

SOME GUIDELINES FOR ONSITE STUDIES OF PESTICIDE LEACHING IN THE UNSATURATED AND SATURATED ZONES

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CONVERSION FACTORS

<i>Multiply</i>	<i>By</i>	<i>To obtain</i>
inch	2.54	centimeter
foot	0.3048	meter
square inch	6.452	square centimeter
square foot	0.09290	square meter
acre	4,047	square meter
cubic inch	16.39	cubic centimeter
quart	0.9464	liter
gallon per minute	0.06309	liter per second
degree Fahrenheit (°F)	(1)	degree Celsius (°C)

¹ °C = (°F-32)/1.8.
°F = 1.8(°C)+32.

SOME GUIDELINES FOR ONSITE STUDIES OF PESTICIDE LEACHING IN THE UNSATURATED AND SATURATED ZONES

By Charles A. Perry¹, Catherine Eiden², Philip L. Barnes³,
and John Tessari⁴

ABSTRACT

Onsite leaching studies can be categorized into two groups--prospective and retrospective studies. The prospective study described in this report is designed to track the movement of pesticide residues from the time of application of the pesticides to a predetermined level of dissipation or length of time. The retrospective study is designed to determine if a previously applied pesticide has already reached the ground water. Onsite information is similar for both study designs and includes climatic data, hydrogeologic properties, and soil properties.

The equipment used and the methods employed for the sampling of soil, soil water, and ground water can be applied to both study designs. The scheduling of sampling varies somewhat between study types, with the prospective study focusing on the unsaturated zone and the retrospective study focusing on the saturated zone. Sample collection can be economized by sample compositing, and tracer applications can provide representative samples while economizing the sampling scheme. Finally, quality-assurance methods need to be incorporated in the collection and transportation of all samples.

INTRODUCTION

Background

Interest in the unsaturated (vadose) zone, the lithologic zone that extends from the soil surface to just above the saturated zone, has increased substantially in recent years as a result of the flux of synthetic organic compounds into it. Physical, chemical, and biological processes operate in the unsaturated zone to

allow water and soluble compounds, such as agriculturally applied pesticides, to move down to the ground-water reservoir. These processes are complex and, in some cases, difficult to measure.

Studies of the unsaturated and saturated zones are used to determine either the likelihood of a pesticide moving to the ground water or the presence of a pesticide in the ground water. Onsite studies are important because degradation and migration are affected by environmental factors, such as soil, climate, the presence of crops, irrigation practices, and microbial activity, which cannot be fully duplicated in the laboratory or by numerical-modeling studies. For example, pesticide mobility may be affected by macropore flow. Macropore flow is the movement of water under the effect of gravity through the worm holes, desiccation cracks, and root cavities rather than the more typical capillary flow through the soil matrix. There is evidence that solutes can be transported to the ground water through macropores more quickly than flow through a porous media (Gish and Helling, 1989).

In order to aid in organizing investigations that address the complex environmental processes just described or that measure the factors that define or quantify these processes, the U.S. Geological Survey, in cooperation with the Kansas Department of Health and Environment, has developed guidelines for designing and conducting onsite studies of pesticide leaching.

Purpose and Scope

This report provides some guidelines for

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designing and conducting efficient unsaturated- and saturated-zone studies of pesticide leaching. The information presented will be useful to those conducting a study on pesticide leaching for the first time and those who monitor ground-water quality. Methodologies of subsurface research and monitoring are continually improving. Therefore, the guidelines presented in this report can be considered a primer for investigators, and the latest techniques need to be investigated before initiating a study.

The guidelines presented in this report include:

1. The design of before-the-fact (prospective) and after-the-fact (retrospective) studies;
2. Collection of hydrologic and geologic information;
3. Methods and schedules for sampling of soil, soil water, and ground water;
4. Quality-assurance and control procedures; and
5. Description of laboratory analysis presently (1991) available.

DESIGN OF PESTICIDE-LEACHING STUDIES

For this report, pesticide-leaching, studies were categorized into two types. Prospective-type studies document pesticide leaching from preapplication conditions to a predetermined level of dissipation throughout a soil and aquifer profile. A pesticide is applied to a specific area, and its movement is monitored by various methods until it can no longer be detected. Retrospective-type studies begin some time after pesticide application, as much as several years. In many retrospective studies, the pesticide in question has already reached the saturated zone.

Prospective Study

A prospective study is defined as one that tracks the movement and fate of pesticides in soil, soil water, and ground water from the time of application to a predetermined level of

dissipation or length of time. The pesticide either degrades, reaches the saturated zone, or reaches a depth significantly greater than the root zone. The dissipation can be monitored by collecting soil-core data, soil-water data, and ground-water data from existing wells or those specifically installed for the study. A major objective of this type of study design typically is to define the maximum depth of pesticide movement and the rate of degradation of the pesticide (half-life) under onsite conditions. This design is appropriate for newly developed pesticides for which a leaching potential is suspected and for new application rates and untested soil types using established pesticides for which a leaching potential exists. Leaching potential exists for those pesticides that are water soluble and persist for a period long enough to move beyond the root zone.

