CH_3CN	Saponification Florisil	TLC	No	Semiquant.	10 ppm	No	Watts, 1980
EPA (9,B)	Milk	Acetone/ hexane	CH_3CN Florisil Silica acid	PGC/ECD	Yes	Ind. peaks	50 ppb	Yes	Watts, 1980 Sherma, 1981

Table 21 (Continued)

Procedure designation	Matrix	Extraction	Cleanup[c]	Determination method	Qualitative assessment	Quantitation method	LOD	QC discussed	Reference
AOAC (29)	Food	CH_3CN/Pet. ether	Florisil MgO/ Celite Saponification	PGC/ECD	No	Total area or Ind. peaks	NS[a]	No	AOAC, 1980a
Japan	Food	Pet. ether/ CH_3CN	Silica gel Saponification (Florisil)	PGC/ECD	Yes	Summed areas perchlorination	NS	No	Tanabe, 1976
PAM	Food	Pet. ether/ CH_3CN	Silicic acid (Saponification) (Oxidation) (Florisil)	PGC/ECD (PGC/HECD) (NP-TLC) (RP-TLC)	No	Area	NS	No	FDA, 1977
AOAC (29)	Paper and paperboard	Saponification	Florisil MgO/ Celite Saponification	PGC/ECD	No	Total area or Ind. peaks	NS[a]	No	AOAC, 1980b
D3303-74	Capacitor Askarels	DI[b]	None	SCOT HRGC/FID	No	Total area	2.8×10^{-8} mol/L	No	ASTM, 1980a
D4059-83	Mineral oil	Dilute with hexane or isooctane	Florisil slurry (H_2SO_4) (Florisil column)	PGC/ECD (PGC/HECD)	Yes	Ind. peaks or Webb-McCall	50 ppm	No	ASTM, 1983
EPA (oil)	Transformer fluids or waste oils	DI	(H_2SO_4) (Florisil) (Alumina) (Silica gel) (GPC), (CH_3CN)	PGC/HECD or /ECD or /EIMS (HRGC)	No	Total area or Webb-McCall	1 mg/kg	Yes	EPA, 1981 Bellar and Lichtenberg, 1981
EPA (by-products)	Products or wastes	Several	Several	HRGC/EIMS	Yes	Ind. peaks	NS	Yes	Erickson et al., 1982, 1983d; Erickson, 1984a
DCMA	3 pigment types	A. Hexane/ H_2SO_4 B. CH_2Cl_2	None Florisil	PGC/ECD	No	10 isomers	~ 1 ppm/homolog	Yes	DCMA, 1982
DOW	Chlorinated benzenes	DI	None	PGC/EIMS	Yes	Total peak height/homolog	NS	Yes	Dow, 1981
EPA (isomer groups)	Unspecified	Not addressed	Not addressed	HRGC/EIMS	Yes	Ind. peaks	NS	Yes	EPA, 1984d

Source: M. D. Erickson, The Analytical Chemistry of PCBs, Butterworths, Boston, MA, 1985, in press.

a No specific details.
b Direct injection or dilute and inject.
c Techniques in parentheses are described as optional in the procedure.
d Or PGC with microcoulometric or electrolytic conductivity.

a. Gas Chromatograph/Electron Capture Detection

Packed column gas chromatography with electron capture detection (GC/ECD) is generally the method of choice for analysis of spill site samples, transformer oils, and other similar matrices which must be analyzed for PCB content prior to disposal (Copland and Gohmann 1982). GC/ECD is very sensitive, highly selective against hydrocarbon background, and relatively inexpensive to operate. The technique is most appropriate when the PCB residue resembles an Aroclor® (Aroclor® is a registered trademark of Monsanto Company; the trademark designation is not used throughout this report) standard and other halogenated compounds do not interfere.

While it is considered a selective detector, ECD also detects non-PCB compounds such as halogenated pesticides, polychlorinated naphthalenes, chloroaromatics, phthalate and adipate esters, and other compounds. These compounds may be differentiated from PCBs only by chromatographic retention time. Elemental sulfur can interfere with PCB analysis in sediment and other samples which have been subjected to anaerobic degradation conditions. There are also common interferences which do not give discrete peaks. An example of a nonspecific interference is mineral oil (ASTM 1983). Mineral oil, a complex mixture of hydrocarbons, can cause a general suppression of ECD response. Mineral oils from transformers often contain PCBs as a result of cross-contamination of transformer oils.

