PART B - CHAPTER 5

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SOIL RESIDUE DISSIPATION
GUIDELINE 875.2200

5.1 INTRODUCTION

This Guideline provides a description of the techniques and sampling strategies commonly used to characterize soil residue dissipation (SRD). Soil-borne residues, for purposes of this Guideline, represent total (not dislodgeable) chemical residues that are found in both surface and subsurface soils. Surface soil residues are of primary concern because contact with surface soils is usually more common than with subsurface soils. However, contact with subsurface soil may also be a concern for certain reentry activities such as potato harvesting, and where a mechanical apparatus is used. For the purpose of this guideline, surface soils are considered as those soil particles in the top 1 cm thick layer of soil. Subsurface soils are considered as anything below the surface layer of soil. SRD data may be used in conjunction with concurrent human exposure data to establish chemical transfer coefficients which are then used to determine restricted-entry intervals in occupational settings and exposures in residential scenarios. As an alternative, SRD data have been used in conjunction with dermal adherence data to estimate potential human exposures (U.S. EPA, 1988). Kissel et al. (1996a) have developed dermal adherence values for various human activities.

5.2 SAMPLE COLLECTION

5.2.1 Test Substance

As stated at 40 CFR 158.390, the test substance to be used for inhalation exposure measurements must be a typical end-use product. Where metabolites, breakdown components, or contaminants of pesticide end-use products pose a potential toxicological concern, investigators may need to consider sampling for them on a case-by-case basis.

5.2.2 Timing of Application

Sample collection should be conducted during the intended use season or under climatic conditions that are essentially identical to those encountered during the intended use season. Weather forecasts should be studied to avoid initiating the testing immediately (e.g., within 24 hours) before a precipitation event. For further information on climatological considerations, see Part B, Chapter 2 - Study Design.

5.2.3 Pesticide Application Rate and Frequency

Generally, the end-use product chosen for the study should be applied at the maximum rate specified on the label. In addition to applying the product at the maximum label rate, it is suggested that the product be applied using a lower application rate, if possible. For example, typical rates are often used in cancer assessments (U.S. EPA, 1997). Monitoring at more than one rate will also provide additional information about the relationship between the application and deposition rates. Also, testing at a lower rate may prove to be beneficial in the event that the data from use of the product at the maximum application rate results in an unacceptable risk.

Where multiple applications are recommended, the minimum time interval between applications should be used. Also, testing at a longer time interval between applications may prove to be beneficial if unacceptable risks may result. Registrants should note, however, that if the maximum rates or minimum application intervals are not monitored, subsequent label changes may be necessary. Also, the potential accumulation of residues from multiple applications should be considered. The application method and equipment typical for the selected test substance should be used.

5.2.4 Sampling Parameters

The following paragraphs provide a description of: where geographically sampling should occur; how long the dissipation must be characterized (i.e., the sampling period); the times within the sampling period that samples should be taken (i.e., sampling intervals); and the number of samples that should be taken at each sampling interval along with a description of where at the sampling location to sample.

5.2.4.1 *Number of Geographic Locations*

SRD samples are typically collected from at least three geographically distinct locations. This is usually necessary to ensure that varying climatic conditions, crops, and pest types are represented. Sampling locations should be selected based on the chemical use patterns, activities associated with the chemical use, and soil characterization data for selected locations. (See Chapter 2, Study Design, for more guidance.)

5.2.4.2 *Sampling Period*

Data should be collected in a manner that characterizes the dissipation mechanisms for the compound (e.g., three half-lives). Further, the sampling period should be reflective of the exposure conditions and toxicological endpoint of concern (i.e., acute or chronic). Typically, SRD dissipation rates are characterized for at least 35 days postapplication unless the compound has been found to fully dissipate in less than this time period. EPA has observed that this sampling period is adequate for characterizing pesticide dissipation under most use conditions; for most pesticides, significant dissipation occurs within the first week of application. Please note, however, that for more persistent pesticides a longer sampling period may need to be used.