Study Plot Selection

Small research plots (normally less than 5 acres) within a specific field are preferable to large plots because the intent of a prospective study is to comprehensively follow the movement of a pesticide, and this is more easily managed in a small area. Furthermore, a small study plot decreases the number of samples needed to adequately define the distribution of pesticides in a soil profile.

A plot with uniform soil-slope and soil-texture characteristics, permeable soil, and a shallow water table, generally less than 30 feet from the land surface, simplifies interpretation of results. Ideally, the plot should be level. Also, the plot should have only one "soil series," as defined in the U.S. Soil Conservation Service taxonomic system (Brady, 1984). If the plot possesses more than one soil series, all of the series should be of the same texture; for example, all series should be sandy loam. This criterion does not preclude plots with layered soils (soil with distinct horizons) as long as the entire plot is characterized by this layered soil. The more uniform the plot, the easier will be the interpretation of the results. U.S. Soil Conservation Service county soil surveys give sufficient detail to characterize a field for selection. A permeable soil and shallow water table will make it possible for the pesticide to move through the saturated zone and be detected in the ground water before the

scheduled end of the study.

Ideally, there should be no prior usage of the pesticide on the study plot or adjacent fields. This assures that ground water beneath the plot has not been affected by pesticide leaching from adjacent fields. However, if past application records are available and sufficient background pesticide concentrations are determined, this requirement can be waived.

The location of a study plot should be examined for any artificial-drainage systems. Many fields have either underground drainage tiles, constructed terraces and waterways, or nearby irrigation ditches that could alter the surface and subsurface flow characteristics. Plots with these artificial-drainage systems should be avoided if possible.

Field-Application Practices

It is important that field-application processes in a study plot follow the current practices for pesticide use (label instructions). Application specifics include rate and timing of application and method of application. These pesticide-application specifics can be varied to evaluate margins of error or worst-case scenarios. Standard agricultural practices, such as tillage or harvesting methods, should be used.

The one exception to the current-practice rule is irrigation. It may be desirable to provide supplemental irrigation even if irrigation is not the current practice for the area. Because the objective of the prospective study is to determine leaching potential, the study should be conducted under average rainfall conditions. Irrigation can guarantee this condition.

Study Duration

Prospective studies should take a minimum of 3 years to complete, including plot selection, well construction, at least 2 years of sampling and analyses, and preparation of results. Prospective studies may require additional time to trace the movement of pesticides if soils in the test plots are of slight permeability or the pesticide is persistent or has slight solubility in water, which would retard downward transport.

Retrospective Study

Retrospective studies can be used to study the known or suspected potential for leaching of pesticides currently being used. The studies often are a result of documented ground-water contamination, particularly findings that can be attributed to normal use and leaching. These studies attempt to determine the degree to which a pesticide has leached to the ground water and normally focus on water-table aquifers.

The primary objective of retrospective studies is to determine the degree that a specific pesticide has leached to ground water in specific fields characteristic of a certain crop use and associated agricultural practices. Like the prospective study, the other main objective is to characterize the leaching pattern in the unsaturated soil profile. By carefully selecting a study plot representative of conditions in which the crop is grown, it may be possible to extrapolate the results to larger areas, such as counties or drainage basins.

Study Plot Selection

Retrospective studies normally require that larger areas be investigated than the prospective studies require. Plots or small fields of about 10 or more acres will enable determination of relations among pesticide use, agricultural practices, and hydrogeology. The larger area of plot or field is necessary to prevent the surrounding fields from affecting the soil, soil water, and ground water beneath the field of interest. Factors such as local ground-water gradient, soil permeability, and slope of the field must be considered. The ratio of the distance between a sampling point and the edge of the field to the depth to the water table should be greater than 10 to 1. The effective size of a field can be increased by finding a location where the surrounding fields have the same general hydrogeology, the same crop, and the same pesticide-application factors. Several fields may require study to provide information on a range of agricultural practices or hydrogeologic conditions. For example, for a commonly planted crop such as soybeans, it may be desirable to select several fields to allow comparison of various factors, such as soil type, slope, and tillage practices. Conversely, for an uncommon crop such as artichokes, only one or two fields may be appropriate.

Selection of specific fields must be based on hydrogeology. The selected fields must be representative of the majority of the acreage to which the pesticide is applied with respect to soil permeability, depth to water, and type of aquifer.

