FORESTRY FIELD AND LABORATORY MANUAL FOR HERBICIDE RESIDUE SAMPLING, SAMPLE PROCESSING AND REPORTING.

FPM-X-72

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

Registration of new forestry herbicides in Canada requires data on the environmental fate of residues, including their persistence, degradation, mobility and movement in a variety of forest components and substrates. In addition, obtaining provincial use permits for newly registered herbicides requires further studies on their environmental fate under local conditions. Techniques for environmental sample collection, their preparation, and residue reporting for forest research studies are generally adapted from those used in agricultural research, owing to the relative youth of forestry herbicide research in Canada. The characteristics of forests, which distinguish them from agricultural land, also create difficulties in applying agricultural residue sampling techniques.

Selection of appropriate residue sampling techniques to derive needed data on environmental fate of forestry herbicides are required in: 1) on- and off-target deposit collection, 2) residue dissipation in stream waters and sediments, 3) residue persistence and degradation in soils and foliage, and 4) residue leaching and its lateral downslope movement in soils. Developments in recent studies on glyphosate (Roundup®) and hexazinone (Velpar®) conducted by the Forest Pest Management Institute (FPMI) in cooperation with the British Columbia Ministry of Forests (BCMOF), CFS Maritimes, Pacific Forestry Centre (PFC) and the Ontario Ministry of Natural Resources (OMNR), have improved sampling, handling and residue reporting techniques for herbicide residues in forest areas. In aerial application of forestry herbicides in certain environmentally sensitive areas, the large droplet sizes provided by the MICROFOIL®[1] boom and the THRU-VALVE BOOM®[2] controlled off-target drift better than the smaller droplet sizes provided by conventional boom and nozzle spray systems (Amchem 1972). The new collection technique developed prevented sample loss from the large droplets splashing and spilling as was found with the previously used plate collectors (Kieley and Ernst 1984) and spray deposit cards (USDA 1984). Two other deposit collectors developed for smaller droplet sizes and different measurement purposes are also described in this manual.

Sediment transportation patterns of streams in steeper forested watersheds differ from those of slower flowing streams typical of agricultural areas in moving larger sediment particles. Selection of appropriate sampling techniques is required in order to collect residues adsorbed to these sediments.

Traditionally, forest soil sampling techniques and methods of residue reporting (Neary et al. 1983; Newton et al. 1984) are adapted from those used for relatively homogeneous agricultural soils. These non-volumetric sampling techniques are inappropriate for dealing with the heterogeneity of the undisturbed forest floor. Forest soils have distinct differences and substantial variation in bulk densities for different soil horizons and geographical locations. Reporting residue values in other than area (kg/ha) or volumetric (mg/L) bases does not enable adequate comparison between different forest soils. Herbicide residue values derived by soil sampling and chemical analysis are often reported on a weight to weight (µg/g) basis (Barring and Torstensson 1983; Neary et al. 1983; Newton et al. 1984; Smith and Hsiao 1985)), whereas residue values are often reported on an area basis (kg/ha) when derived through bioassay techniques (Harrington et al. 1982; Peter and Weber 1985) or through accountability in runoff water by ecologists (Rueppel et al. 1977). Difficulties in interpreting the different units indicate a need for conformity in presenting

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[1] Registered trademark of Union Carbide, Ambler, Pa.

[2] Registered trademark of Waldrum Specialties Inc., Ambler, Pa.

residue data in a standardized format. Further need for reporting residues in soil on a weight to area basis (kg/ha) is apparent when relating initially applied amounts of herbicide (kg/ha) to residue persistence data, as well as lateral residue movement in soil to the initial background level of residues contributed by the off-target drift deposit (reported as kg/ha) from an aerial application. A new soil sampling procedure developed in recent studies provides the capability to transform traditional residue data from a weight to weight basis (i.e., µg ai/ g soil) to a standardized format using a weight to area (kg/ha) or volumetric basis (mg ai/L soil). The procedure provides a correction factor for individual residue values on the basis of bulk density which accounts for much variation in soil porosity, density of minerals and organic matter, and their combined physical composition found in different soil horizons and locations. Forest managers and regulatory agencies can therefore directly compare the residue data generated from different forest areas, different sampling dates and different application rates.

Some important aspects of herbicide residue sampling that this manual does not discuss include: a) herbicide application techniques, which are specific to herbicide, dispersal systems and field conditions involved, b) statistical and experimental design for randomization, replication and sampling schedule duration, which are specific to the objectives and goals of the research, and c) analytical procedures for residue determination, which are specific to the nature of the samples, and are modified frequently to produce accurate and reproducible results. However, these aspects have been intensively studied, and relevant references and guides to them are readily available.

The main objective of this manual is to provide foresters and field researchers with techniques to obtain reliable environmental samples and some critical pre-analytical measurements that will facilitate further data processing, evaluation and comparison from the residue data traditionally generated in an analytical laboratory.

Scope

This manual specifically addresses techniques for obtaining reliable residue samples for forestry environmental studies on aerially applied hexazinone and glyphosate, unless otherwise specified. However, the techniques described may also apply to other pesticide residues and studies on their environmental fate. Materials and methods, including preparation of sampling plots, and sample collection, packaging, shipping and storage, are described for assessing spray deposition and monitoring herbicide residues in five forestry substrates, including stream water, suspended sediments, streambed sediments, soils and foliage/leaf-litter. Pre-analysis preparation of deposition and soil samples, and reporting of residue data for all substrates, are also described.

SPRAY DEPOSITION

Scope

The procedure in this section describes collection of herbicide deposit from aerial application. Equipment preparation, packaging, storage, shipping and sample extraction are also described.

Summary

Three types of collectors are described for collecting on- and off-target deposit generated from various atomizers used in forestry aerial applications. These include: 1) aluminum foil collectors, 2) petri-dish collectors with filter paper linings, and 3) large Teflon sheet collectors. Aluminum foil collectors (400 cm^2; Fig. 1, 2) were designed for spray with conventional booms and nozzles which generate

Figure 1. Assembly of an aluminum foil herbicide deposition collector.

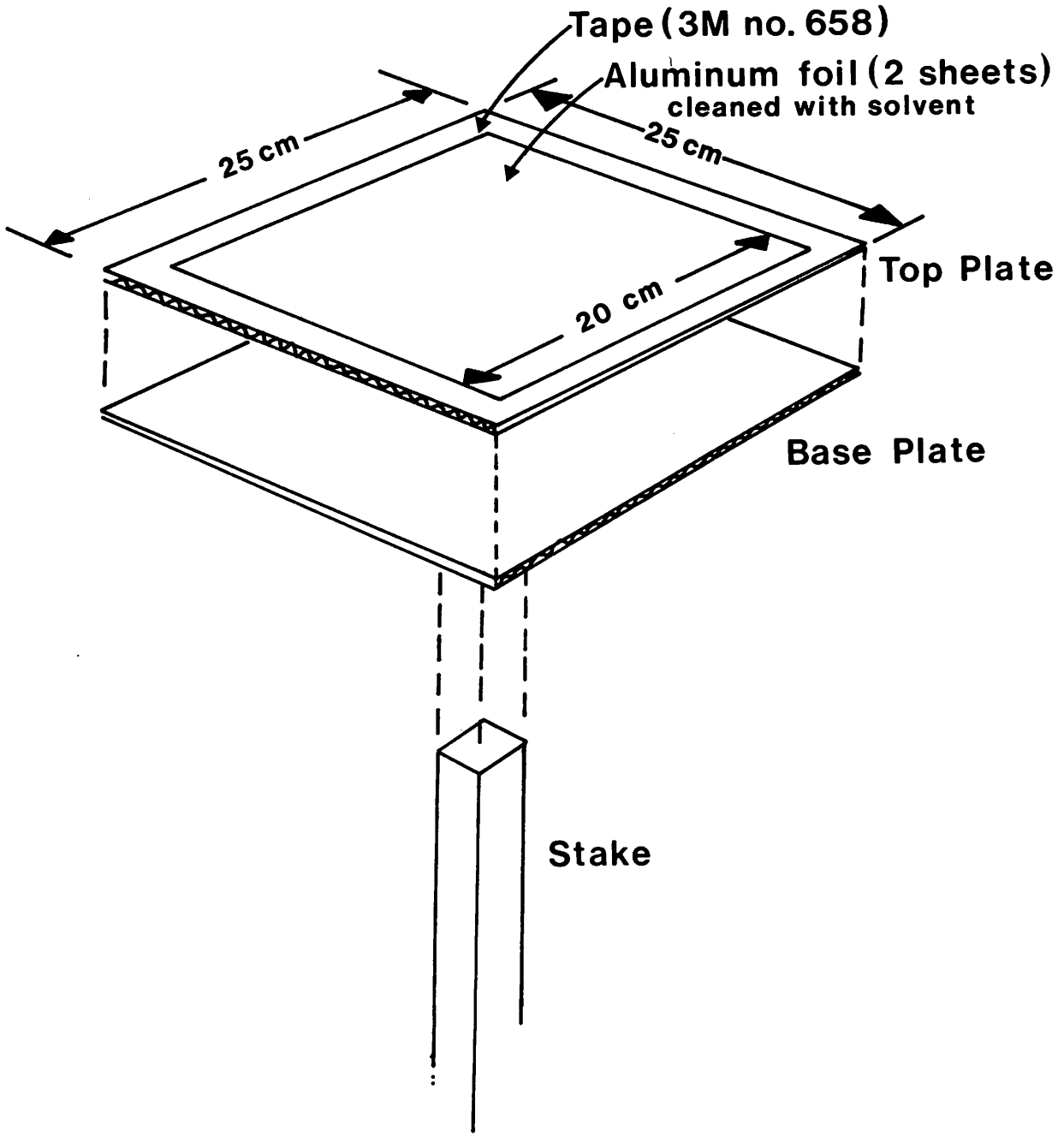
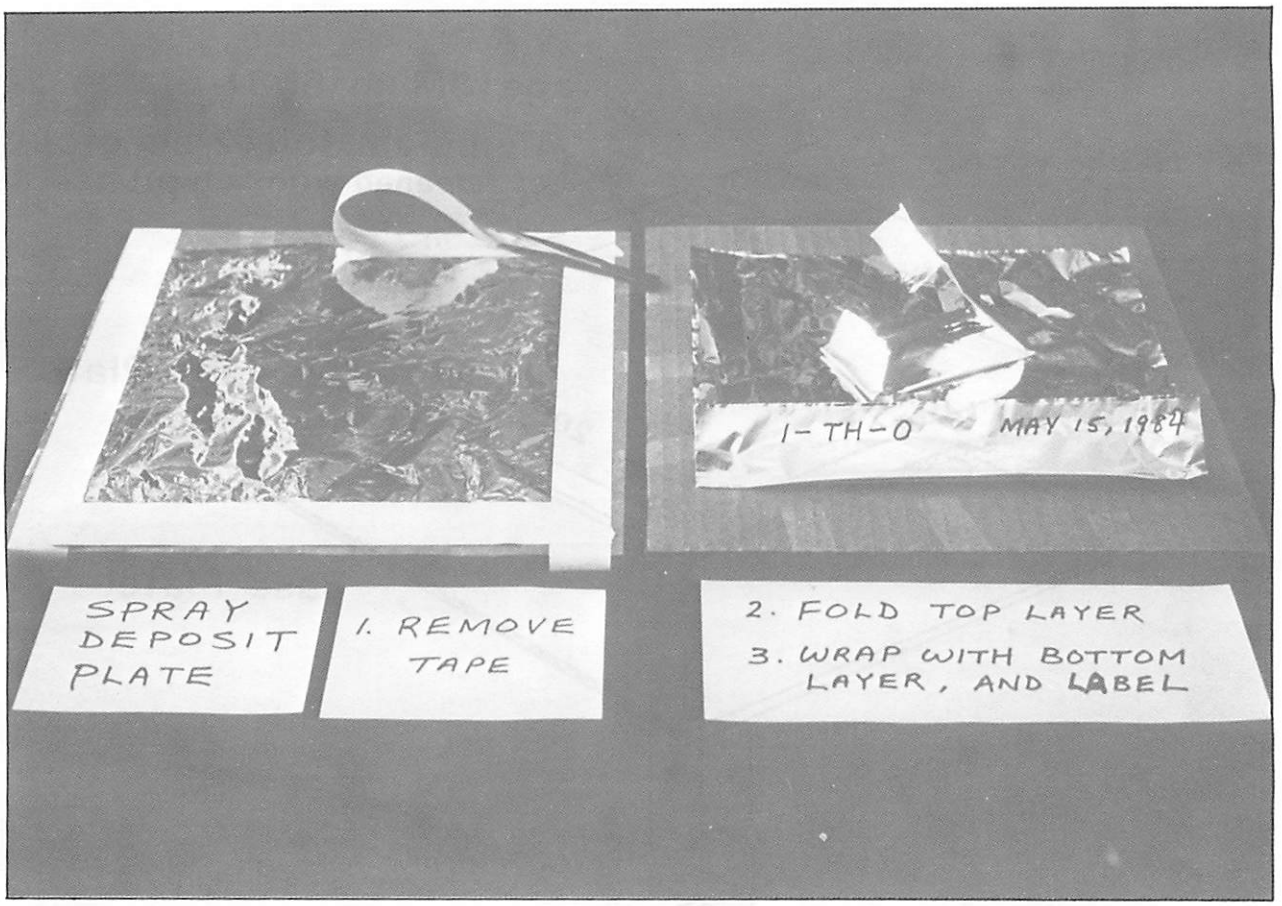