5.2.4.3 *Sampling Intervals*

Generally, the length of time between sampling days should be relatively short in the beginning and should lengthen as the study progresses. EPA recommends that samples be collected prior to application on the day of application; on the application day at various hourly intervals after application (e.g., 4 hours and 12 hours may be appropriate); and on various days postapplication. For example, sampling on days 1, 2, 4, 7, 10, 14, 21, 28, and 35 after application may be appropriate. Please note that for certain pesticides (e.g., one that degrades quickly) shorter sampling intervals may suffice. However, the sampling should continue for 35 days, but all of the samples may not need to be analyzed if the pesticide has fully dissipated (i.e., nondetects for two sampling intervals). On the other hand, sampling may need to be continued beyond 35 days for more persistent pesticides. Special consideration should also be given to pesticides that exhibit biphasic dissipation kinetics.

If typical chemical use patterns involve a sequential series of treatments (i.e., multiple applications), samples in addition to the ones indicated above should be collected. Generally for multiapplication scenarios, the Agency recommends that samples be collected prior to and after each application on the day of application. Additionally, for all but the final applications (see above), samples should be collected at least every 7 days after each application during the intervals between application events (e.g., if multiple applications occur on a 14 day interval, then samples should be collected prior to and after each application and 7 days after each application). However, modifications to this sampling scheme may be proposed to the Agency if the market and use pattern will accept that reentry is prohibited between applications, or if the registrant is willing to accept the results and restrictions imposed by the alternative sampling scheme.

The proposed sampling intervals should be presented to EPA for review in the study protocol prior to the initiation of the study to ensure that they are agreeable to the Agency.

5.2.4.4 *Number of Samples and Sampling Positions*

The Agency recommends that at least three replicate samples be collected at each sampling interval. Each replicate sample should be taken from designated, distinct areas within the treated location. Samples should be collected in the worker contact zone (i.e., in those areas where workers will be conducting their activities). A sufficient number of subsamples must be collected and composited from each designated sampling location to generate samples that are sufficient for analysis. Exact sample collection procedures must be documented in any submission to the Agency. Control plots should also be established. Sufficient control samples should be collected to ensure that the same bulk sample can be used as a negative control matrix throughout all sample analyses. Additionally, samples from the control plots should be collected at each interval for assessment of the field sample collection and storage procedures.

Several approaches have been utilized by investigators to determine where to sample within treated sites. These include, but are not limited to: nondirected sampling and the planned approach for row crops. In nondirected sampling, field technicians enter a treated area and sample selected areas within the treated location at random. In the planned approach, investigators develop a scheme that predetermines sample collection locations. (See Figure B5-1.) EPA recommends that a planned approach be used for SRD sample collection.

5.2.5 Technique Validation

Validation of the soil sampling method is not required. Soils are to be analyzed for total residue levels contained in the sample. Validation of the analytical method used to evaluate chemical residues contained in soil is required, based on the guidance provided in Part C, Quality Assurance/Quality Control.

5.2.6 Sampling Techniques

Two sampling techniques are available for the conduct of a soil residue dissipation study. The first technique is surface soil sampling where the top layer of the soil (i.e., 1 cm thick) is removed and retained for analysis. The second technique is soil core sampling where samples are collected in 6-inch layers to depths that represent the exposure activity of concern. For most human activity patterns that are of concern, surface soil sampling is the recommended technique. However, there are activities such as potato harvesting and nursery stock transplanting where significant exposure to soils below the surface layer can occur.