One way to locate fields for possible inclusion in a retrospective study is to use an indexing system known as "DRASTIC" (Aller and others, 1987). DRASTIC was developed to evaluate ground-water pollution potential using hydrogeologic-setting data. Each letter of this acronym refers to a hydrologic aspect that is rated according to its vulnerability. As part of the National Pesticide Survey of the U.S. Environmental Protection Agency, every county in the United States was evaluated using the DRASTIC index. It should be emphasized that DRASTIC is only an approximate rating of average county vulnerability. The results of this indexing system can be used as a guide in locating fields for retrospective studies. For sites considered vulnerable to the leaching of pesticides, the factors of primary importance are depth to ground water (D), recharge rate (R), and top soil (S in DRASTIC). The selection of individual study plots should be made to include a range of these factors that are typical of the crop and pesticide to be evaluated. To fully characterize an area, consultation with state geologists, hydrogeologists, and county extension agents is suggested (Aller and others, 1987).

Because a retrospective study examines the historical movement of pesticides to the water-table aquifer, documentation of prior use of pesticides at selected sites is necessary. Also, farmer cooperation is imperative, as it will be necessary to have full access to fields for instrument installation and sampling. Plots located on university-owned research farms, State land, or Federal land can be ideal locations.

Field-Application Practices

It is important that current practices for pesticide use in the area of the study be followed in a retrospective study. Specifics of pesticide use include rate and timing of application, method of application, and standard agricultural practices for the crop in question,

including such factors as tillage or harvesting methods. Unlike the prospective study, the farm operator should have been irrigating and applying chemicals according to standard practices for his crop and region, including the possibility of no irrigation.

Study Duration

Retrospective studies should take 2 years to complete, including study plot selection, well construction, sampling and analyses, and final reports.

COLLECTION OF ONSITE INFORMATION

Essential earth-science information is needed to evaluate the hydrologic processes occurring within a study plot. This information includes (1) climatic, (2) general hydrogeologic, and (3) soil data. Climate controls the supply of water that activates most pesticides, makes them available to the plants, and provides them with a means to percolate downward. The depth and time distribution of the supply of water are critical to these processes, some of which are nonlinear functions. General hydrogeologic data provide information on the ability of the underground materials to hold or transmit the water upward as well as downward. Soil data provide information concerning infiltration and runoff, both mechanisms for transporting pesticides. The elements within each type of information, as well as suggestions for obtaining the information, are presented in this section.

Climate

Meteorological Data

Monthly and annual climatic trends can be estimated from meteorological data obtained from the National Weather Service (NWS) observation network. With the exception of rainfall, most of these monthly and annual data can be interpolated between NWS observation stations.

Daily rainfall, evaporation, solar radiation, wind, barometric pressure, and temperature data, however, are best gathered at the site because of significant spatial and temporal variability in most measurements. This requires

either a full-time observer or an automated, data-logging, weather station (Sophocleous and Perry, 1984) (fig. 1). The automated station may be preferred because of its reliability and computer-interface capabilities. Also, it can be programmed to record other information, such as soil moisture and ground-water levels. All sites should have a reliable recording rain gage because rainfall depth and intensity are important variables in leaching and runoff determinations.

Irrigation Scheduling

The importance of water application to leaching and runoff requires that irrigation water depths be recorded. Sprinkler irrigation can be measured with auxillary rain gages. Total depth of flood irrigation can be computed by dividing gaged or metered discharges by the total area flooded.



Figure 1. Automated weather station.

Hydrogeology

Stratigraphy

Stratigraphic descriptions of the subsurface indicate the presence of sediments or lithologic units of decreased permeability, such as clay and silt-clay lenses. Onsite drilling and geophysical logging provide the best information. Keys and MacCary (1971) provide a good summary of the application of borehole geophysics to water-resource investigations. Borehole cuttings or undisturbed samples from split-spoon or press-core barrel samplers can be used to verify geophysical-logging data.

Regional ground-water studies provide general descriptions of aquifer type and materials. A detailed analysis should be conducted when describing specific study plots. A good procedure is to obtain samples of the aquifer material during the installation of observation wells.

Depth to Water Table

The vertical distance from the ground surface to the depth where the soil becomes saturated and hydraulic pressure equals atmospheric pressure is the depth to the water table. This can be found by measuring the water level in wells. Care must be taken if using existing wells in which the screen depth or length is unknown. To give a true measure of the depth to the water table, the well must be screened near the top of the saturated zone.

Aquifer Permeability

Vertical and lateral movement of ground water and of solutes in the ground are controlled by the permeability of the underground materials. Permeability is calculated from measurements of the hydraulic conductivity and the transmissivity of the soil or aquifer matrix.

Hydraulic Conductivity

Hydraulic conductivity (K) of porous material is defined as the volume of water that will move per unit of time under a unit hydraulic gradient through a unit cross-sectional area. Hydraulic conductivity for saturated geologic materials (an aquifer) can range through 12

orders of magnitude (Heath, 1983).