Figure 2. Packaging samples from an aluminum foil deposit collector.



relatively small droplets and a wide range of droplet spectra. Advantages to using this collector include easier storage and shipping, and a collection surface larger than the traditional 50 cm^2, which reduces variation caused by the hit or miss of the relatively smaller number of large droplets. Herbicide residues are also easily extracted from the aluminum foil sheets.

The petri-dish collectors (15 cm diameter) are designed to accommodate the extremely large droplets (> 1700 µm) generated by MICROFOIL BOOMS and THRU-VALVE BOOMs. The energy of impact of the larger droplets needs to be absorbed to prevent loss through splashing. The two layers of filter paper at the bottom of the petri-dish collectors help absorb this impact. The filter paper and walls of the petri dishes also reduce potential for deposit coalescence and runoff from collectors that are not perfectly horizontal.

Teflon sheet collectors (300 cm^2) are designed to monitor off-target drift over the greater distances required for calculation of drift pattern equations and computer modelling. These calculations may involve several variables and different types of dispersal systems. The larger surface area of the Teflon sheets and their proximity to the ground more fully represent deposition on ground or water surfaces than do other collectors. Teflon collectors are difficult to handle without cross-contamination both in the field and in the analytical laboratory, and their extractions involve large volumes of solvents. Teflon collectors are therefore recommended only for sophisticated statistical studies. Descriptions of other methods for monitoring spray drift, including foliage-shaped collectors, rotorod aerosol collectors (Payne and Feng)[3] and various types of solid and liquid impingers were beyond the scope of this manual.

Results of herbicide residue analysis from deposit collectors are calculated on a weight to area basis (µg ai/cm^2 of collector surface) and converted to kg ai/ha for reporting.

Equipment and Materials

Equipment and materials required for herbicide deposit assessment include:

1) Aluminum foil collectors (Fig. 1)

- Glass petri dishes (150 x 15 mm with covers)
- Teflon or Mylar sheet (30 x 100 cm) collectors

2) Insulated shipping boxes

3) Cooler packs, ice or dry ice

4) Meteorological instruments:

- Anemometer
- Recording thermographs at ground and 2 m heights
- Hygrometer (for humidity)
- Precipitation gauge
- Wind direction indicator

5) Whatman No. 114 Qualitative, wet strengthened filter papers (15.0 cm diameter)

6) Masking tape

7) Marking pens

8) Vinyl gloves

9) Forceps

10) Paper towels

[3] N.J. Payne and J.C. Feng. 1986. Estimating the buffer required around water during Roundup applications. Can. For. Serv., For. Pest. Manage. Inst. Information Report. Sault Ste. Marie, Ont. P6A 5M7. In preparation.

Equipment and materials required for herbicide extraction in a field lab or analytical lab include:

1) 15 cm Buchner funnel (Porcelain, Coors, Canlab Cat. No. F7300-9)

2) Aspiration apparatus

3) Vacuum Rotary Evaporator (optional - depending on type of extraction and cleanup procedure involved)

4) Glass funnel (20 cm diameter)

5) Filtering flask (size dependent on volume of washing used)

6) Teflon bottles (0.5 or 1 L) or large mouth Nalgene (Nalge 2107) bottles

7) Mechanical shaker (reciprocal type, 2-3 speeds)

8) Forceps

9) Wash bottle (500 mL, Canlab B7895-500)

10) Round bottom flask (size dependent on volume of washing used)

11) Solvents appropriate for the herbicide to be extracted

12) Vinyl disposable gloves

13) Glass stirring rods

Preparations for Deposit Collection

Aluminum foil collector assemblies consist of upper collection and lower base plates (Fig. 1). The plates can be made from corrugated cardboard 25 x 25 cm. Line the upper plate with two clean (rinsed with appropriate solvents) sheets of aluminum foil (22 x 22 cm) taped on the edges of the upper sheet, leaving an untaped collection surface of 20 x 20 cm. Tape the two plates together on two opposite corners with short pieces of masking tape after securing the basal plate to the station stake with a carpet tack.

Petri-dish collector assemblies require insertion of two filter papers in each base and cover dish (Fig. 3). The papers should be slightly larger than the inside diameter of the petri dishes and fit snugly when creased along the inside walls. Fit masking tape along the outside walls and extend over the lip of the petri plates to maintain an uncontaminated contact surface underneath the tape, essential for placing the cover dish over the base dish during shipping and storage after deposit collection. Pre-label the plates and tape together in pairs (base and cover) for transport to the site.

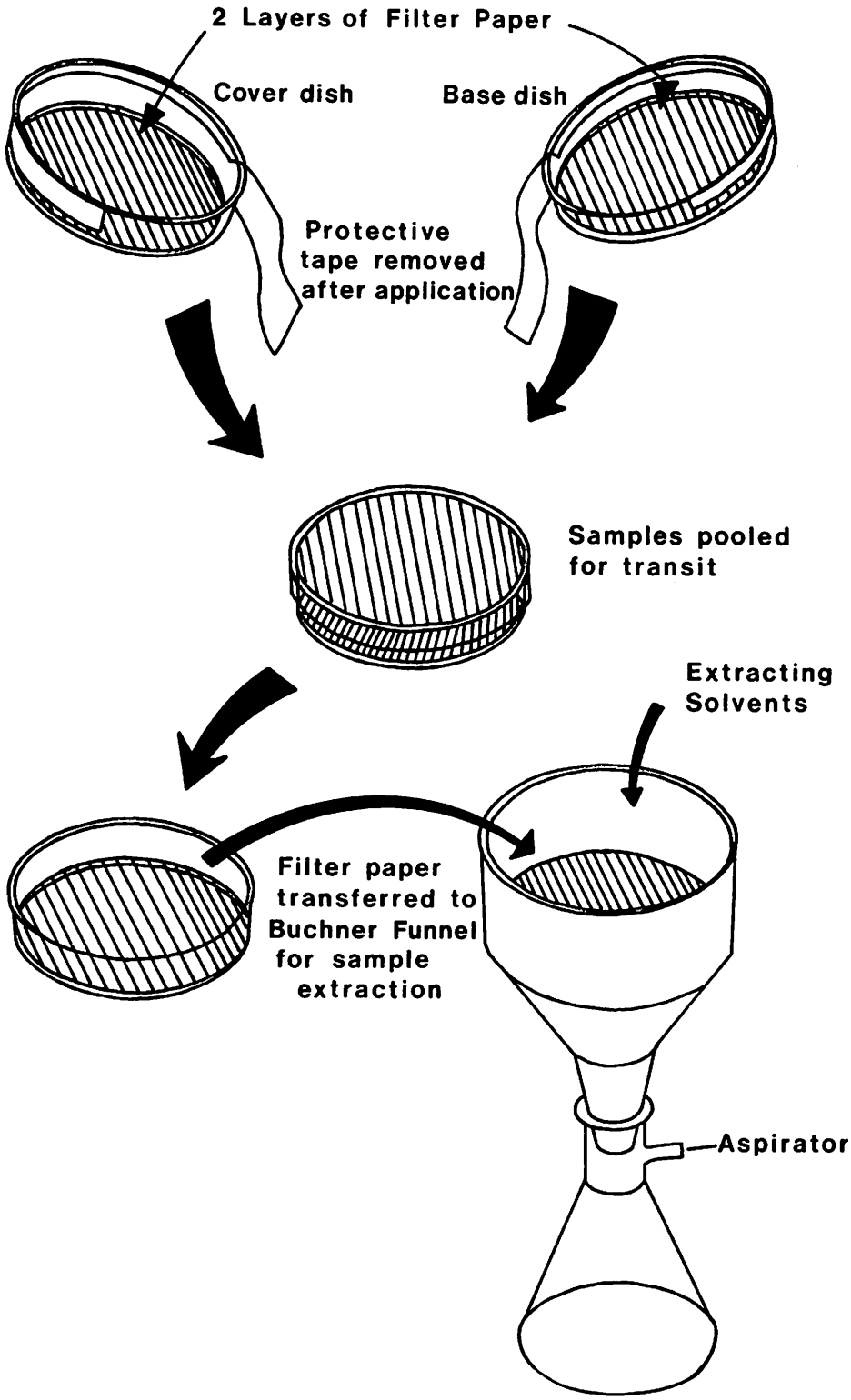
Teflon sheet deposition collectors work similarly to aluminum foil collectors and can be assembled in a similar manner but on a larger scale.