A major disadvantage of ECD is the range of response factors which different PCB congeners exhibit. Zitko et al. (1971) and Hattori et al. (1981) published response factors ranges of about 540 and 9000, respectively. Boe and Egaas (1979), Onsuka et al. (1983) and Singer et al. (1983) have also published ECD response factors. The range of response factors seriously inhibits reliable quantitation of individual PCB congeners or non-Aroclor PCBs unless the composition of the sample and standard are the same.

When PCBs are analyzed by packed column gas chromatography, the PCBs are usually quantitated by total areas or individual peaks. In the total areas method, the areas of all peaks in a retention window are summed and this total compared with the corresponding response of an Aroclor standard. With the individual peak quantitation method, response factors are calculated for each peak in the packed column chromatogram. The most prominent individual peak quantitation method was originated by Webb and McCall (1973). These results may be reported as an Aroclor concentration or as total PCB. Packed column GC techniques are generally useful for quantitation of samples which resemble pure Aroclors but are prone to errors from interfering compounds or from PCB mixtures that do not resemble pure Aroclors (Albro 1979). For this reason analysts have been using capillary gas chromatography for the analysis of PCBs. Capillary gas chromatography offers the analyst the ability to separate most of the individual PCB isomers. Bush et al. (1982) has proposed a method of obtaining "total PCB" values by integration of all PCB peaks, using response factors generated from an Aroclor mixture. Zell and Ballschmiter (1980) have developed a simplified approach where only a selected few "diagnostic peaks" are quantitated. In a similar approach Tuinstra et al. (1983) have quantitated six specific, diagnostic congeners which appear to be useful for regulatory cutoff analyses.

b. GC/Hall Electrolytic Conductivity Detector

Electrolytic conductivity detectors have also been used with packed column gas chromatography to selectively detect PCBs (Webb and McCall 1973, Sawyer 1978). The Hall electrolytic conductivity detector (HECD) measures the change in conductivity of a solution containing HCl or HBr which is formed by pyrolysis of halogenated organic GC effluents. The HECD exhibits 10^5-10^6 selectivity for halogenated compounds over other compounds. It also gives a linear response over at least a 10^3 range. HECD and ECD were compared for their use in detecting PCBs in waste oil, hydraulic fluid, capacitor fluid, and transformer oil (Sonchik et al. 1984). They found both detectors acceptable, but noted that the HECD gave higher results with less precision than the ECD. The method detection limits ranged from 3-12 ppm for HECD and 2-4 ppm for ECD. Greater than 100% recovery of spikes analyzed by HECD indicated a nonspecific response to non-PCB components, since extraneous peaks were not observed. Another comparison of HECD and ECD for the analysis of PCBs in oils at the 30-500 ppm levels found that the type of detector made no significant difference in the results (Levine et al. 1983). The authors noted that they had expected higher accuracy from the more specific HECD. They postulated that the cleanup procedures (Florisil, alumina, and sulfuric acid) all had effectively removed the non-PCB species which would have caused interferences in the ECD and reduced its accuracy.

c. GC/Mass Spectrometry

Highly specific identification of PCBs is performed by GC with mass spectrometric (GC/MS) detection. High resolution gas chromatography is generally used with mass spectrometry, so individual PCB isomers may be separated and identified. A GC/MS produces a chromatogram consisting of data points at about 1 second intervals, which are actually full mass spectra. The data are stored by a computer and may be retrieved in a variety of ways. The data file contains information on the amount of compound (signal intensity), molecular weight (parent ion), and chemical composition (fragmentation patterns and isotopic clusters).

GC/MS is particularly suited to detection of PCBs because of its intense molecular ion and the characteristic chlorine cluster. Chlorine has two naturally occurring isotopes, ^{35}Cl and ^{37}Cl, which occur in a ratio of 100:33. Thus, a molecule with one chlorine atom will have a parent ion, M, and an M+2 peak at 33% relative intensity. With two chlorine atoms, M+2 has an intensity of 66% and M+4, 11%.