Hydraulic conductivity not only varies among materials but also within a specific material. If the hydraulic conductivity is essentially the same in any given area, the aquifer in that area is said to be homogeneous; if it differs from one part of the area to another, the aquifer in that area is said to be heterogeneous. Hydraulic conductivity also may differ directionally. If the hydraulic conductivity is similar in all directions, the aquifer is said to be isotropic. If it is different in different directions, the aquifer is said to be anisotropic. The most commonly encountered situation, especially in unconsolidated deposits and in flat-lying, consolidated sedimentary rocks, is for the hydraulic conductivity to be greater in the lateral direction than it is in the vertical direction.

Hydraulic conductivity of saturated materials is best measured onsite by the auger-hole method or the piezometer method (Black, 1965). If a sample of aquifer material can be obtained, an estimate of the hydraulic conductivity can be made in the laboratory by the permeameter method. However, it is often difficult to obtain undisturbed samples of the aquifer material.

Transmissivity

Transmissivity (T), is equal to the hydraulic conductivity (K) multiplied by the saturated thickness of the aquifer (b). Transmissivity of an aquifer also may be calculated from the equation:

$$T = \frac{Q}{W} \left(\frac{dh}{dl} \right), \quad (1)$$

where

Q = a quantity of water discharging from a known width of aquifer per unit time;

W = the width of the aquifer; and

$\frac{dh}{dl}$ = is the slope of the water table parallel to the direction of ground-water flow (hydraulic gradient).

Direction and Velocity of Lateral Ground-Water Flow

The general direction of ground-water flow can be determined from regional surveys and assessments of ground-water resources but is best determined from an analysis of water-table altitudes from at least three ground-water observation wells. This analysis is detailed in the "Ground Water" section of this report.

The rate of water movement through porous media is particularly important to understanding contaminant movement. Velocity can be calculated from Darcy's law and the velocity equation of hydraulics:

$$Q = Av, \quad (2)$$

where A is the cross-sectional area, and v is the velocity of the water. Allowance must be made for the porosity (open space between particles) of the aquifer material because water moves only through these openings. Therefore, equation 2 becomes:

$$v = \frac{Kdh}{ndl}, \quad (3)$$

where K is the hydraulic conductivity, and n is the porosity of the aquifer material. Porosity is defined as the percentage of the bulk volume not occupied by the solids (Black, 1965).

Direction and Velocity of Vertical Ground-Water Flow

Plots or fields selected to investigate pesticide movement and fate should have the potential for downward movement of water. Locations at which the ground water is moving upward or is stagnant should be avoided. Nearby topography variations can cause local vertical ground-water gradients that increase with depth, reversing normal gravity flow and bringing up ground water to saturate the surface soil layer. Impermeable clay lenses near the ground surface can create perched water tables that can extend to the surface preventing downward flow of ground water. A large percentage of water-tolerant plant species, such as cattails or marsh grass, present within a field is an indication of either upward movement of ground water or stagnant conditions, both of which should be avoided in selection of a study plot. A more quantitative method of determining direction and velocity of vertical

ground-water flow involves a flow-net analysis (Linsley and Franzini, 1972), which uses series of piezometer nests to map the ground-water hydraulic heads in three dimensions.

Soil

Soil-Series Classification

The U.S. Department of Agriculture Soil Conservation Service has compiled detailed information on most soils in the United States. Descriptions of each soil series are published along with tables of various soil-fertility factors and physical properties. The soil series are contoured on aerial photographs for most counties and field verified. Soil surveys are available through any U.S. Department of Agriculture Soil Conservation Service office.

Particle-Size Distribution

Particle-size analysis of soil expresses the proportions of the various sizes of particles that make up the soil. Rough estimates of bulk density and permeability can be made if the particle-size distribution is known. Most analyses describe the percentage of sand, silt, and clay. Sand has a diameter of greater than 0.05 millimeter; silt ranges between 0.05 and 0.002 millimeter; and clay is less than 0.002 millimeter. Several methods are used to determine the entire range in particle-size diameters. They include filtration, dispersion, and the sieve-pipette method (Black, 1965).

Bulk Density

Bulk density can be determined either gravimetrically by the core method or indirectly by the nuclear-density-gage method (Black, 1965). The core method is simplest. It requires a soil-sampling device that will cut an undisturbed sample from the ground. The dimensions of the core are noted in order to compute the volume. The core then is oven-dried at 105 °C and weighed. Bulk density is the dry weight divided by the volume of the sample. When undisturbed samples are impossible to obtain, a nuclear-density-gage method can be used. This method uses a gamma-radiation source and a detector, which are housed in a single probe. This probe can be lowered into the soil through an access tube to the desired depth. The more dense the soil, the greater the gamma

radiation. The measurement includes the mass of the water between the soil particles so a correction must be made to account for soil moisture. Many of the new density probes include a neutron probe for soil-moisture determinations.