It is important to establish a meteorological station near the experimental plots. Weather conditions, including air temperature, relative humidity and wind velocity and direction at the time of application greatly affect herbicide deposition patterns. A record of these conditions enables comparison of deposit results to that from different application and areas.

Spray Deposition Collection and Packaging

Where the actual rate of aerial application of herbicide is required for specific locations, the deposit from a group of several collectors may be combined to produce an average deposition. The pooling of like samples may be required to provide sufficient amounts of residue for reliable analysis and accurate results. Pooling samples from four aluminum or petri dish collectors, or one Teflon collector per soil or other plot enables calculation of average deposition across the plots. Center the deposit collectors along the four sides of the plot away from overhead obstructions. Drive

Figure 3. Residue extraction procedure for petri-dish deposit collectors.



stakes to 25 cm above the ground for aluminum foil collectors. For Teflon or petri-dish collectors, level a small area of ground at each deposit station.

Allow herbicide deposited on aluminum foil collectors to dry (about 20-30 minutes after application) before handling. Use clean vinyl gloves and forceps for removing the tape from the surface of the collectors (Fig. 2), being careful not to contact any surface of the aluminum sheet with contaminated articles. Fold the samples on the upper sheet. Wrap the lower aluminum sheet over the folded upper sheet, and place in individually labelled plastic bags (25 x 40 cm). Place the samples in a cold container immediately after packaging.

If petri-dish collectors are used, open the dishes immediately prior to herbicide application and place horizontally on several layers of paper towels on the ground. The paper towel will help to stop spray landing outside of the depostion plates from splashing into the collectors. Collect samples immediately following application to prevent loss through volatilization. Remove the contaminated protective tape from around the outside wall to provide a clean contact surface between the cover and base plates. Prevent contamination of the freshly exposed glass surfaces by wearing clean vinyl gloves and using forceps to peel back the tape. When the tape has been removed, place the cover plate over the base plate of the same set, thus pooling the sample. The samples are ready for transport after placing them into a plastic bag and tying it closed. The shipping cases the petri dishes came in are suitable for transport to and from the field. Place samples in a cold container immediately after packaging.

Shipping and Storage

Freeze deposition samples within several hours of sample collection. Store samples below -10°C until ready for extraction to minimize chemical decompostion of the herbicide collected. To minimize sample handling, keep the samples in the shipping cases during storage. Transport samples in well-constructed commercial coolers or in insulated boxes (40 x 50 x 60 cm waxed cardboard with built-in insulation further lined with 2.5 cm styrofoam) covered with a layer of frozen cooler packs, ice or dry ice to keep samples near or below 0°C.

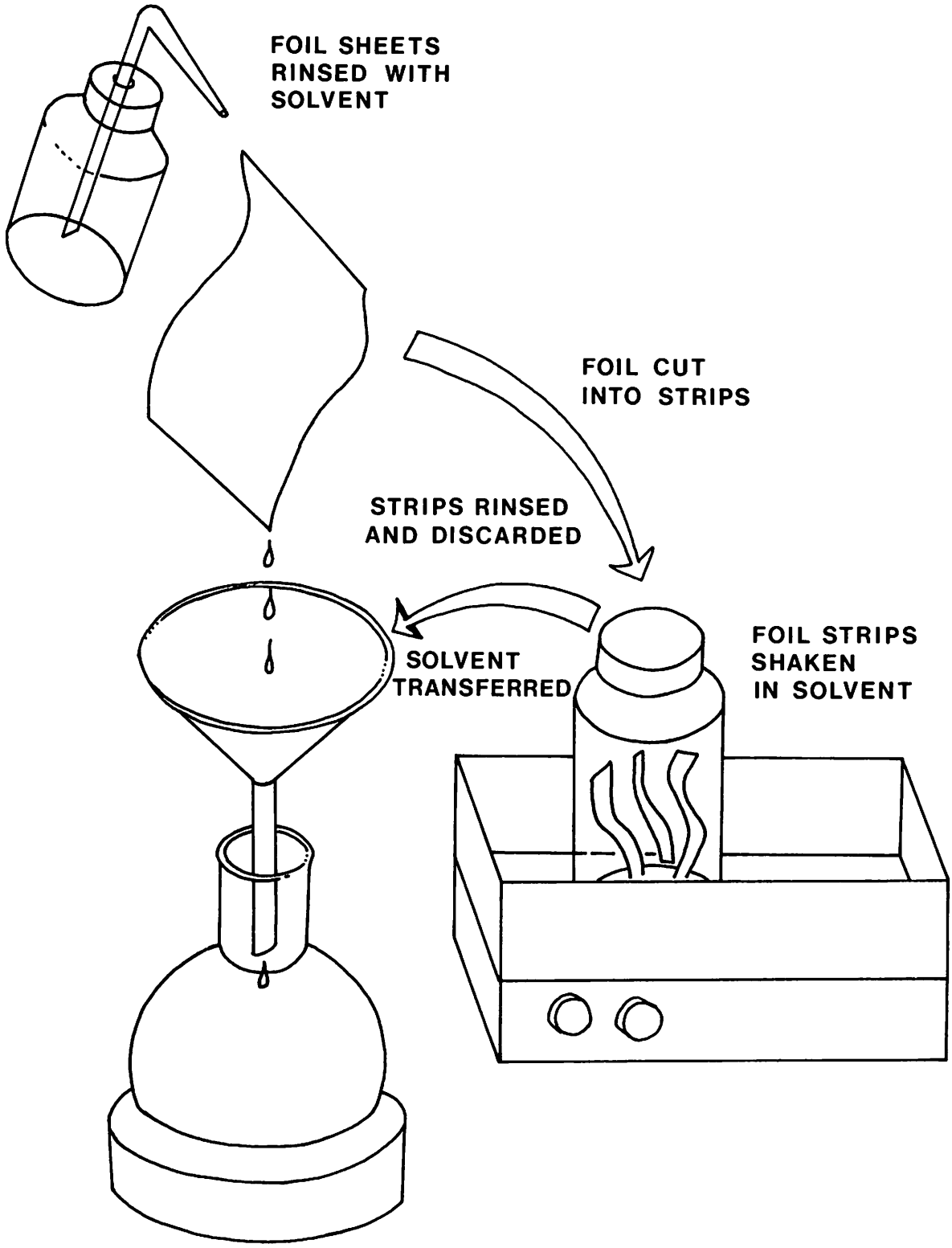
Residue degradation during sample storage should be assessed if previously undetermined. Residue degradation can be monitored by fortifying field samples so that they undergo the same schedule (freezing, shipping and storage) as the actual samples.

Sample Extraction

Deposit samples are extracted from aluminum foil collectors with multiple rinses of solvent(s) appropriate for the herbicide collected (Fig. 4). Collect the solvent through the funnel into a round bottom flask. After the initial rinsings, tear the foil into strips, using forceps and wearing clean vinyl gloves, and place the foil strips in a Teflon (or Nalgene) bottle. Use of bottles other than Teflon with pesticides other than glyphosate and hexazinone may require trials to determine that adsorption or desorption of chemicals is insignificant. Add solvent to the bottle, then sequentially sonicate and shake on a mechanical shaker for a defined length of time. Transfer extracts to the round bottom flask and repeat the extraction 2-3 times. Remove foil strips from the bottle and give them a final rinse into the round bottom flask. Either bring the extracts to a standardized volume with extracting solvents, or concentrate the deposit sample extracts with use of a vacuum rotary evaporator.

Extraction of deposit samples on petri-dish collectors involves re-inserting the filter papers from the petri-dishes into a Buchner funnel assembly (Fig. 3). Rinse the empty petri dishes with extracting solvents for the herbicide and add to the Buchner

Figure 4. Method of herbicide sample extraction from aluminum foil deposit collectors.



funnel. Extract the filter papers in the Buchner funnel several times under reduced pressure and discard. Bring the filtrate to, or concentrate to, a standardized volume ready for sample analysis. The method described above provides rapid and efficient extraction with minimum handling.

Extraction of deposit samples on Teflon sheet collectors is similar to extraction from aluminum foil collectors. Carefully cut the sheet into smaller squares before the initial rinsing, and then into strips before extracting by sonicating and shaking on a mechanical shaker.

HERBICIDE RESIDUES IN STREAMWATER

Scope

These procedures describe streamwater collection for both point samples and time-integrated samples. Methods of water sample collection, handling, shipping and storage are described.

Summary

Concentrations of herbicide residues dissolved in streamwater vary with amount of source input from overspraying, drift and runoff, the dilution effect of stream discharge, and the degree of residue degradation and re-adsorption between source and point of sampling. Repeated samplings should therefore be conducted at the same downstream locations where previous samples were collected.

While monitoring an oversprayed stream channel, frequent water samples should be integrated over short time periods (e.g., 1 hour) during the initial 6-12 hours to smooth irregularities in concentrations caused by minor pulses. Sample integration also reduces the need to analyze as many samples, thereby reducing analytical costs. For monitoring residue runoff contamination of streamwater, identify storm events by a predetermined threshold based on stream discharge and rainfall data according to the specific goals of the research project.

Results from streamwater residue analysis are reported on a weight to volume (mg/L or ppm, W/V) basis.

Equipment and Materials

Equipment and materials required for water sample collection include:

1) Graduated cylinder (200 mL)

2) Insulated shipping boxes (see page 8)

3) Cooler packs, ice or dry ice

4) Water sample bottles (1 L - Teflon or Nalge 2002)

5) Masking tape

6) Marking pens

7) Wooden stakes (4 x 4 x 120 cm)

Preparations for Streamwater Collection

Teflon or Nalgene bottles can be used for both hexazinone and glyphosate samples. There is no evidence of adsorption on the wall of these types of bottles. There is no need to acidify samples for storage. Requirements of bottle materials and acid treatment for other herbicides or pesticides should be checked before sampling. To prepare for streamwater sampling, thoroughly wash sample bottles with appropriate solvents (e.g., wash with methanol and distilled water for hexazinone and glyphosate sampling, respectively). Label bottles with experiment, location and sample identification numbers, date and time of collection, and name of operator on a strip of masking tape rather than writing directly on the bottle where labelling may rub off. Mark

sampling locations on the streambank for future reference with a stake labelled with the station number.

Streamwater Collection

Base a sampling schedule for streamwater collection on both time from application and phase within a storm hydrograph (i.e. the increase and decrease in stream discharge over time within a storm event). Sample streamwater before, and hourly after application, gradually decreasing sample frequency to daily, weekly and monthly. In addition, for long term or storm event monitoring, select a recognizable phase of a storm hydrograph with a threshold discharge that will provide an expected minimum number of storms that exceed the threshold during sampling period. Obtain discharge or rainfall records from site history reports or a local weather station. Initiate sampling on a daily, decreasing to weekly basis when this threshold discharge is achieved.