Because of its expense, complexity of data, and lack of sensitivity, GC/MS has not been used as extensively as other GC methods (particularly GC/ECD), despite its inherently higher information content. As the above factors have been improved, GC/MS has become much more popular for analysis of PCBs, and will probably continue to increase in importance. Several factors including the introduction of routine instruments without costly accessories, decreasing data system costs, and mass-marketing, have combined to keep the costs of GC/MS down while prices of other instruments have risen steadily. With larger data systems and more versatile and "user-friendly"

software, the large amount of data is more easily handled. However, data reduction of a GC/MS chromatogram still requires substantially more time than for a GC/ECD chromatogram. In addition, the sensitivity of GC/MS has improved.

d. Field-Portable Gas Chromatography Instrumentation

Gas chromatography may be used for analysis of samples in the field. Gas chromatography is a well-established laboratory technique, and portable instruments with electron capture detectors are available (Spittler 1983, Colby et al. 1983, Picker and Colby 1984). A field-portable GC/ECD was used to obtain rapid measurements of PCBs in sediment and soil (Spittler 1983). The sample preparation consisted of a single solvent extraction. The PCBs were eluted from the GC within 9 min. In a 6-h period, 40 soils and 10 QC samples were analyzed, with concentrations ranging from 0.2 to 24,000 ppm. The use of field analysis permits real-time decisions in a cleanup operation and reduces the need for either return visits to a site.

Mobile mass spectrometers are also available. An atmospheric pressure chemical ionization mass spectrometer, marketed by SCIEX, has been mounted in a van and used for in situ analyses of soil and clay (Lovett et al. 1983). The instrument has apparently been used for field determination of PCBs in a variety of emergency response situations, including hazardous waste site cleanups. Other, more conventional mass spectrometers, should also be amenable to use in the field.

2. Thin-Layer Chromatography (TLC)

Thin-layer chromatography is a well-established analytical technique which has been used for the determination of PCBs for many years. Since the publication of a TLC method for PCBs by Mulhern (Mulhern 1968, Mulhern et al. 1971), several researchers have used TLC to measure PCBs in various matrices. Methods have been reported by Willis and Addison (1972) for the analysis of Aroclor mixtures, by Piechalak (1984) for the analysis of soils, and by Stahr (1984) for the analysis of PCB containing oils. Even with a densitometer to measure the intensity of the spots, TLC is not generally considered quantitative. Order-of-magnitude estimates of the concentration are certainly obtainable, but the precision and accuracy probably do not approach that of the gas chromatographic methods.

A spill site sample extract will probably need to be cleaned up before TLC analysis. Levine et al. (1983) have published a comparison of various cleanup procedures. Stahr (1984) has compared the Levine sulfuric acid cleanup to a SepPak® C_{18} cleanup method.

Different TLC techniques have been used to improve the sensitivity and selectivity of the method. Several researchers have reported that the use of reverse-phase TLC (C_{18}-bonded phase) achieves a better separation of PCBs from interferences (DeVos and Peet 1971, DeVos 1972, Stalling and Huckins 1973, Brinkman et al. 1976). Koch (1979) has reported an order of magnitude improvement in the PCB limit of detection through use of circular

TLC. The two most common methods of visualization are fluorescence (Kan et al. 1973, Ueta et al. 1974) and reaction with $AgNO_3$ followed by UV irradiation (DeVos and Peet 1971, DeVos 1972, Kawabata 1974, Stahr 1984).

No direct comparison of the performance of TLC with other techniques for analysis of samples from spill sites has been made. Two studies (Bush et al. 1975, Collins et al. 1972) compared TLC and GC/ECD. In both studies, the PCB values obtained were comparable. However, the study by Bush et al. indicated that the TLC results were generally lower than GC/ECD.