Organic Matter

The amount of organic material in the soil is a controlling factor in adsorption and immobilization of pesticides in the soil matrix. The greater the organic content the greater the volume of pesticides that can be held in the soil.

To determine the amount of soil organic matter it is necessary to separate organic and inorganic material. The organic material is removed by burning in a combustion furnace with a stream of oxygen (Black, 1965). Many laboratories routinely perform organic-material analysis and furnish organic-carbon and inorganic-carbon concentrations or percentages.

Permeability

Knowing the permeability of the soil and underlying materials is essential in estimating pesticide flux through the unsaturated zone. Permeability is the measure of the ability of water to move through a material under a specified hydrostatic head. Estimates of soil permeability can be based on the soil particle-size distribution. Permeability can be measured either in the laboratory or onsite. A laboratory measurement can be made by the constant-head method. In this method, a sample of the soil is placed in a container with a basal screen or porous ceramic plate in the bottom that supports the soil and allows unperturbed drainage. Preferably, the soil is obtained by coring and is relatively undisturbed. If necessary, the soil is compacted to a density comparable to onsite conditions. A constant head of water is applied to the top of the sample, and the volume of water percolating through the column during a given time interval is measured. The following equation can be used to compute the permeability (modified from Black, 1965):

$$k'_w = \frac{\eta k}{\rho_w g} = \frac{\eta}{\rho_w g} \frac{VL}{A \Delta h \Delta t} \quad (4)$$

where

k'_w = intrinsic permeability with water, in square inches;

η = viscosity of water at the recorded temperature, in dyne seconds per inch squared (poises);

ρ_w = density of water, in grams per cubic inch;

g = acceleration of gravity, in inches per second squared;

k = hydraulic conductivity, in inches per second;

V = volume of percolate in time Δt , in cubic inches;

L = length of soil column, in inches;

A = cross-sectional area of the soil column, in square inches;

Δh = difference in hydraulic head between the inflow and outflow ends of the soil column, in inches; and

Δt = time interval for volume of percolate V to pass through the soil, in seconds.

An alternative method of determining soil permeability is a constant-head permeameter that operates on the Mariotte-siphon principle (fig. 2). It can be used onsite to determine field-saturated hydraulic conductivity, matrix-flux potential, and sorptivity. Saturated hydraulic conductivity (K_{sat}) is the measure of the ability of a soil to transmit water under saturated conditions. Field-saturated hydraulic conductivity refers to the saturated hydraulic conductivity of soil containing entrapped air, which is common in the unsaturated zone. Matrix-flux potential is the measure of a soil's ability to move water, by capillary force, through a unit cross-sectional area in a unit time. Sorptivity is the measure of the ability of a soil to absorb a wetting liquid. In general, the greater the value of sorptivity, the greater the volume of water that can be absorbed, and the more rapidly it is absorbed.