Collecting a water sample integrated over time requires filling the 1 L sample bottle with equal sample aliquots taken at regular time intervals. For example, 150 mL per 10 minute interval to produce a 900 mL per hour integrated sample. Samples collected by this method should be measured with a graduated cylinder before being added to the integrated sample bottle.

Collecting a water sample at one point in time requires filling the sample bottle with water representative of the stream at that station. However, precautions are necessary to prevent contamination of water samples. Do not allow water to pass across ones hands as it flows into the bottles. Avoid collecting water that is disturbed when entering the stream by collecting samples from upstream of where one is standing. For further discussion on sample replicates and station locations, see Pledger (no date). Depth-integrate the water samples by repeatedly raising and lowering bottles from the surface to the bottom of the water column. Once the bottle is full, pour off enough water so the surface level falls below the shoulder of the bottle (about 900 mL) so that about 10% free space is available to prevent breakage during freezing. Immediately place samples into a cold container and freeze within several hours of collection.

Shipping and Storage

Procedures for shipping and storage are similar to those described on page 8. If bottles are frozen in an upright position, they will not develop bulges in the bottom that make for awkward handling later.

HERBICIDE RESIDUES IN SUSPENDED SEDIMENTS

Scope

This procedure collects and isolates soil particles suspended in streamwater. The quantity of water filtered to obtain the sediments is used for calculations of herbicide residue per volume. Sample packaging, shipping and storage procedures are also described.

Summary

Herbicide residues that bond to soil particles may be transported via fluvial activity in bedload or suspended in the water column. Suspended sediment concentrations vary within a system, being related to stream discharge, stage condition, relative sequence of the storm in the annual cycle and possibly the rate of rise of the stream (Brown 1980). By sampling stream water at consistent stages and intervals through selected storm hydrographs, changes in herbicide residue levels transported on suspended sediments may be monitored over time. The methods described in this section are also applicable to individual spot samples, such as immediately after treatment prior to storm events, as described for streamwater sampling schedule above.

Known volumes of streamwater are filtered to isolate suspended sediments. Filtration can be done in a field lab so that only the sample on the filter paper need be shipped (frozen) to the analytical lab. The amount of residue detected in later analysis may be then related to the volume of water filtered to yield weight to volume (mg/L) or weight to weight (µg/g) values for reporting.

Equipment and Materials

Equipment and materials required to collect suspended sediment samples include:

1) 12 L plastic buckets with lids

2) 1 L graduated cylinder

3) 1 L filtering flask

4) 15 cm Buchner funnel (Porcelain, Coors, Canlab No. F7300-9)

5) Aspiration assembly

6) 500 mL beaker

7) Insulated shipping boxes (see page 8)

8) Cooler packs, ice or dry ice

9) Whatman No. 114 filters (270 or 320 mm diameter)

10) Marking pens

11) Plastic bags (25 x 40 cm)

12) Vinyl disposable gloves

Suspended Sediment Collection, Filtration and Packaging

Initiate a sampling schedule for suspended sediment collection on a recognizable phase of a storm hydrograph to permit comparison between storm events. Sampling at consistent phases or intervals within storm hydrographs (e.g., during the rising limbs of hydrographs or at x days after peak discharges) minimizes intra-storm variation in sediment load sampled. Select the initiation point for storm sampling at a critical or desired threshold discharge, such as based on storm return frequency (i.e. expected frequency of a selected stream discharge, based on past discharge records), or on a "bank-full" stage. Select an appropriate threshold discharge to provide an expected minimum number of storms to be monitored. In addition to using the threshold discharge to initiate during-storm sample collection, also use it to initiate post-storm sampling schedules.

The quantity of suspended sediments in samples is a function of the volume of water filtered. In systems where relatively large quantities of sediments are transported, smaller volumes of water may be required to yield sufficient amounts of sediment samples for herbicide residue analysis and to avoid saturating many filter papers per sample. In streams in forested watersheds, it may be necessary to filter 20 to 40 L for an adequate suspended sediment sample, based on field experience. Residue analysis requires greater than 0.1 and 0.2 µg of hexazinone and glyphosate per sample, respectively. For example, when sediment samples contain 0.1 ppm (w/w) of residue, at least 1 g and 2 g of sediments are required for their analysis, respectively.

Several precautions are necessary to collect representative suspended sediment samples. Use clean containers and lids washed in solvent, and avoid contact of their inside surfaces with contaminated articles. Avoid collecting water that passes over contaminated articles such as hands or clothing as it flows into the containers. Ensure that streambed sediments stirred into the water column when entering the stream are not sampled by collecting samples from upstream of where one is stand-

ing. Depth-integrated samples are more representative of the stream water than are samples collected only from the surface.

Filtering the sample should directly follow sampling to avoid desorbtion of residues. Fold the filter paper and fit it over the bottom of a 15 cm diameter beaker before insertion into the Buchner funnel, being careful to avoid cross-contamination. Measure the volumes of sample water before vacuum filtering them. Suspended sediments will settle as a function of particle density and time. Ensure that the sediments settled at the bottom of the collecting containers are also filtered by rinsing the containers with sample water previously filtered. After filtration, remove the loaded filter paper with forceps and allow to briefly air dry. Fold the loaded filter paper into a labelled plastic bag and tie closed. Triple-bag the samples to prevent contamination. Place the samples in a cold container immediately, and freeze within several hours of filtration to minimize decomposition of the herbicide. Aliquots of 1 L water filtrate should be collected and analyzed for cross-references if separate water samples are not collected.

Shipping and Storage

Procedures for shipping and storage are similar to those described on page 8.

HERBICIDE RESIDUES IN STREAMBED SEDIMENTS

Scope

Two procedures described permit streambed sediment sample collection in either fast or slowly flowing streams. Methods of sediment sample collection, handling, shipping and storage are described.

Summary

Herbicide residues may be transported in streams in at least three modes: 1) dissolved in water, 2) adhered to suspended sediments, and 3) adhered to bedload (i.e. larger movable particles associated with the streambed) or streambed sediments. Residues may be deposited along the stream, particularly in deposition areas where streambed sediments form bars and suspended sediments fall out of suspension. Additional residue deposition may occur where dissolved residues come into contact with and adhere to stationary sediments. Residues adsorbed onto soil particles are primarily transported during storm events and hence, sediment sample collection should be linked to storm frequency to minimize sample variability (see page 12). An appropriate sampling schedule would be similar to that for streamwater (page 11).

Two methods of sediment collection are described to accommodate sampling sediments of different consistencies. A core sampler is suitable for collecting fine sediments, as would be encountered along slower sections of a stream. For faster flowing sections of forest streams where sediments are coarser and less cohesive, direct collection into a sample bottle is more appropriate.

Values of herbicide residues associated with streambed sediments are reported on a weight to weight (µg/g) basis.

Equipment and Materials

Equipment and materials required for sampling streambed sediments include either of two sets:

Core sampler method for cohesive sediments:

1) Hand core sampler (Wildco No. 2420-G55; 5 cm diameter, 15 cm core length)

2) Insulated shipping boxes (see page 8)

3) Cooler packs, ice or dry ice

4) Liner tubes (5 cm diameter x 15 cm, Wildco)

5) Liner tube caps (15 cm diameter, Wildco)

6) Egg shell core catchers (Wildco)

7) Plastic bags (25 x 40 cm)

8) Marking pens

9) Wooden stakes (4 x 4 x 120 cm)

Open bottle method for coarser sediments:

1) Widemouth bottles (Nalge 2107, 250 mL)

2) Insulated boxes (see page 8)

3) Cooler packs, ice or dry ice

4) Masking tape

5) Marking pens

6) Wooden stakes (4 x 4 x 120 cm)

Preparations for Streambed Sediment Sampling

To prepare for streambed sediment sampling, label bottles washed in solvent with experiment, location and sample identification numbers, date and time of collection, and name of operator on strips of masking tape. Install labelled stakes at sampling locations for future reference.

Sample Collection and Packaging

Core Sampler Method

Insert a clean, pre-assembled core sampler with liner tube, caps and egg shell core catcher into the stream substrate. To extract, twist and slowly remove the assembly with the sample contained in the liner tube. Be careful to prevent cross-contamination while capping the liner tubes by avoiding sample contact with contaminated articles and by triple-bagging the sample. Immediately place samples in a cold container and freeze within several hours of collection.

Open Bottle Method

Precautions against sample contamination are necessary during streambed sediment collection with a bottle. Rinse the labelled sample bottle and cap in streamwater three times prior to sample collection. Locate deposit of fine sediments below the streamwater surface, and scoop the sediments in the bottle. Ensure that the sample sediments are not in contact with contaminated hands nor with the sediments disturbed when entering the stream. Exclude larger organic debris from the sample. Before capping the sample bottle, pour out as much water as possible. Immediately place samples in a cold container and freeze within several hours of collection.

Shipping and Storage

Procedures for shipping and storage are similar to those described on page 8.

HERBICIDE RESIDUES IN SOIL

Scope

These procedures describe soil site selection, pre-sampling preparations, sample collection and recording procedures, sample packaging, storage, shipping, and pre-analysis sample preparation. An improved method for residue reporting is also described.

Summary

A study design for assessing herbicide residues in soil should ensure that samples collected are representative of the treated area. Although outlining study designs for statistical representation was beyond the scope of this manual, guidelines for selection of appropriate sampling schedules, sampling equipment and plot locations are provided to achieve proper representation. Maintaining representation of the samples by preventing cross-contamination and residue degradation is also necessary. Cross-contamination between soil samples is mini-

mized by the sampling and packaging techniques described in this section. Minimizing degradation of herbicide residues in samples during shipping and storage is also discussed.

After samples have been analyzed, calculating the residue values so that they are representative of the treated area is necessary for comparison between samples or studies. By calculating the sample bulk densities from the known areas, depths and total weights of soil samples, a correction factor may be applied to analytical data in a weight to weight (µg/g) format, converting values to an area basis (kg/ha), which provides consistent residue reporting between horizons, soil types and regions. Vertical subsampling described in this section is designed to accommodate soil horizons and their different bulk densities.