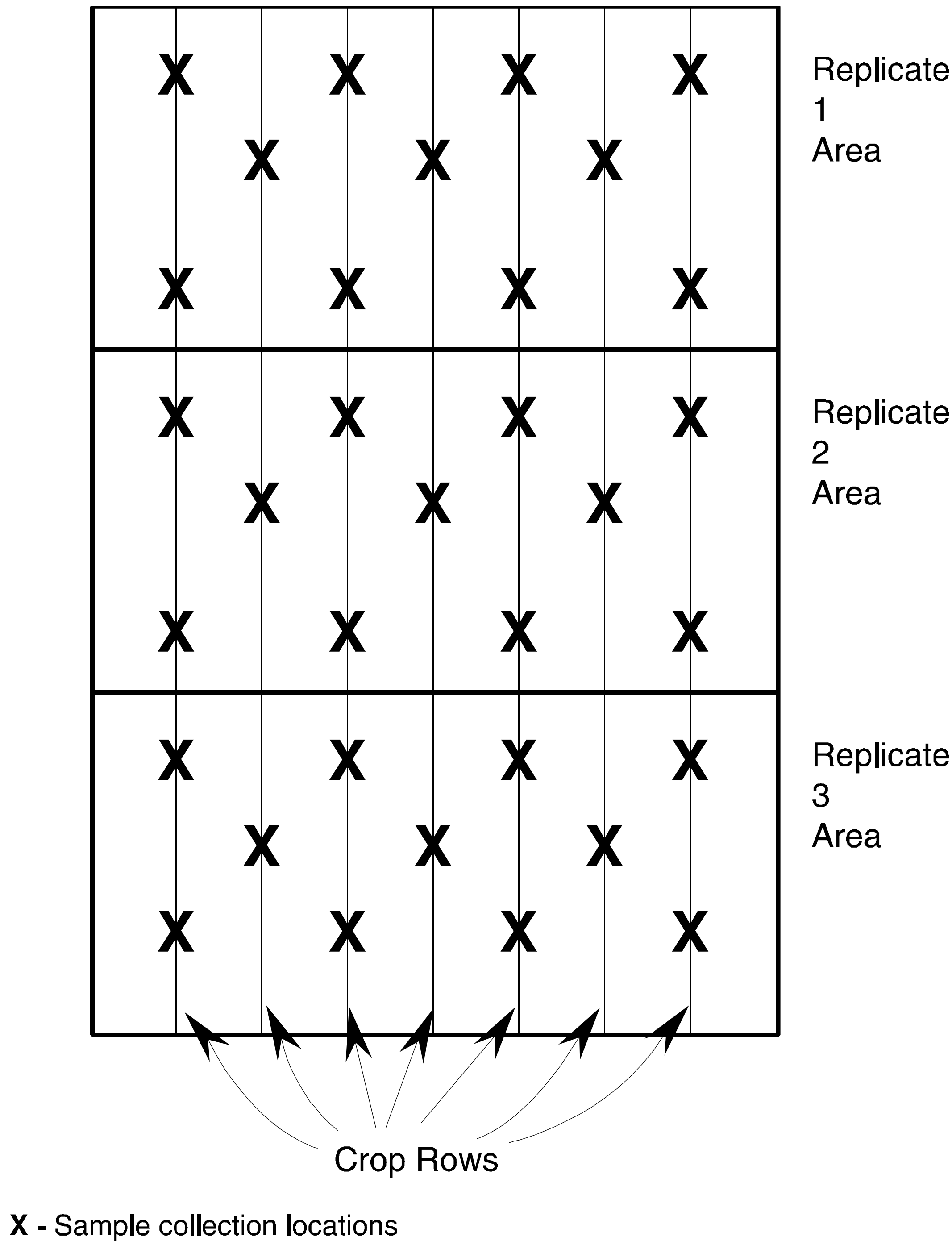
Replicate
1
Area
Replicate
2
Area
Replicate
3
Area
Crop Rows
X - Sample collection locations

Figure B5-1. Planned Approach for Field Crop Sampling

Surface soil samples may be collected using common equipment such as scoops, scrapers, and shovels. A template of known surface area (e.g., 1 foot by 1 foot) should be placed over the sampling area and the entire surface layer within the template should be removed as a replicate sample. The purpose of the template is to provide data that can be used to normalize residue levels based on the surface area sampled as well as on a weight basis. In cases where the treated plot has been tilled into furrows, samples should be collected from the top area of the furrow as this field arrangement is typically used for irrigation purposes and contact with the irrigation water may impact the dissipation of the analyte of interest.

If other surface soil sampling techniques are used, the sampling equipment must be thoroughly described in submissions to the Agency. Alternative types of techniques include: sweeping soil surface dusts (Berck et al., 1981); excavation of soil from the upper soil layers using templates (Zweig et al., 1985); and vacuuming soil dusts (Spencer et al., 1977).