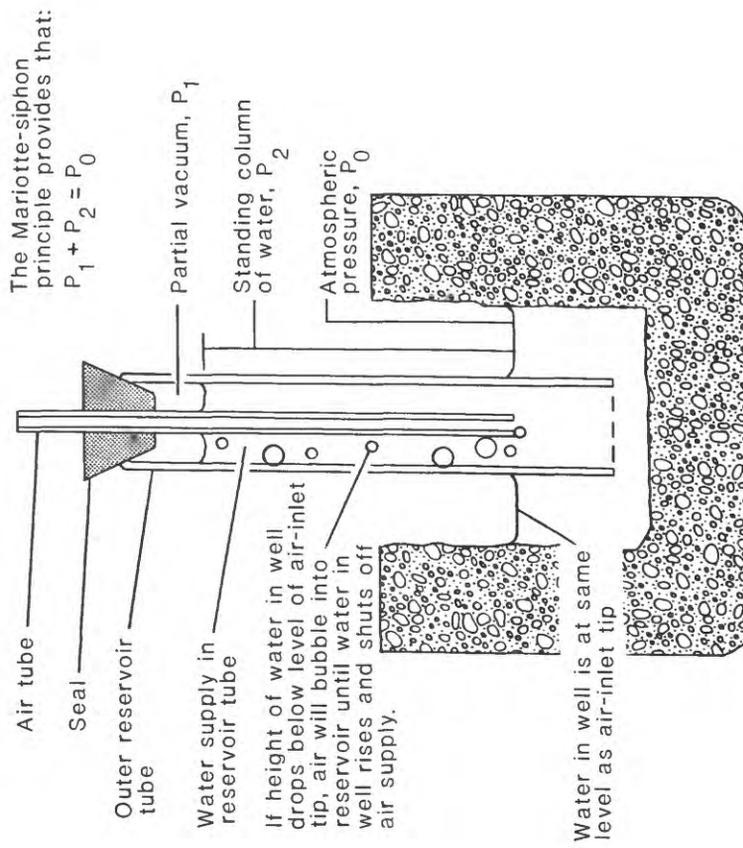
The constant-head permeameter is an

in-hole permeability measuring device. The device is used to measure the steady-state rate of water recharge through the bottom and sides of a cylindrical borehole in which a constant depth (hydraulic head) of water is maintained in the unsaturated soil. Constant-head level in the borehole is established and maintained by regulating the level of the bottom of an air tube (fig. 2) that is located in the center of the permeameter. As the water level in the reservoir declines, a vacuum is created in the air space above the water. The vacuum can be relieved only when air, which enters at the top of the air tube, bubbles out of the lower end of the air tube and rises to the top of the water reservoir. This in turn allows water to flow from the reservoir into the borehole, causing the water level to rise slightly. An equilibrium is established with the partial vacuum and the pressure of the water column within the reservoir, balancing the atmospheric pressure on the water surface within the borehole. This is the Mariotte-siphon principle.

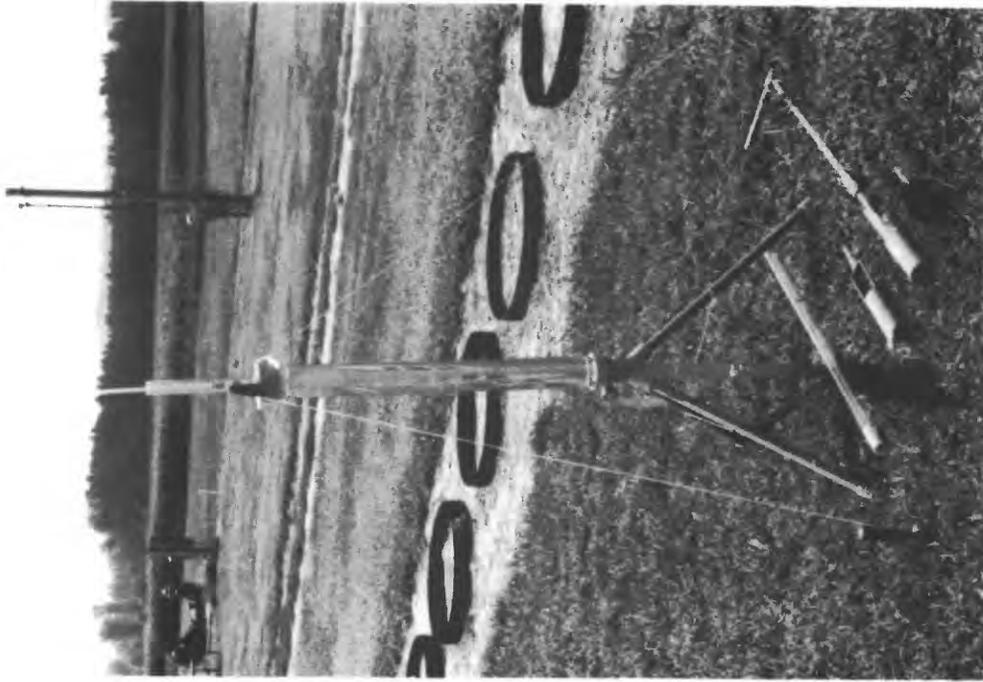
When a constant height of water is established in the borehole in the soil, a "bulb" of saturated soil with specific dimensions is quickly established. This bulb is very stable, and its shape depends on the type of soil, the radius of the borehole, and the hydraulic head of water in the borehole. The shape of the bulb is described numerically by Reynolds and Elrick (1985).

Once the unique bulb shape is established, the outflow of water from the borehole reaches a steady-state flow rate. The measured flow rate, diameter of the borehole, and the height of water in the borehole can be used to determine field-saturated conductivity, matrix-flux potential, and sorptivity of the soil.

Unsaturated hydraulic conductivity (K_{unsat}) is the measure of the ability of unsaturated soil to transmit water. Unsaturated hydraulic conductivity is determined by a nonlinear function dependent upon the volumetric moisture content of the soil. K_{unsat} can vary several orders of magnitude under moisture conditions typically occurring in the soil zone. An example of determining unsaturated hydraulic conductivity is provided in Sophocleous and Perry (1987).



A.



B.

Figure 2. (A) Constant-head permeameter illustrating the Mariotte-siphon principle used to determine soil permeability and (B) permeameter installed onsite.