Equipment and Materials

Equipment and materials required for soil sampling include:

1) Campbell soil auger (reinforced steel; see Fig. 6)
2) Box auger (steel; see Fig. 7)
3) Sledge hammer (1 kg or 5 kg)
4) Scoops for box auger
5) Shovel
6) Water container (20 L)
7) Packsack
8) Trowel, customized with rounded tip (4.5 cm radius)
9) Ruler
10) Scissors
11) Scalpel
12) Wash bottle (500 mL, Canlab No. B7895-500)
13) 3 Paint brushes (2.5 cm wide)
14) 2 Scrub brushes (5 x 15 cm)
15) Calculator (optional)
16) Flathead screwdriver
17) Work table (0.5 x 1 m minimum)
18) Forceps
19) Rinse water (about 2 L per sample)
20) Kraft paper towels (about 30 per sample)
21) Aluminum foil (pre-cut to 15 x 30 cm)
22) Masking tape
23) Marking pens
24) Plastic bags: 25 x 40 cm (15 pre-labelled per sample station)
    36 x 53 cm (one per core)
25) Cloth residue bags (34 x 60 cm; one per core)
26) Data sheets
27) Plastic sheets to cover work table (e.g. opened garbage bags)
28) Vinyl disposable gloves
29) Wooden stakes (4 x 4 x 120 cm)

Equipment and materials required for storage and transport include:

1) Freezing facilities
2) Insulated shipping boxes (see page 8)
3) Cooler packs, ice or dry ice

Equipment and materials required for pre-analysis preparation include:

1) Drying room (darkened with minimum temp. about 15°C)

2) Dehumidifier (Viking Model 30271)

3) Shelves in drying room

4) Drying trays (about 35 x 50 x 1 cm)

5) Scale (3 kg accurate to 1 g)

6) Commercial blender: base (Waring no. S-61643-50)
containers (Waring 1 L and 4 L heavy duty stainless)

7) Blending room with fume hood

8) Protective ear muffs

9) Apparatus washing facilities

10) Sieves (Tyler no. 10; 2.00 mm)

11) Spatulas (various sizes)

12) Aluminum foil

13) Marking pens

14) Vinyl disposable gloves

15) Plastic bags (36 x 57 cm; heavy duty)

16) Breathing masks (SAK-102, non woven)

17) Acetone or other solvents for cleaning and drying

Preparation for Soil Sampling

Experimental design can only be completed after a reconnaissance of the area. Several factors must be considered in selecting soil sampling plots. Plots for persistence and vertical leaching studies should be relatively flat to minimize overland runoff and subsequent residue movement. Soil plots should be located away from the edges of the treatment blocks. The plots should be of sufficient size to permit sampling more than the required number of replicates (e.g., roughly 16 m^2 for a 2-year study). The soil profile should not be disturbed to a greater degree than occurs in commercial silvicultural practice (Pesticides Division, EPS 1985) to represent typical conditions. Soil profiles where rocks and large gravel are frequently encountered should be avoided to minimize bias in analysis introduced through the loss of residues adsorbed to unprocessable rocks, and variation in recoverable amounts of soil particles (less than 2 mm diameter). Soil auger life expectancy and ease of sampling are greater if these rocky areas are avoided. Ease of access should be considered in selecting a site, taking into consideration the proposed frequency of sampling.

The number of plots and replicate stations per plot to adequately represent a treated area also need to be selected. The number of samples required will vary with the nature of the study and the variation in forest floor composition. Different experimental designs have been discussed in detail by Pledger (no date) and Pesticides Division, EPS (1985). If the soils are sufficiently uniform to assume that soils are spatially homogeneous within a plot, one sample at each of three or more plots per sampling may be adequate to represent a treated area. Appropriate sampling depths are necessary to achieve representation of the treated area. Select a lower core subdivision below the maximum depth of residue leaching expected for the herbicide in the soil type encountered. An appropriate sample schedule includes pre-treatment, zero-time, and post-treatment samples on a daily basis, gradually decreasing in sample frequency to weekly, monthly and annually. A rigorous study may include 20 scheduled samplings in its first year. Determination of the persistence of hexazinone in clay soils may require a 3-year or 4 growing-

season study. However, for glyphosate and hexazinone in sandy soils, determination may require 2-3 growing seasons.

Simulating a "worst-case scenario" under local operational conditions, has been the objective of pesticide registration and many experimental designs. To achieve the worst case for herbicide impact on soils from forestry aerial spraying, direct application of the maximum allowable rate on the exposed forest floor is desired. Exposing the forest floor also provides a more uniform application than if standing vegetation were available to partially intercept the herbicide. To expose the forest floor, remove all understory and overstory vegetation using chainsaws, brushsaws, hedge clippers and hand rakes as required. Do not disturb the soil profile during clearing. Trim vegetation within the sampling plots down to below 1 cm and remove large debris and slash (Fig. 5). Clear vegetation from around the soil plots to prevent spray interception and to provide access to all sides of the plots. In areas under a high canopy, the width of canopy opening should be three or more times the canopy height to minimize the vortex effect during aerial application and to provide uniform treatment across the soil plot.

Once the plot has been cleared, use corner posts to mark sampling plot boundaries and identify the plots for future reference. For a 2-year residue study, plot sizes of 3 x 3 m or 4 x 4 m are adequate. To discourage inadvertent movement of herbicide onto the plots from human foot traffic or that of large animals such as deer or bears, hang removable fence rails from the corner posts (Fig. 5) and hang flagging from the rails to improve their effectiveness.

When the goal of a study is to verify the herbicide input to the forest floor through initial penetration and subsequent leaf fall, and its persistence in soils under a "real-life scenario" in a forest area occupied by a high tree canopy of weed species, leave the overstory canopy intact and clear only the lower growth and understory vegetation. Use tree stems for marking plot boundaries or for supporting removable fence rails.

Assessment of herbicide deposition rate at the soil sample plots provides actual baseline application rates for later soil analyses. It is more appropriate to use this actual application rate than to use the less accurate nominal application rate, as estimated from concentration of active ingredient (ai) in the tank mix, operational calibration of the dispersal system, aircraft speed and elevation, and swath overlap. In order to accurately assess deposition, designate four areas for deposition collectors centered along the edges of the soil plots (Fig. 5). Just prior to herbicide application, remove the fence rails and lay out the deposition collectors as described in the section on spray deposition collection and packaging on page 6.

Pre-treatment samples (or those from controls) are required for the background contamination analysis and spike-recovery tests for analytical procedures involved. Zero-time samples are crucial for evaluation of all subsequent samples (Pesticides Division, EPS 1985). Early analysis of zero-time soil samples and/or spray deposition is required to confirm that the plots were treated and that further sampling is warranted.

A great variety of soil sampling techniques have been developed, largely for agricultural pesticide studies (Coile 1936; Cline 1945; Hormann et al. 1974; Wilson and Lavy 1975; Bannink et al. 1977; Apperson et al. 1980; Sieczka et al. 1982; Rother and Millbank 1983; Pledger no date). Two techniques recently developed for sampling forest soils are discussed in this section. The types of soil encountered in soil plots largely determines which of the two sampling methods is most suitable. If the soils are deeper than 40 cm and if rocks and large gravel are infrequent, the most appropriate

sampling method is with the Campbell soil auger (Fig. 6). Conversely, if the soils are shallow or are very high in gravel content, a box auger (Fig. 7) should be used. The box auger should also be used in studies where residue distribution over depth is not the concern, such as in monitoring the off-site movement of residues in runoff.

Prior to soil sampling, several preparations are required:

1) Pre-label soil sample bags (three per subsample), indicating date, location, nominal herbicide rate and date applied, sample number and name of the person responsible for sampling (Table 1). Large bags designed to contain all subsamples of one soil core should also indicate which subsamples are enclosed.

2) If the Campbell soil auger is to be used, cut aluminum foil into 15 x 40 cm strips. The foil is used for covering the contaminated outer surface of the Campbell soil auger.

3) Draft data sheets with columns for sample numbers and depths encountered (Table 2, 3).

4) If using the Campbell soil auger, mark it at the depths desired for subdividing the soil core (e.g., corresponding to 0, 5, 15, 30 and 35 cm from the ground surface when the auger is inserted 40 cm)

5) Thoroughly clean all equipment and tools in contact with the samples from any contamination, including the soil sampler, scissors, scalpel and forceps.

6) Pack all equipment and materials listed in the preceding sections in a suitable container for transport (e.g., packsack).

Soil Collection and Packaging Using a Campbell Soil Auger

The main design of the following procedure is to provide data required to calculate the weight to volume ratio or sample bulk density of each subsample, and to package the samples without any contamination from adjacent samples or from outside sources. The importance of providing weight to volume ratios or bulk density values of soil samples lies in residue accountability calculations, described further on page 31.

Begin sampling at the edge of the soil plots and work in towards treated but undisturbed areas at the plot centers. Maintain a maximum reserve of undisturbed sampling area by restraining foot traffic within the plot. However, it is best to space samples more than 40 cm apart to minimize the effect of precipitation entering holes of previous samples in influencing residue infiltration patterns. Fill sample holes with uncontaminated or pesticide-free soils wherever it is possible to maintain a supply of these soils near the sampling plots.

In auger insertion, steady the auger by bracing it with a stick jammed behind a handle (Fig. 8). Drive the auger in with a 5 kg sledge hammer until the top mark (0 cm depth line) on the auger reaches the ground surface. Extract the auger by twisting and pulling. When the soils are either very dry and loose, or very wet and cohesive (e.g., swampy areas), dig an auxiliary hole adjacent to the auger before extracting the auger and soil core. In these areas, the soil core may fall or be sucked out of the auger as it is extracted. An auxiliary hole, dug deep enough to allow the auger to be tilted and a cover or hand to be placed over the bottom, will aid in retaining soils. In very cohesive soils, slicing the soils across the bottom of the auger with a shovel

Fig. 5. Plot for residue collection in soils.

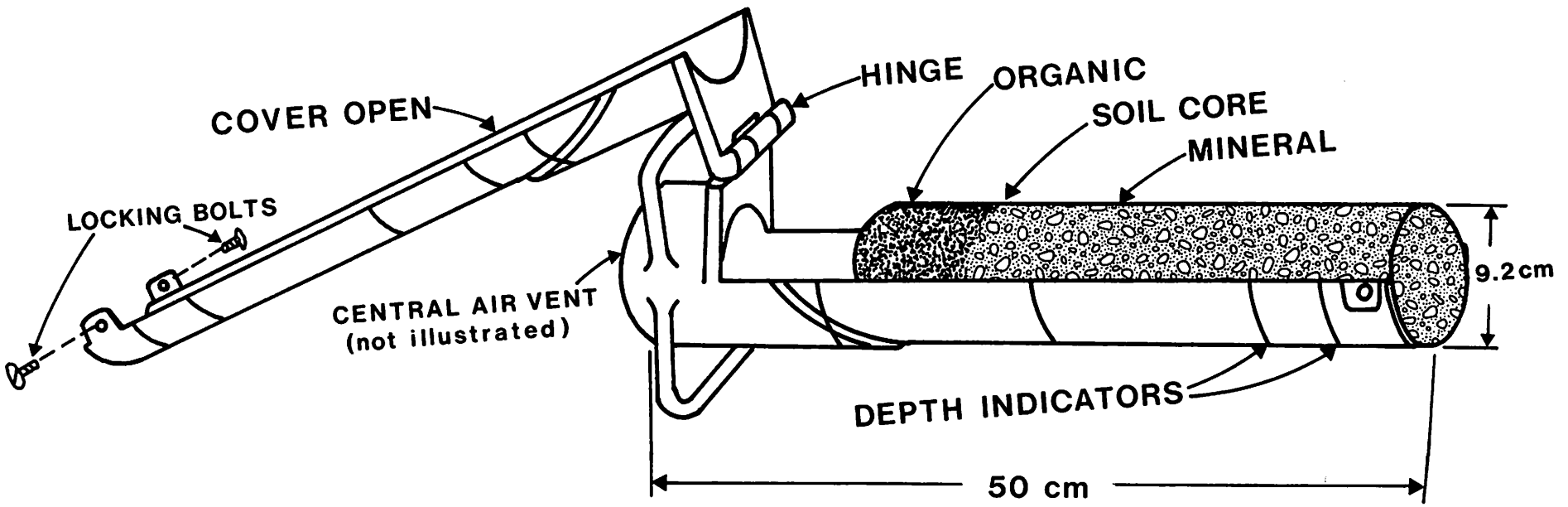


Fig. 6. The Campbell soil auger.