Soil core samples may be collected using common techniques such as hand probes and mechanical soil coring machines. Both techniques are based on the principle of driving a cylinder into the ground, withdrawing the cylinder, and retaining the column of soil contained therein for analysis. Investigators are cautioned to use zero contamination devices wherever possible, particularly when sampling over several 6-inch depth levels. Zero contamination devices are double cylinder systems in which the outer cylinder is the soil core sampler and the inner tube is a clean cylinder (i.e., residue free sample container) that is driven into the ground concurrently and collects the sample. The inner cylinder prevents contamination between layers by retaining the sampled soil column intact and by preventing particles from shaking off the soil column and falling to the lower layers. Generally, the soil samples are retained for analysis in the inner cylinder. A number of subsamples should be collected to ensure that a sufficient quantity of soil is obtained for analysis at each sampled 6-inch layer.

5.2.7 General Considerations for Field Sample Collection

Control or background samples should be collected from the test plot prior to application of the test substance. Sufficient control samples should be collected so that fortified controls can be prepared on each sampling day. These fortified controls should be packaged, transported, stored, and analyzed concurrent with the dislodgeable residue samples. Please see Part C for detailed considerations on Quality Assurance and Quality Control recommendations.

5.2.8 Sample Preparation Procedures

Sample preparation procedures depend upon the objectives of the study. Based on the following data, investigators must consider soil conditions in the study design process and justify the soil sample preparation process. Dermal soil adherence data indicate that both particle size and percent moisture influence soil adherence to skin (Kissel et al., 1996b**)**. Kissel et al. (1996b) used various soil types (i.e., loamy sand, two sandy loams, a silt loam, and sand) to evaluate factors that affect dermal adherence. Dermal soil adherence levels were determined using whole soils and soils at three size fractions (i.e., <150 µm, 150 to 250 µm, and ≥250 µm to ≤425 µm). Percent moisture levels were also varied for each adherence test. Adherence of size**-** fractioned soils was evaluated at three percent moisture levels (i.e., <0.1 to 9, 10 to 19, and 21 to 27). Kissel et al. (1996) indicated that particles less than 150 µm are the primary contributors to soil adherence when the soil is dry (i.e., moisture is less than 2 percent). In contrast, particles greater than 250 µm are the primary contributors to soil adherence when soil is wet (i.e., percent moisture is between 12 and 18). Based on the whole soil test results, soil adherence increases as the percent moisture levels increase (e.g., 21 to 27 percent moisture soil adherence was generally an order of magnitude greater than adherence levels at percent moistures <2 percent). Generally, the Agency recommends that if moisture levels are ≤10 percent, then soils should be prepared for analysis by sieving to obtain a sample for analysis that contains all particles ≤250 µm. Conversely, if moisture levels are >10 percent, then soils should be prepared by sieving to obtain a sample for analysis that contains all particles ≤425 µm. Typically, whole soil samples should never be submitted for analysis as these samples may contain coarse materials that would not likely adhere to skin but may contribute to a measured residue level (e.g., twigs and small stones).

The Agency prefers that common, mesh screen sieves be used to separate fine soil particles from more coarse soil components (Figure B5-2). Soil samples may be sieved using one of two approaches. The first approach requires that investigators sieve soil samples immediately after collection prior to freezing, storage, and analysis. The second approach involves freezing whole soil surface samples after collection and preparing those samples prior to analysis. Samples should be sieved while they are malleable, yet still partially frozen to ensure that there is no chemical residue loss (e.g., volatilization, soil metabolism, etc.). Aliquots of the fine soil components should be retained for three types of analysis: determination of chemical residues; soil characterization purposes; and determination of the percent water in each sample.

5.2.9 <u>Soil Characterization</u>

Investigators must characterize whole soil samples from each site used in the study (i.e., samples that have not been sieved) and samples that have been prepared for analysis. The Agency requires that