Soil Moisture

An important factor in determining the transport and fate of pesticides in the unsaturated zone is the volume of water present between the soil particles, referred to as soil-moisture content. Two important measures of soil moisture are field capacity and wilting point. Field capacity is defined as the volume of water held in the soil after excess gravitational water has drained and after the rate of downward water movement has materially decreased. Wilting point is the moisture content of the soil at which permanent wilting of plants occurs. These two reference points can be expressed in terms of soil tension. Colman (1947) has shown that field capacity is essentially the water retained in soil at a tension of one-third atmosphere. The wilting point commonly is assumed to be equivalent to the moisture content at a tension of 15 atmospheres.

Available water (the difference between field capacity and wilting point) can be measured best using a weighable pressure cell, as outlined by Black (1965). First, the pressure cell with soil in it is allowed to drain by gravity. Then it is weighed to obtain the volume of water at field capacity. Pressure then is applied to the cell in increments, and the cell is reweighed after each pressure increase. Pressure is increased to 15 atmospheres, which is considered the tension of the soil at the wilting point. The difference in the volume of water between the field capacity and at 15 atmospheres is considered the available water.

Soil-moisture content can be measured by several methods. The gravimetric method is most accurate. It requires oven-drying a soil sample and dividing the difference between wet weight and dried weight by the dried weight. The result is the percentage of moisture by weight. Another method is to measure the soil tension by a tensiometer, which consists of a porous-ceramic cup filled with water and inserted into the soil. Because of the negative matrix potential in the unsaturated soil, water flows from the cup into the soil, and a negative-pressure gage indicates the soil tension (Stannard, 1986). Tensiometers can measure soil-water tension from saturation (0.0

millimeter of mercury) to 1 atmosphere (760 millimeters of mercury). The resistivity method uses a porous dielectric, which has a pair of embedded electrodes. The resistivity between the electrodes changes as a function of the moisture content of the dielectric material, which is in equilibrium with the soil moisture. Resistance is measured with an alternating-current bridge. Maximum sensitivity of this method is near saturation; the moisture-resistivity relation is not stable, and as the sensor ages, frequent recalibration is required. The neutron-scattering method (Gardner and Kirkham, 1952) uses a source of fast neutrons, which is lowered into an access tube installed in the soil. Fast neutrons become slow neutrons after colliding with hydrogen atoms within the water molecule. The more water molecules that are present in the soil, the greater the number of slow neutrons that will be detected and counted (fig. 3). This measurement usually is given in percentage of moisture by volume. The neutron meter usually is calibrated by using the oven-drying method along with a measure of the bulk density of the soil.

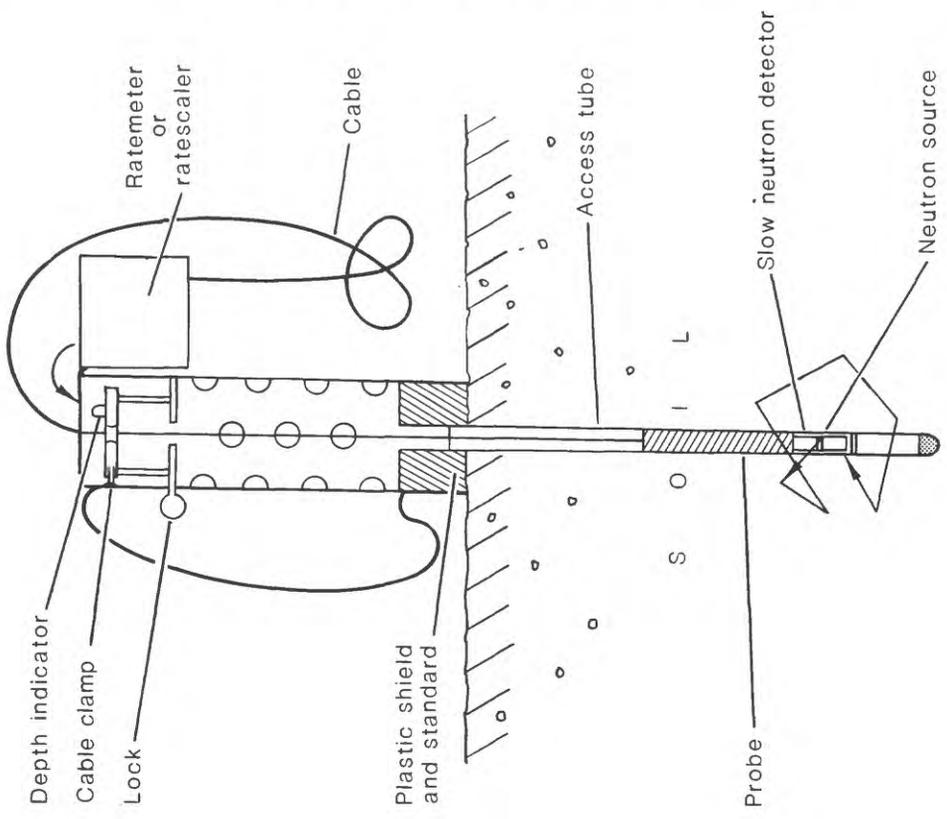
CONDUCTING SOIL, SOIL-WATER, AND GROUND-WATER SAMPLING

Pesticide movement and fate are documented by measurements of pesticide concentrations. Distributions of these measurements in time and space provide the evidence for determining leachability and persistence of a pesticide. These measurements must be determined from representative samples of soil, soil water, and ground water.