Fig. 7. The box auger.

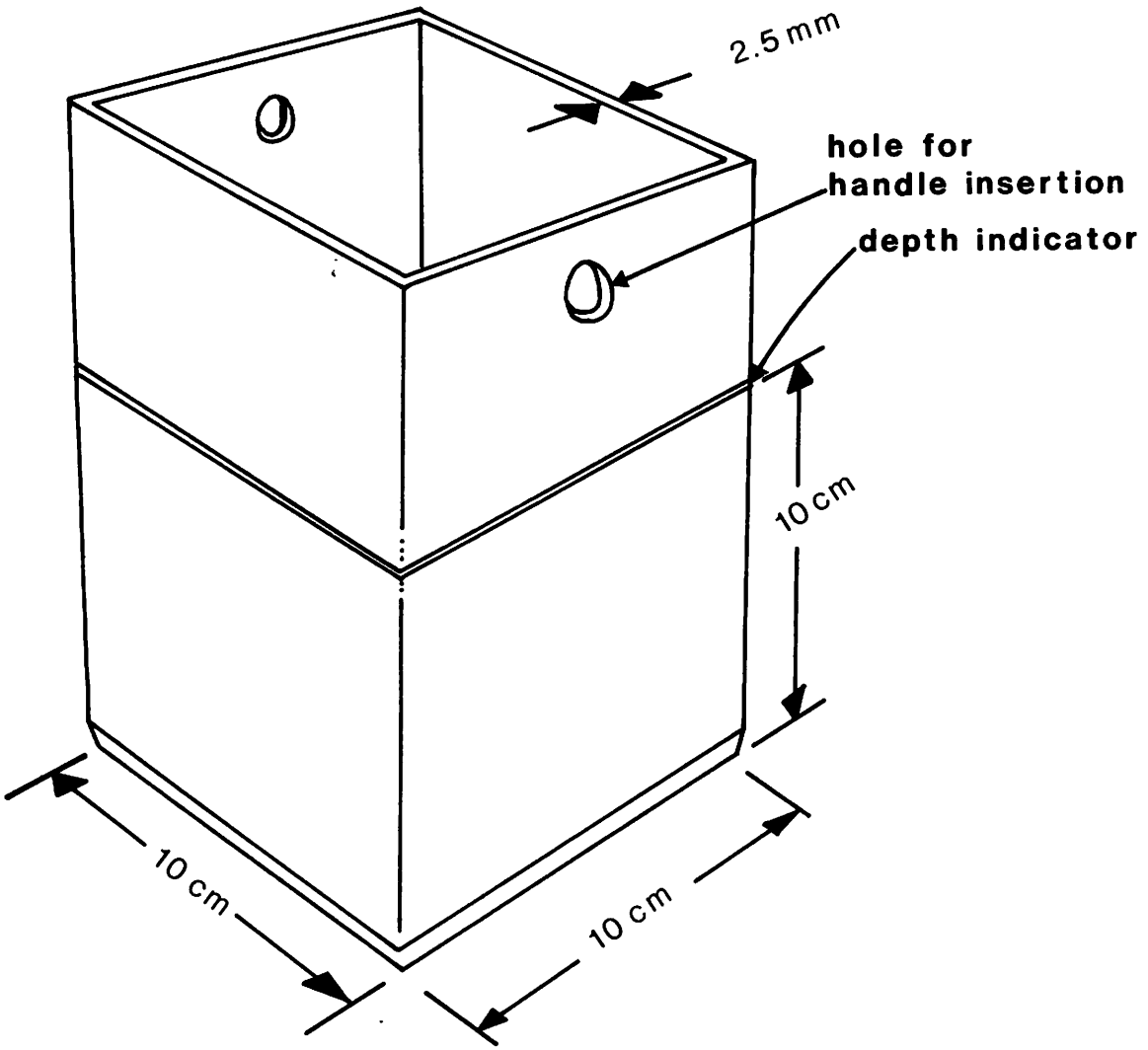


Table 1. Sample bag labelling for herbicide residues in soils

Location: _____

Herbicide: _____

Rate of Application: _____

Sample Number: _____

Date: _____

Names of Samplers: _____

Table 2. Data sheet for soil residue sampling where organic and mineral horizons are to be kept separate

Herbicide: _____

Sample date: _____

Time of sampling: _____

Sample number: _____

Location: _____

Names of samplers: _____

Sample Code*	Horizon	Compacted Thickness (cm)	Corresponding Initial Thickness (cm)
1-05H-1	humus		
1-05M-1	mineral		
1-15H-1	humus		
1-15M-1	mineral		
1-30H-1	humus		
1-30M-1	mineral		
1-35H-1	humus		
1-35M-1	mineral		
2-05H-1	humus		
2-05M-1	mineral		
2-15H-1	humus		
2-15M-1	mineral		
2-30H-1	humus		
2-30M-1	mineral		
2-35H-1	humus		
2-35M-1	mineral		

* Where the first digit of the code represents the station number, the second series indicates the depth and horizon type, and the third series indicates the time of sample (in this case, 1 represents the first sample after treatment).

Table 3. Data sheet for soil residue sampling where organic and mineral samples need not be kept separate

Herbicide: _____

Sample date: _____

Time of sampling: _____

Sample number: _____

Location: _____

Names of samplers: _____

Sample Code*	Compacted Thickness (cm)	Corresponding Initial Thickness (cm)
1-05-1		
1-15-1		
1-30-1		
1-35-1		
2-05-1		
2-15-1		
2-30-1		
2-35-1		
3-05-1		
3-15-1		
3-30-1		
3-35-1		

* Where the first digit of the sample code represents the plot number, the second series indicate the depth of the sample, and the third indicate the time of sampling (in this case 1 represents the first sampling after treatment).

Fig. 8. Inserting a Campbell soil auger.

prior to extraction prevents loss of the soil core due to suction. In all soil types, extraction is facilitated by initially twisting the auger.

The next step is designed to present a clean auger surface to the sample bags and minimize any possible contamination. Clean the outside of the auger with a stiff brush and paper towel. Remove the bolts locking the two halves of the sampling cylinder together. Tape on the aluminum foil, covering the contaminated outside of the basal half of the sample cylinder (Fig. 9). Transpose the desired depth division lines (i.e., 0, 5, 15, 30 and 35 cm) onto the tapes. Ensure that the foil and tape do not become contaminated by moving the auger to a clean portion of the plastic-covered work table (i.e., the tailgate of a pickup truck or a work bench adjacent to the sampling plot).

After prying open the auger with a screwdriver, measure soil compaction and calculate where to subdivide the soil core. The soil core is divided to correspond to the selected depths originally encountered for that sample. If the soil core top is at the 0 cm depth line, i.e., to where the auger was driven into the ground, there was no compaction and the division lines on the tape are appropriate sample divisions. If the top of the soil core lies below the 0 cm depth line, either the core has slipped out of the auger on extraction, usually observed only in wet soils or occasionally in very dry and loose soils, or there was soil compaction, usually observed when there is a thick organic layer or high gravel content in the core. If the core has slipped, discard the sample, clean the auger and repeat the above procedures. Experience gained through sampling approximately 1000 times with the Campbell soil auger suggests that compaction is not likely to occur in mineral soils (sands, silts and clays). Compaction is observed in humus, duff, cores of high gravel content (> 50% in volume) and in swampy wet soils. Humus and duff generally account for compaction in normal forested areas. However, several trial samples should be taken prior to the experimental samples on or near the sampling site to confirm the pattern of compaction of different soil horizons. If the humus layer present is too thin to account for distance of compaction (i.e., <100% of the distance of compaction), then the soil core has probably slipped on auger extraction. To calculate a correction factor to account for compaction, first measure the actual distance from the top to the bottom of the compacted humus layer and mark it on the tape alongside the soil core. Second, divide this distance by the distance from the 0 cm line on the auger to the bottom of the humus layer (i.e., the depth of the humus layer before compaction). Multiply the desired sample depths of humus (i.e., the top 5 cm, next 10 cm, next 15 cm and etc.) by the dividend and mark on the tape, starting at the soil core surface. Apply this correction factor only to the humus layers and not to the mineral layers. Below the humus/mineral interface, use the marks previously indicated to divide samples. If the humus/mineral interface lies at other than a previously indicated sample division mark, two subsamples will be required for that desired depth category if the organic layers are to be separated from mineral layers.

Example:

The desired sample division depths for this example are: 5, 15, 30 and 35 cm (Fig. 10). Humus samples are to be kept separate from mineral samples. The humus/mineral interface is encountered at the 25 cm level. The soil core surface is at 10 cm, therefore the humus layer was 25 cm before compaction but now is 15 cm thick.

1) 15 cm / 25 cm = 0.6

2) multiply: 0.6 x 5 cm = 3.0 cm from the core surface is the top division, accounting for 5.0 cm of original thickness.

Fig. 9. Aluminum foil protection on the base of a Campbell soil auger.