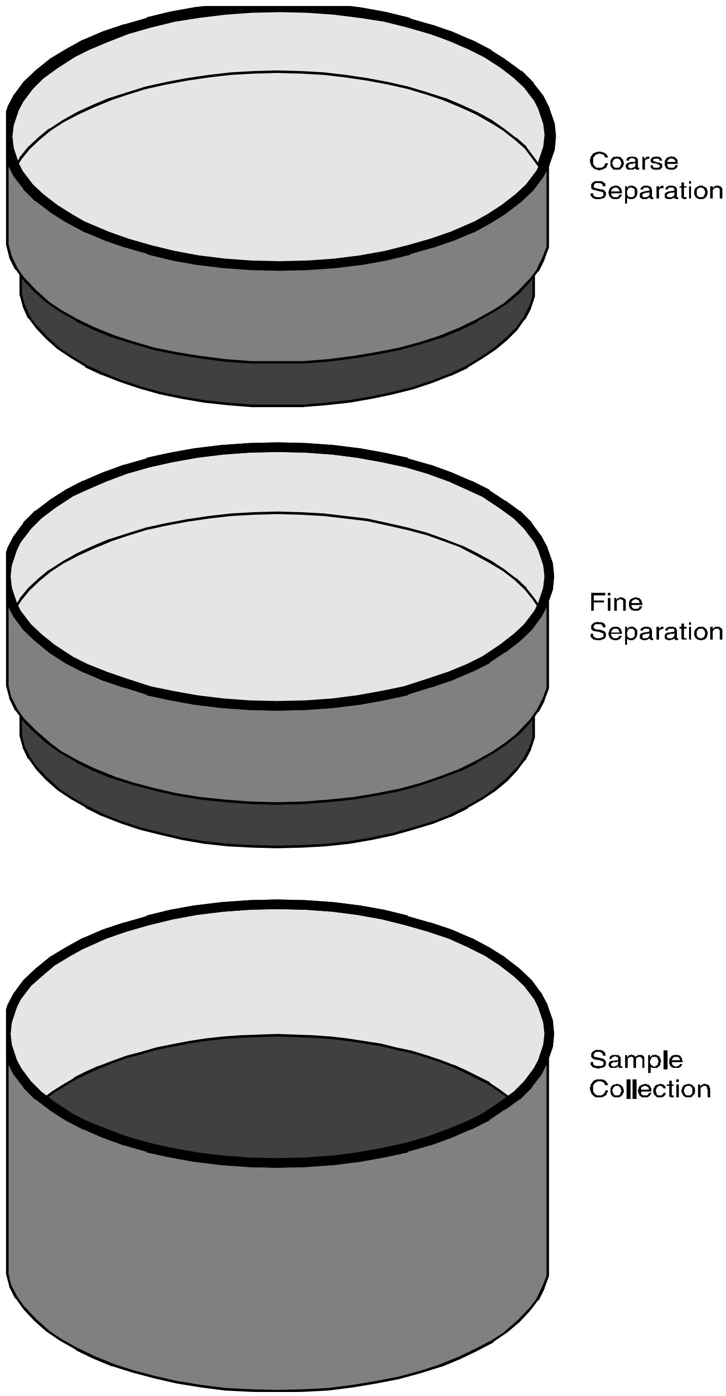

Figure B5-2. Soil Sieve/Screen Schematic characterization be completed with at least triplicate samples collected from each study site. Soil characterization testing is a required element of all surface soil residue dissipation studies. Characterization of soils is based on the soil texture triangle illustrated in Figure B5-3 (U.S. EPA, 1991). Soil characterization data are required to ensure that the site selection process was adequate. Additionally, these data may provide useful information when attempting to evaluate soil residue dissipation kinetics especially when compared to any existing environmental fate data for the pesticide.

5.2.10 Water Content

In addition to the soil characterization requirements described above, the percentage of water contained in each soil sample intended for chemical residue analysis must be determined. Two gravimetric methods are available for determining the percentage of water in a soil sample. The first method involves preparing an aliquot of wet soil, placing the aliquot in a drying oven, and, after a predetermined time interval, removing the aliquot from the oven and weighing it to gauge water loss. The second method involves the use of a percent moisture meter (Figure B5-4). The device typically contains a high intensity visible light source (e.g., heat lamp), an analytical balance, and a timer for the light source (USGS, 1977). Other direct and indirect methods are available to determine the percent water in soil including alcohol burning, neutron scattering, and gamma-ray attenuation (USGS, 1977).

5.3 SAMPLE STORAGE

Soil residue samples and extracts should be stored in a manner that will minimize deterioration and loss of analyte between collection and analysis; more detailed information on sample storage is provided in Part C, Quality Assurance and Quality Control. The study investigator is responsible for demonstrating storage stability.

5.4 SAMPLE ANALYSIS

Validated methods of appropriate or sufficient sensitivity are needed for all sample analyses. See Part C, Quality Assurance and Quality Control for more detailed information on sample analysis.