3. Total Organic Halide Analyses

Total organic halide analysis can be used to estimate PCB concentrations for guiding field work, but is not appropriate for verification or enforcement analyses. A total organic halide analysis indicates the presence of chlorine and sometimes the other halogens. Many of the techniques also detect inorganic chlorides such as sodium chloride. The reduction of organochlorine to free chloride ion with metallic sodium can be used for PCB analysis. The free chloride ions can be then detected colorimetrically (Chlor-N-Oil®) or by a chloride ion-specific electrode (McGraw-Edison). The performance of these kits has not been tested with any matrix other than mineral oil. X-ray fluorescence (XRF) has also been studied as a PCB screening technique (McQuade 1982, Schwalb and Marquez 1982).

D. Selection of Appropriate Methods

1. Criteria for Selection

The primary criterion for an enforcement method is that the data be highly reliable (i.e., they are legally defensible). This does not necessarily imply that the most exotic, state-of-the-art methods be employed; rather that the methods have a sound scientific basis and validation data to support their use. Many other criteria also enter into selection of a method, including accuracy, precision, reproducibility, comparability, consistency across matrices, availability, and cost.

For PCB spills, it is assumed that the spills will be relatively fresh and therefore that PCB mixtures will generally resemble those in commercial products (i.e., Aroclor®). It is further assumed that, for most of the matrices likely to be encountered, the levels of interferences will be relatively low.

2. Selection of Instrumental Techniques

Based upon the above criteria and assumptions, either GC/ECD or GC/MS should provide suitable data. Since GC/ECD is included in more standard methods and since the technique is more widely used, it appears to be the technique of choice. The primary methods recommended below are all based on GC/ECD instrumental analysis. Some of the secondary and confirmatory techniques are based on GC/EIMS.

3. Selection of Methods

Ideally, a standard method would be available for each matrix likely to be encountered in a PCB spill. The matrices of concern include solids (soil, sand, sediment, bricks, asphalt, wood, etc.), water, oil, surface wipes, and vegetation. The methods for these matrices are summarized in Table 22 and discussed in detail below. A primary recommended method is given and should be used in most spill instances. The secondary method may be useful for confirmatory analyses, or where the situation (e.g., high level of interferences) indicates that the primary method is not applicable. The methods used must be documented or referenced.

a. Solids (Soil, Sand, Sediment, Bricks, Asphalt, Wood, Etc.)

EPA Method 8080 from SW-846 (USEPA 1982e) is the primary recommended method. The secondary methods, Method 8250 and Method 8270, are GC/MS analogs. Method 8080 entails an acetone/hexane (1:1) extraction, a Florisil column chromatographic cleanup, and a GC/ECD instrumental determination. A total area quantitation versus Aroclor standards is specified. No qualitative criteria are supplied. A detection limit of 1 µg/g is prescribed. No validation data are available.

Bulk samples (bricks, asphalt, wood, etc.) should be readily extractable using a Soxhlet extractor according to EPA Method 8080 (USEPA 1982e). The sample must be crushed and subsampled to ensure proper solvent contact.

b. Water

EPA Method 608 (USEPA 1984e) is recommended as the primary method. This is one of the "priority pollutant" methods and involves extraction of water samples with dichloromethane. An optional Florisil column chromatographic cleanup and also an optional sulfur removal are given. Samples are analyzed by GC/ECD and quantitated against the total area of Aroclor standards. No qualitative criteria are given. This method has been extensively validated and complex recovery and precision equations are given in the method for seven Aroclor mixtures. The average recovery is about 86% and average overall precision about ± 26%. The average recovery and precision for the more common Aroclors (1242, 1254, and 1260) are about 78% and ± 26%, respectively. Detection limits are not given in the current version (USEPA 1984a), although they were listed as between 0.04 and 0.15 µg/L for the seven Aroclor mixtures listed as priority pollutants in the method validation study (Millar et al. 1984).

c. Oils

Spilled oil samples should be analyzed according to an EPA method (Bellar and Lichtenberg 1981). The method is written for transformer fluids and waste oils, but should also be applicable to other similar oils such as capacitor fluids. In this method, samples are diluted by an appropriate factor (e.g., 1:1000). Six optional cleanup techniques are given.