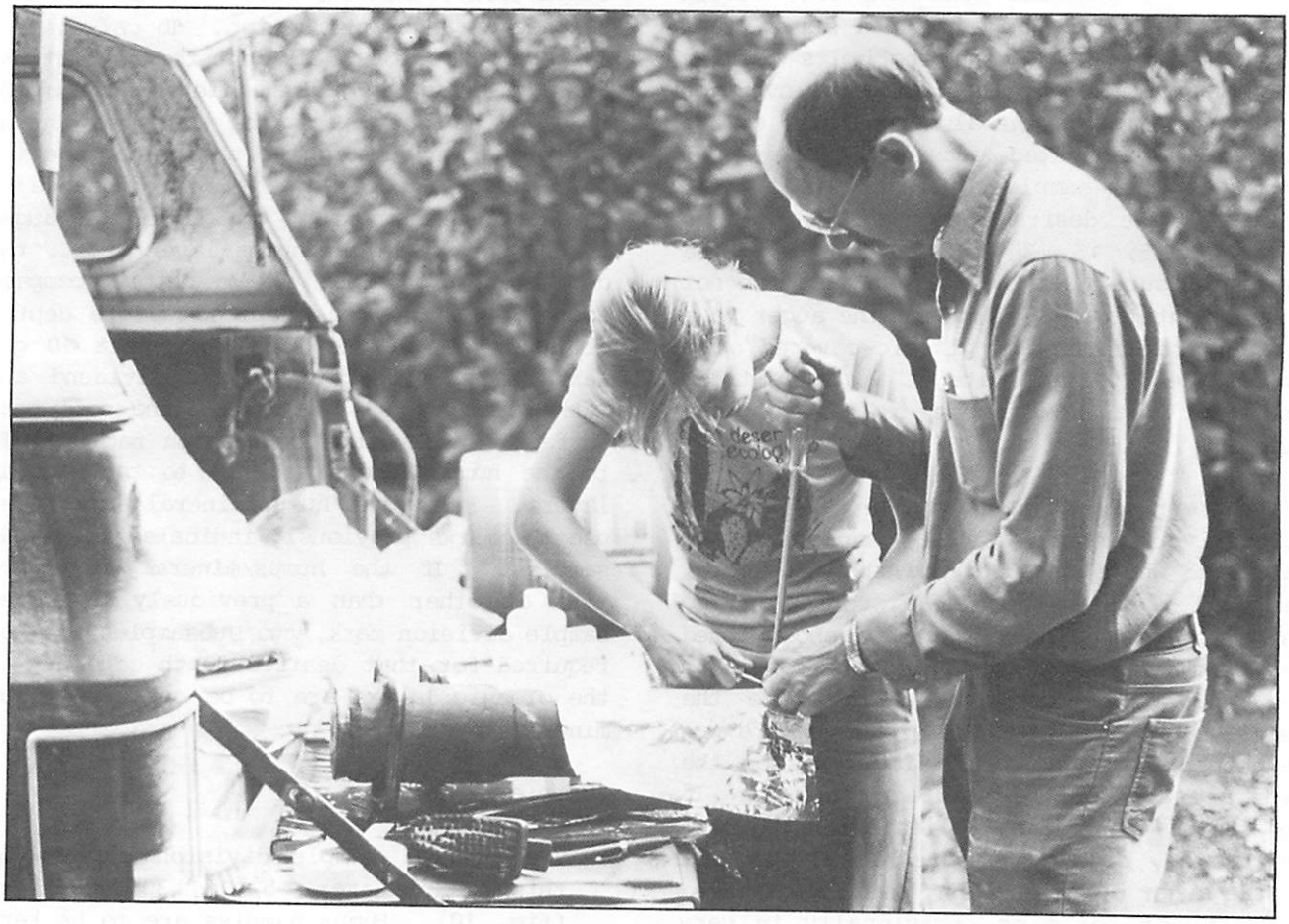
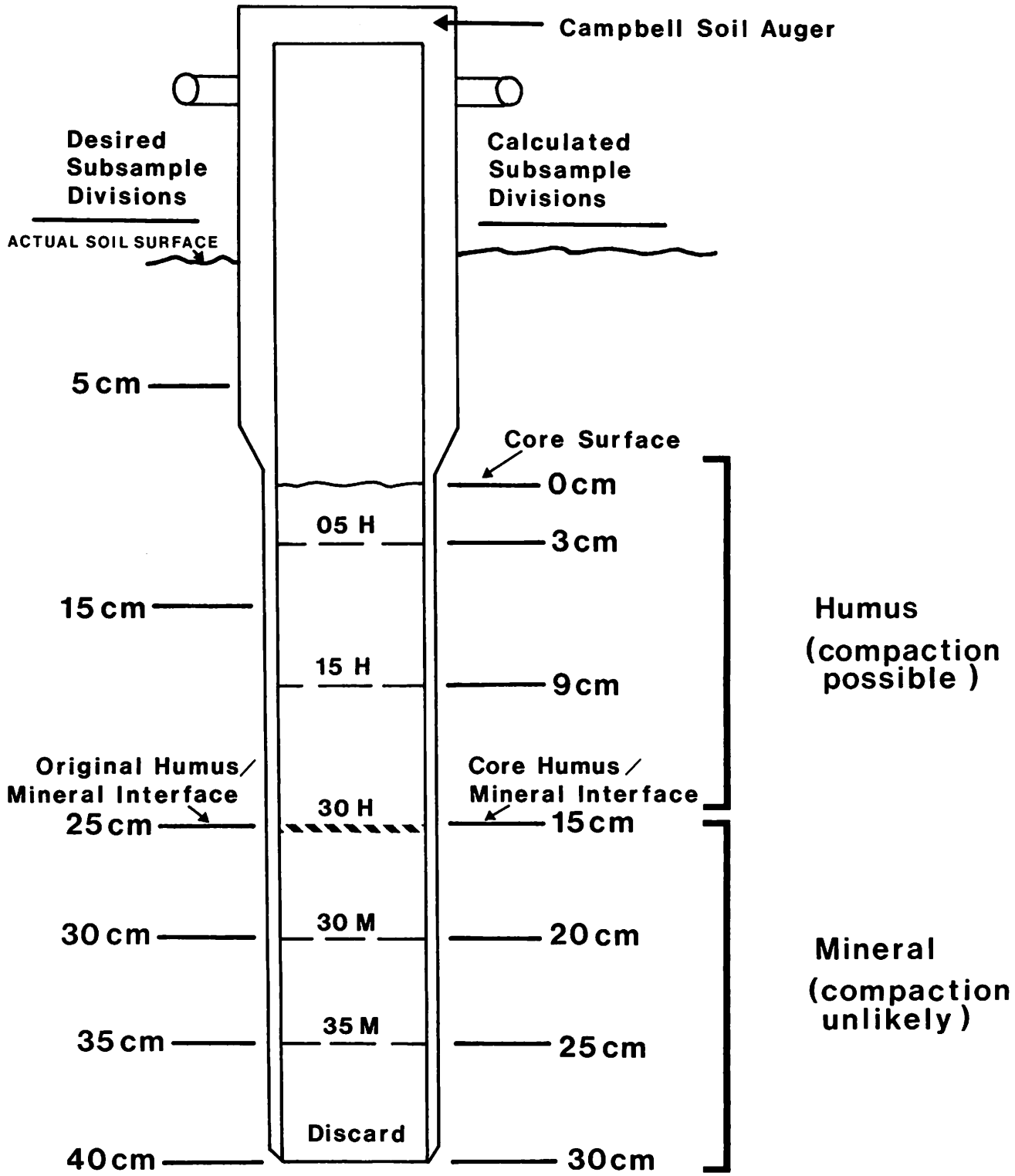


Fig. 10. Sample divisions of a soil core collected with a Campbell soil auger.



0.6 x 15 cm = 9.0 cm; second division from the core surface.
0.6 x 25 cm = 15 cm; third division from the core surface.

This last division should correspond to the original humus/mineral interface. The fourth and fifth sample divisions are the original 30 and 35 cm lines previously marked on the auger. Table 4 illustrates proper data recording for this example.

Subdivide the soil core by first transposing the division marks from the tape to the core itself. These reference marks on the core are useful should the core slide during cutting and dividing operations. Using a trowel and other cutting tools as necessary, cut and discard the bottom 5 cm protective layer; it has been contaminated as the auger passed through soil closer to the surface having, theoretically, higher residue concentrations. The trowel may now be contaminated and should be cleaned before re-use. An assistant with clean vinyl gloves slides an appropriately labelled sample bag over the end of the auger and holds it to receive the first sample. With the present sophisticated means of detecting residues in trace quantities, it is paramount that no contaminated objects enter or even touch the inside of the sample bags. Use the trowel to cut and slide the sample into the bag (Fig. 11). If a portion of the intended sample falls onto the clean surface of the work table, or remains inside the auger, use a clean paint brush to sweep the soil into the bag. Use a separate properly labelled brush for each layer to be collected. Carefully add portions of the sample that adhered onto the cover half of the sampling cylinder to the appropriate sample. Squeezing the sample bag to remove air before tying it closed decreases the risk of puncture and facilitates handling. Triple-bag the samples for added protection. Repeat the slicing and packaging process for the designated number of sample layers while maintaining uncontaminated equipment for each layer. Group all separately bagged samples from one core together as a set in an appropriately labelled bag. Place sets of related core samples in cloth residue bags for further protection.

Table 4. Soil thickness data accounting for soil compaction from insertion of a Campbell soil auger

Sample Code*	Horizon	Compacted Thickness (cm)	Corresponding Initial Thickness (cm)
1-05H-1	humus	3.0	5.0
1-05M-1	mineral	---	---
1-15H-1	humus	6.0	10.0
1-15M-1	mineral	---	---
1-30H-1	humus	6.0	10.0
1-30M-1	mineral	5.0	5.0
1-35H-1	humus	---	---
1-35M-1	mineral	5.0	5.0

* Where the first digit of the code represents the station number, the second series indicates the depth and horizon type, and the third series indicates the time of sample (in this case, 1 represents the first sample after treatment).

Fig. 11. Subdividing a core from a Campbell soil auger.

Soil Collection and Packaging using a Box Auger

Use the box auger where the Campbell soil auger is not appropriate (page 18). Follow the sampling schedule described for the Campbell soil auger on page 16. Insertion of a box auger (designed for 5 or 10 cm depth sampling) requires a driving force supplied by a hand sledge hammer transmitted through a 2 cm thick plywood capping that rests on top of the auger. Insert the auger to the depth indicated on the side of the auger. Use a shovel to dig an access hole (30 cm wide) along two or three sides of the auger. Use a flat trowel (wider than the auger base) to slice off the soil column across the bottom of the auger. If the trowel cannot be worked through the soil column, clean and re-insert the auger elsewhere.

Lift the auger and soil core using the trowel and empty the contents into a prelabelled plastic bag. Triple-bag the samples to prevent cross-contamination. Teflon- or vinyl-lined soil bags are useful to transport sets of samples.

Shipping and Storage

Immediately chill samples and freeze within several hours of sample collection to minimize microbial, chemical, photolytic and hydrolytic decomposition of herbicide residues. This requirement precludes shipping unfrozen samples long distances directly from the field. Start cooling as soon as possible by covering samples with frozen cooler packs or ice inside insulated containers. This configuration is recommended for transport to nearby freezing facilities. Samples should be kept frozen for prolonged storage or long distance shipping. Residue degradation can be monitored by fortifying field samples on site, if it is feasible, so that they undergo the same schedule (freezing, shipping and storage) as the actual samples.