5.5 CALCULATIONS

Refer to Part D of this document for a description of the calculations needed for estimating dissipation rates, exposure, and risk.

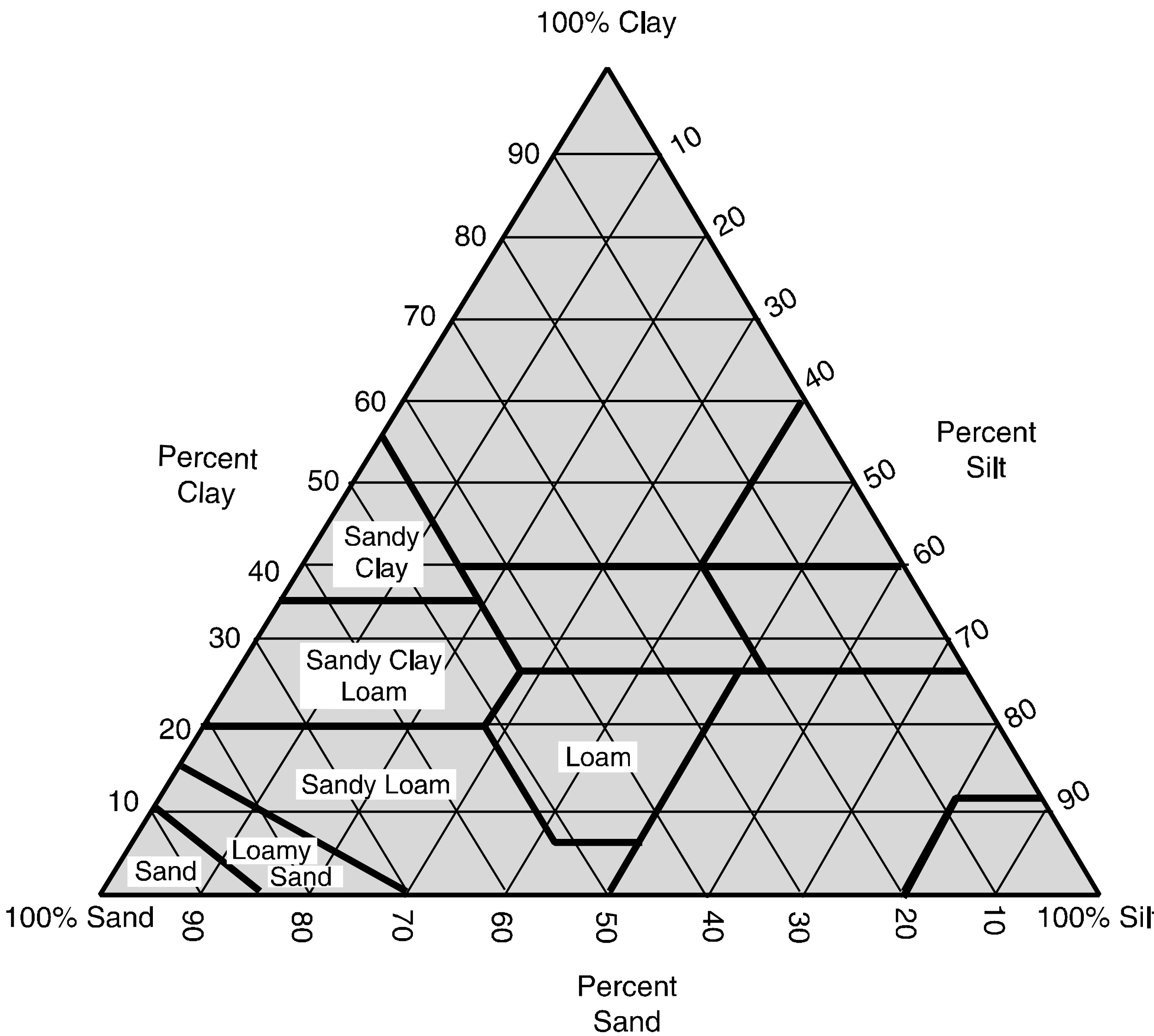

Figure B5-3. Soil Texture Triangle

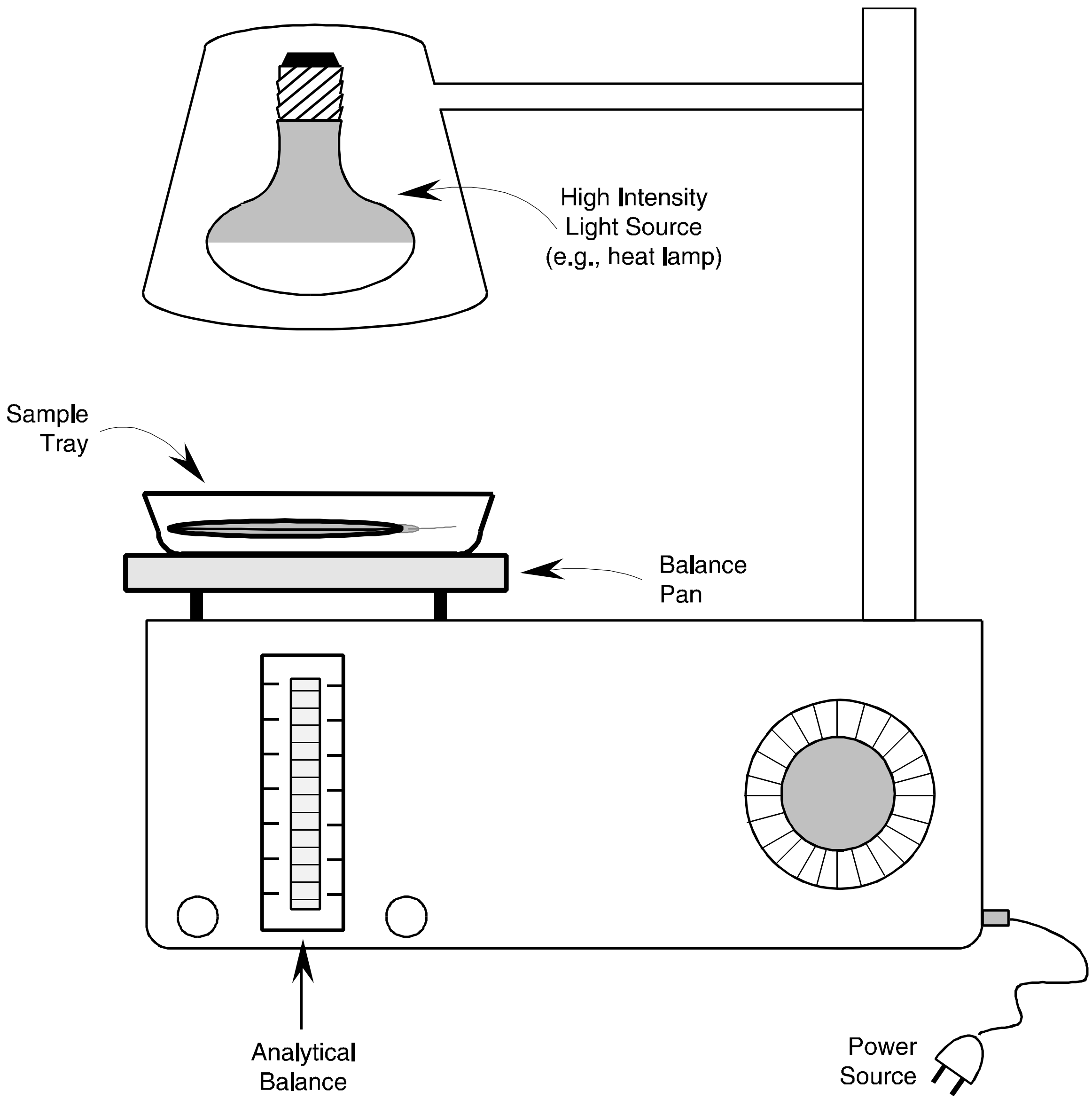

Figure B5-4. Percent Moisture Meter

5.6 DATA PRESENTATION

Soil residues should be reported as mg or µg of pesticide active ingredient on a per weight sampled and on a unit area sampled basis as appropriate (i.e., unit area for soil cores represents depth and diameter). These data should be reported in tabular form for each sampling day. In addition, the best fit dissipation curve should be plotted (typically log-linear) with soil residues on the Y-axis and time on the X-axis. Distributional data should be provided, to the extent possible.

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