Table 22. Summary of Recommended Analytical Methods

Matrix	Primary method (GC/ECD)		Secondary method		
	Designation	Reference	Designation	GC detector	Reference
Solids	8080	USEPA 1982e	8250, 8270	MS	USEPA 1982e
Water	608	USEPA 1984a	625	MS	USEPA 1984b
Oil	"oil"	USEPA 1981a; Bellar and Lichtenberg, 1981	"oil"	MS	USEPA 1981a; Bellar and Lichtenberg, 1981
Surface wipes	Hexane extraction/608	None	Hexane extraction/625	MS	None
Vegetation	AOAC (29)	AOAC 1980a	None	None	None

The sample may be analyzed by GC/ECD as the primary method. Secondary instrumental choices, also presented in the method, are GC/HECD, GC/MS, and capillary GC/MS. PCBs are quantitated by either total areas or the Webb-McCall (1973) method. No qualitative criteria are given. QC criteria are given. A detection limit of 1 mg/kg is stated, although it is highly dependent on the amount of dilution required. An interlaboratory validation study (Sonchik and Ronan 1984) indicated 81 to 126% recoveries for different PCB mixtures, with an average of 97% for Aroclors 1242, 1254, and 1260, as measured by ECD. The overall method precision ranged from ± 11 to ± 55%, with an average of ± 12% for Aroclors 1242, 1254, and 1260. The method validation statistics were presented in more detail as regression equations.

d. Surface Wipes

No standard method is available for analysis of PCBs collected on surface wipes. However, since this matrix should be relatively clean and easily extractable, a simple hexane extraction should be sufficient. Samples should be analyzed according to EPA Method 608 (USEPA 1984a), except for Section 10.1 through 10.3. In lieu of these sections, the sample should be extracted three times with 25 to 50 mL of hexane. The sample can be extracted by shaking for at least 1 min per extraction in the wide-mouthed jar used for sample storage. Note that the rinses should be with hexane so that solvent exchange from methylene chloride to hexane (Section 10.7) is not necessary.

e. Vegetation

The AOAC (1980a) procedure for food is recommended for analysis of vegetation (leaves, vegetables, etc.). This method involves extraction of a macerated sample with acetonitrile. The acetonitrile is diluted with water and the PCBs extracted into petroleum ether. The concentrated extract is cleaned up by Florisil column chromatography by elution with a mixture of ethyl ether and petroleum ether. The sample is analyzed by GC/ECD with quantitation by total areas or individual peak heights as compared to Aroclor standards. No qualitative criteria are given. Validation studies with chicken fat and fish (Sawyer 1973) are not relevant to the types of matrices to be encountered in PCB spills.

4. Implementation of Methods

Each laboratory is responsible for generating reliable data. The first step is preparation of an in-house protocol. This detailed "cookbook" is based on methods cited above, but specifies which options must be followed and provides more detail in the conduct of the techniques. It is essential that a written protocol be prepared for auditing purposes.

Each laboratory is responsible for generating validation data to demonstrate the performance of the method in the laboratory. This can be done before processing of samples; however, it is often impractical. Validation of method performance (replicates, spikes, QC samples, etc.) while analyzing field samples is acceptable.

Changes in the above methods are acceptable, provided the changes are documented and also provided that they do not affect performance. Some minor changes (e.g., substitution of hexane for petroleum ether) do not generally require validation. More significant changes (e.g., substitution of a HECD for ECD) will require documentation of equivalent performance.

E. Quality Assurance

Quality assurance must be applied throughout the entire monitoring program including the sample planning and collection phase, the laboratory analysis phase, and the data processing and interpretation phase.

Each participating EPA or EPA contract laboratory must develop a quality assurance plan (QAP) according to EPA guidelines (USEPA 1980). Additional guidance is also available (USEPA 1983). The quality assurance plan must be submitted to the regional QA officer or other appropriate QA official for approval prior to analysis of samples.

1. Quality Assurance Plan

The elements of a QAP (U.S. EPA, 1980) include:

Title page
Table of contents
Project description
Project organization and responsibility
QA objectives for measurement data in terms of precision, accuracy, completeness, representativeness, and comparability
Sampling procedures
Sample tracking and traceability
Calibration procedures and frequency
Analytical procedures
Data reduction, validation and reporting
Internal quality control checks
Performance and system audits
Preventive maintenance
Specific routine procedures used to assess data precision, accuracy and completeness
Corrective action
Quality assurance reports to management

2. Quality Control

Each laboratory that uses this method must operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial and continuing demonstration of acceptable laboratory performance by the analysis of check samples, spiked blanks, and field blanks. The laboratory must maintain performance records which define the quality of data that are generated.