Long distance transport, including overnight air freight, is possible without the samples thawing if precautions are taken. Well-constructed commercial coolers or insulated boxes further lined with 2.5 cm styrofoam have been sufficient in keeping samples frozen for 1-2 days, depending on the seasonal temperature. However, it is important that the samples start out well frozen. A layer of frozen cooler packs, ice or dry ice, covering the samples helps keep the temperatures near 0°C.

Pre-Analysis Sample Preparation

Processing soil samples prior to analysis is required for representative subsampling. Unprocessed samples may have a total weight as high as 2 kg whereas residue analysis only requires 10-50 g of soil. However, it is essential to homogenize the field samples before subsampling. It is difficult to prepare a homogenous fresh sample, especially when the moisture content is high or variable. Therefore, air drying before blending is recommended whenever possible. Owing to possible residue losses of some herbicides by decomposition or volatilization, it is very important to ensure through spiked trials that there is no loss or consistently low loss of the herbicide through air drying. An insulated dark room or chamber with a dehumidifying system on maximum should be maintained at room temperature (20°C) for relatively fast (2-4 days) drying to a moisture level of approximately 5 %. It is important to exclude sunlight from the drying room to prevent photolytic decomposition of the residues. Subsequent blending and sieving will provide fine particles or powder which can be mixed thoroughly for controllable subsampling.

Organization is the key to processing samples efficiently. The procedures for air drying and subsequent processing are described as follows:

1) Label data sheets (Table 5), drying trays and sample bags with a unified coding system

designed to facilitate efficient sample handling.

2) Line the drying trays with clean aluminum foil ahead of time to speed the actual sample handling.

3) Weigh the frozen samples in the bags and spread on the trays to dry.

4) Subtract the weight of the bags to yield the total fresh weight of the samples.

5) Crumble the samples into fine pieces after they have thawed and partially dried (after about 12 hours in the drying room) to facilitate subsequent homogenization.

6) Once dry, transfer all samples into prelabelled sample bags and weigh.

7) The bag weight subtracted from this yields the gross dry weight of the samples.

8) Remove rocks from the samples, scrape them clean of soil particles and place in separate discard containers for later weighing. The surface areas of rocks contributing to the adsorption of herbicide residues in soils is negligible relative to that of the smaller soil particles (Table 6).

9) Use a heavy duty stainless steel Waring Blender to pulverize air dried soils.

10) Sift the blended soils through a 2.00 mm mesh sieve with a cover and collection pan. The 2 mm mesh was selected to correspond with the maximum particle diameters defined for mineral soil (Table 6).

11) Repeat the process of blending (2 minutes) the portion of sample retained in the sieve, and sieving. Use a spatula for breaking up clumps of soil missed by the blender blade.

12) When no breakable clumps are retained by the sieve, transfer the soil samples from the collection pans into prelabelled sample bags and transfer the retained gravel to the appropriate discard containers.

13) Weigh gravel and rocks collected in the discard containers and subtract the weights from the gross dry weights to yield the net air-dried weights of each sample.

14) Wash the sieve assemblies and blender containers sequentially in appropriate solvents and water between samples.

Pre-analysis preparation in a properly equipped field lab is recommended when long-distance or delayed shipping to the analytical lab is expected. Several benefits are derived from processing samples at a field lab, including:

1) Better protection against residue degradation is offered by immediately air-drying the samples over storing frozen fresh samples.

2) Freezing facilities become unnecessary. However, when prolonged storage prior to residue analysis is expected, store air-dried samples under refrigeration to further protect the integrity of the samples.

3) Between-sampling periods for field crews can be better utilized by processing samples.

4) Bulk and weight of the samples is reduced for shipping.

Reporting Herbicide Residues in Soil

The significance of the new soil residue reporting method, calculating µg/mL soil or kg/ha rather than the traditional µg/g soil, enables a direct comparison with herbicide application rates (kg/ha) and with

Table 5. Sample data sheet for soil preparation

Herbicide Experiment - Sample Log

Experiment Number: _____

Active Ingredient: _____

Application Date: _____

Lab Sample No.:

Fresh Sample:

Sample Code:

Date Sampled:

Post-Spray Days:

Sample Description:

Weight: Sample (g):
Bag (g):

Net Sample (g):

Date Prepared:

Air Drying:

Weight: Sample (g):

Bag (g):

Total Sample (g):

Discard (g):

Net Sample (g):

Date Blended:

Operators Initials:

Water Content (%):

Table 6. Soil particle classification and their calculated surface areas.

Conventional Name	USDA Classification (Briggs 1904) Diameter Upper Limit (mm)	Total Surface Area (cm^2/mL)	Total Surface Area (cm^2/g)*	International Classification (Lyons et al. 1952) Diameter Upper Limit (mm)	Total Surface Area (cm^2/mL)	Total Surface Area (cm^2/g)*
Very Coarse Sand	2.00	30	11.3			
Coarse Sand	1.00	60	22.6	2.0	30	11.3
Medium Sand	0.50	120	45.2			
Fine Sand	0.25	240	90.4	0.2	300	113
Very Fine Sand	0.10	600	226			
Silt	0.05	1200	452	0.02	3000	1130
Clay	0.002	30000	11300	0.002	30000	11300
Discarded Pebbles	20	3	1.13	20	3	1.13
	10	6	2.26	10	6	2.26

* Calculations based on an average mineral soil density of 2.65 (Robinson 1949).

phytotoxicity data (µg/mL) generated from greenhouse studies. Once the analytical results (µg/g soil) are available, convert them to kg/ha or µg/mL (mg/L) using the following procedure:

1) The soil sample is taken from a defined area (A cm^2) and depth (D cm).

2) The weight of the whole core is W g.

3) The residue from an aliquot of soil sample weighed for residue analysis is reported as ppm (µg/g).

4) The sample Bulk Density B (g/cm^3) = W g / [A (cm^2) x D (cm)]

5) To convert from µg/g to kg/ha:
ppm (µg/g) x W (g) / A (cm^2) x 10^{-9} kg/µg x 10^8 cm^2/ha = (ppm x W) / (A x 10) (kg/ha)

6) To convert from µg/g to g/mL (or mg/L):
ppm (µg/mL) = ppm (µg/g) x B (g/cm^3)

7) To convert from µg/mL to kg/ha:
kg/ha = ppm (µg/mL) x D cm / 10

A protocol for reporting on other aspects of herbicide research methods and results (such as site description and data format) was described in detail by the Pesticides Division, EPS (1985).

HERBICIDE RESIDUES IN FOLIAGE AND LEAF-LITTER

Scope

This procedure describes collection of leaf and leaf-litter samples at desired time intervals. The establishment of collection nets and methods of sample collection, packaging, shipping and storage are described.

Summary

Techniques have been recently developed for studies on herbicide residue persistence in leaves and leaf-litter. Herbicide intercepted by leaves after foliar application in the autumn may persist and be transported onto the forest floor as leaf-litter. Although traditional methods for initial foliage sampling before and immediately after herbicide application remain appropriate, the collection of leaf-litter during senescence has been improved. The collection mesh described elevates fallen leaf-litter, thus precluding contamination of the leaves from residue on the forest floor. The size of the collection surface is not limited and can be easily adjusted to accommodate plots having low leaf densities to yield an estimated sample size of at least 100 g for residue analysis, which requires 20-50 g per subsample.

Residue values from leaf foliage and litter are reported on a weight to weight (ppm) basis.

Equipment and Materials

Equipment and materials required for foliage and leaf-litter sampling include:

1) Hammer
2) Ax
3) Knife
4) Chainsaw
5) Insulated shipping boxes (see page 8)
6) Cooler packs, ice or dry ice
7) Wooden stakes (4 x 4 x 60 cm)
8) Carpet tacks
9) 2 mm Nylon mesh (60-80 cm widths)
10) String
11) Plastic bags (36 x 53 cm)
12) Marking pens
13) Vinyl gloves

Preparations for Foliage and Leaf-Litter Collection

Plots should be selected to collect a desired representation of the weed species to be studied. Establish plots for collecting fresh foliage separate from plots for collecting leaf-litter. For leaf-litter collection, install nylon mesh after herbicide application in order to minimize potential sample contamination. Mesh is easily installed without disturbing target vegetation when it forms a high canopy. However, when the target species forms a low canopy, mesh installation should precede application to avoid disturbing treated target vegetation. In order to maintain sample representation, keep the plots away from the edges of the treatment blocks. Remove all non-target species from the plots, leaving only the target vegetation to be studied. Select plots for foliage collection (involving tree removal) separately to provide a full canopy above leaf-litter plots. Hang mesh for leaf-litter collection from stakes so that it is elevated at least 10 cm above ground surface (Fig. 12) in order to clear any twigs, roots or debris. In plots under large overstory, lay out the mesh in greater than 10 m strips, with access lanes between strips. In small brush areas, fit the mesh around stems to maintain a straight strip by cutting the mesh and later tying the cuts closed with string (Fig. 13). Mesh in a low canopy area installed prior to herbicide application should be protected with plastic sheets during application whenever feasible. Remove the protective sheets about 2-3 hours following herbicide application when the herbicide has dried on the foliage. When the protective sheets are not used, remove all leaf-litter from the collection mesh immediately prior to herbicide application to prevent residue dilution of subsequent samples by untreated materials.

Foliage and Leaf-Litter Collection and Packaging

A sampling schedule should be selected to accommodate leaf senescence in autumn. Collect samples at 2-3 week intervals as late into the season as leaves remain on the target species, and ending when the amount of leaf-litter sample is insufficient for analysis (less than 100 g dry weight).

Fig. 12. Plot for residue collection in willow and alder leaf-litter.

Fig. 13. Plot for residue collection in salmonberry leaf-litter.

Foliage samples near the time of aerial herbicide application usually need to be collected live from standing vegetation. In areas of tall overstory target species, sampling is facilitated by felling a representative tree. For zero-time samples, wait a period sufficient to allow the herbicide to dry on the foliage (0.5 - 1 hour) prior to felling. Collect a balanced proportion of foliage from top-of-crown, mid-crown and below-crown positions.

Precautions should be taken to prevent sample contamination of both living foliage and leaf-litter samples. Wear vinyl gloves during collection and replace for each replicate sample. Use double sample bags to protect from puncture and on-site contamination. Fold the outer bag over the lip of the inner sample bag to prevent contact of sleeves and other non-sample materials with the inner surface of the sample bag. After collection, discard the outer bag, replace with two fresh ones, and remove air from the bags before tying closed. Triple-bagging samples is necessary to reduce possible puncture and subsequent cross-contamination during transport. Chill samples immediately after, and freeze within several hours of collection.

Shipping and Storage

Procedures for shipping and storage are similar to those described on page 8.

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