The exact quality control measures will depend on the laboratory, type and number of samples, and client requirements. The QC measures should be stipulated in the QA Plan. The QC measures discussed below are given for example only. Laboratories must decide on which of the measures below, or additional measures, will be required for each situation.

a. Protocols

Virtually all of the available PCB methods contain numerous options and general instructions. Effective implementation by a laboratory requires the preparation of a detailed analysis protocol which may be followed unambiguously in the laboratory. This document should contain working instructions for all steps of the analysis. This document also forms the basis for conducting an audit.

b. Certification and Performance Checks

Prior to the analysis of samples, the laboratory must define its routine performance. At a minimum, this must include demonstration of acceptable response factor precision with at least three replicate analyses of a calibration solution; and analysis of a blind QC check sample (e.g., the response factor calibration solution at unknown concentration submitted by an independent QA officer). Acceptable criteria for the precision and the accuracy of the QC check sample analysis must be presented in the QA plan.

Ongoing performance checks should include periodic repetition of the initial demonstration or more elaborate measures. More elaborate measures may include control charts and analysis of QA check samples containing unknown PCBs, and possibly with matrix interferences.

c. Procedural QC

The various steps of the analytical procedure should have quality control measures. These include, but are not limited to, the following:

Instrumental Performance: Instrumental performance criteria and a system for routinely monitoring the performance should be set out in the QA Plan. Corrective action for when performance does not meet the criteria should also be stipulated.

Qualitative Identification: Any questionable results should be confirmed by a second analytical method. A least 10% of the identifications, as well as any questionable results, should be confirmed by a second analyst.

Quantitation: At least 10% of all calculations must be checked. The results should be manually checked after any changes in computer quantitation routines.

d. Sample QC

Each sample and each sample set must have QC measures applied to it to establish the data quality for each analysis result. The following should be considered when preparing the QA plan:

Field Blanks: Field blanks are analyzed to demonstrate that the sample collection equipment has not been contaminated. A field blank may be generated by using the sampling equipment to collect a blank sample (e.g., using the water sampling equipment to sample laboratory reagent grade water) or by extracting the sampling equipment (e.g., extracting a sheet of filter paper from the lot used to collect wipe samples or rinsing the soil sampling apparatus into the sample jar). A field blank must be collected and analyzed for each type of sample collected.

Laboratory Reagent Blanks: These blanks are generated in the laboratory and are analyzed to assess contamination of glassware, reagents, etc., in the laboratory. Generally, a reagent blank is processed through the entire analysis process. Although in special circumstances, additional reagent blanks may be generated which are processed through only part of the procedure to isolate sources of contamination. At least one laboratory reagent blank must be generated and analyzed for each type of sample analyzed.

Check Samples: These samples contain known concentrations of PCBs in the sample matrix. They are analyzed along with field samples to demonstrate the method performance. The PCB concentrations may be known to the analyst.

Blind Check Samples: These samples are the same as the check samples discussed above, except the PCB concentration is not known to the analyst.

Replicate Samples: One sample from each batch of 20 or fewer will be analyzed in triplicate. The sample is divided into three replicate subsamples and all these subsamples carried through the analytical procedure, blind to the analyst. The results of these analyses must be comparable within the limits required for spiked samples.

Spiked Samples: The sensitivity and reproducibility must be demonstrated for any method used to report verification data. This can be done by analyzing spiked blanks near the required detection limit. To demonstrate the ability of the method to reproducibly detect the spiked sample, one or more spiked samples should be analyzed in at least triplicate for each group of 20 or fewer samples within each sample type collected. Samples will

be spiked with a PCB mixture similar to that spilled (e.g., Aroclor 1260). Example concentrations are:

Matrix	Spike Level
Soil, etc.	10 µg/g (10 ppm)
Water	100 µg/L (100 ppb))
Wipes	100 µg/wipe (100 µg/100 cm^2)

Quantitative techniques must detect the spike level within ±30% for all spiked samples.

e. Sample Custody

As part of the Quality Assurance Plan, the chain-of-custody protocol must be described. A chain-of-custody provides defensible proof of the sample and data integrity. The less rigorous sample traceability documentation merely provides a record of when operations were performed and by whom. Sample traceability is not acceptable for enforcement activities.

Chain-of-custody is required for analyses which may result in legal proceedings and where the data may be subject to legal scrutiny. Chain-of-custody provides conclusive written proof that samples are taken, transferred, prepared, and analyzed in an unbroken line as a means to maintain sample integrity. A sample is in custody if:

- It is in the possession of an authorized individual;
- It is in the field of vision of an authorized individual;
- It is in a designated secure area; or
- It has been placed in a locked container by an authorized individual.

A typical chain-of-custody protocol contains the following elements:

1. Unique sample identification numbers.
2. Records of sample container preparation and integrity prior to sampling.
3. Records of the sample collection such as:
   - Specific location of sampling.

- Date of collection.
- Exact time of collection.
- Type of sample taken (e.g., air, water, soil).
- Initialing each entry.
- Entering pertinent information on chain-of-custody record.
- Maintaining the samples in one's possession or under lock and key.
- Transporting or shipping the samples to the analysis laboratory.
- Filling out the chain-of-custody records.
- The chain-of-custody records must accompany the samples.

4. Unbroken custody during shipping. Complete shipping records must be retained; samples must be shipped in locked or sealed (evidence tape) containers.

5. Laboratory chain-of-custody procedures consist of:

   - Receiving the samples.
   - Checking each sample for tampering.
   - Checking each sample against the chain-of-custody records.
   - Checking each sample and noting its condition.
   - Assigning a sample custodian who will be responsible for maintaining chain-of-custody.
   - Maintaining the sign-offs for every transfer of each sample on the chain-of-custody record.
   - Ensuring that all manipulations of the sample are duly recorded in a laboratory notebook along with sample number and date. These manipulations will be verified by the program manager or a designee.

F. Documentation and Records

Each laboratory is responsible for maintaining complete records of the analysis. A detailed documentation plan should be prepared as part of

the QAP. Laboratory notebooks should be used for handwritten records. Digital or other GC/MS data must be archived on magnetic tape, disk, or a similar device. Hard copy printouts may also be kept if desired. Hard copy analog data from strip chart recorders must be archived. QA records should also be retained.

The documentation must completely describe how the analysis was performed. Any variances from a standard protocol must be noted and fully described. Where a procedure lists options (e.g., sample cleanup), the option used and specifics (solvent volumes, digestion times, etc.) must be stated.

The remaining samples and extracts should be archived for at least 2 months or until the analysis report is approved by the client organization (whichever is longer) and then disposed unless other arrangements are made. The magnetic disks or tapes, hard copy chromatograms, hard copy spectra, quantitation reports, work sheets, etc., must be archived for at least 3 years. All calculations used to determine final concentrations must be documented. An example of each type of calculation should be submitted with each verification spot.

G. Reporting Results

Results of analysis will normally be reported as follows:

Matrix	Reporting Units
Soil, etc.	µg PCB/g of sample (ppm)
Water	mg PCB/L of sample (ppm)
Surfaces (wipes)	µg PCB/wipe (µg PCB/100 cm^2)

In some cases, the results are to be reported by homolog. In this case, 11 values are reported per sample: one each for the 10 homologs and one for the total. Some TSCA analyses require reporting the results in terms of resolvable gas chromatographic peak (U.S. EPA, 1982c, 1984e). In these cases, the number of results reported equals the number of peaks observed on the chromatogram. These analyses are generally associated with a regulatory cutoff (e.g., 2 µg/g per resolvable chromatographic peak (U.S. EPA, 1982c, 1984). In these cases it may be sufficient, depending on the client organization's request, to report only those peaks which are above the regulatory cutoff.

Even if an Aroclor is used as the quantitation standard, the results are never to be reported as "µg Aroclor®/g sample." TSCA regulates all PCBs, not merely a specific commercial mixture.

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