The following sections describe procedures for collection of soil, soil-water, and ground-water samples, which are applicable in both prospective and retrospective study designs. All of the siting, construction, and sampling information on soil, soil water, and ground water applies to studies conducted in unconsolidated geologic materials; these include alluvial-fill materials, glacial till and stratified glacial materials, coastal-plain deposits, and residual soils developed over the unconsolidated materials and consolidated bedrock. In regions underlain by karstic carbonate rocks, the general approaches described herein for well location and construction may not be applicable.



B.



A.

Figure 3. Diagram (A) and photograph (B) of neutron meter for measuring soil moisture.



Figure 4. Light-weight, trailer-mounted coring rig with press-core barrel poised for sampling.

Soil Cores

Methods of Collection

Both the prospective and retrospective studies require chemical and physical analyses of soil material. Soil samples may be obtained by hand-coring tools or truck-mounted coring rigs. Shallow cores (less than 6 feet below ground surface) are best taken by hand auger or a light-weight coring rig (fig. 4). This prevents compaction of the surrounding soil, which could alter soil permeability. However, initial soil sampling could be performed with a heavier truck-mounted coring rig if tillage of the study plot or field follows.

There are many coring tools that can be used to obtain a soil sample. These include

screw-type augers, bucket augers, and split-spoon samplers or press-core barrels, which can be used in hollow-stem augers (Shuter and Teasdale, 1989). The tool chosen should obtain a soil sample with minimal agitation or mixing and should be easily cleaned to prevent cross contamination between boreholes.

A common problem in soil sampling is the possibility of pesticide residues being pushed downward by the sampling device or by surface material falling into the borehole during sampling and subsequent contamination of deeper samples. Cross contamination between different boreholes is possible if the sampling device is not cleaned thoroughly. Some methods being used successfully to prevent contamination include: (1) careful scraping of outer and upper parts of the sampling device, (2) systematically discarding the upper inch or two of each sample (since it may have been contaminated from the soil above it), (3) obtaining smaller diameter cores for each subsequent sample, and (4) cleaning the sampling device thoroughly between samplings. This problem should be addressed because contamination can invalidate the soil-sample data.

Proper filling of boreholes after soil sampling often is overlooked. Boreholes can become conduits down which surface water can drain. Pesticides at or just below the ground surface can move with water down boreholes much quicker than by percolation through undisturbed soil. This can result in "miniature plumes" that inadvertently may be sampled at a latter date. All boreholes should be backfilled with bentonite and marked with a small flag; the bentonite will seal the borehole, and the flag should prevent sampling near or at a previous borehole.

Sample Scheduling

At least one set of soil samples through the unsaturated zone is required at the onset of a study. The purpose of this set is twofold: (1) To determine the presence and amount of pesticide residue in the soil as the result of the most recent application, and (2) to characterize the soil profile in the root zone in detail and in the unsaturated zone to the water table to the

extent that relatively undisturbed cores can be extracted. Minimally, the root zone needs to be characterized as to the percentages of sand, silt, clay, organic matter, the presence of silt-clay lenses, field capacity, and bulk density. The unsaturated zone needs to be characterized at least as to the various soil textures present--for example, sand loam, silt loam, gravel, and sand.

For the initial soil-characterization sampling, the following depth increments are suggested: 6-inch increments for the first 1 foot of soil, and 1-foot increments to the water table (or as deep as possible while maintaining the integrity of samples). It may be necessary to alter this sampling scheme to fully characterize the soil if one of the depth-increment samples penetrates a distinctly different soil horizon. For example, if a distinct horizon begins at 2.5 feet, then an acceptable alteration to the sampling scheme just proposed would be to take two samples from the 1.0-foot to 2.5-foot depth (8-inch samples), and 1-foot increment samples below that. Preliminary information on soil-horizon development can be obtained from the drilling of onsite wells.

Sampling of the soil for pesticide analysis at later dates will yield important information on the movement and fate of the pesticide. The time interval between first- and second-round sampling would be a function of water availability and the leachability of the soil, with a shorter time interval for wet conditions and a more permeable soil. If the emphasis of a retrospective study is on monitoring of the water-table aquifer, additional rounds of soil sampling may not always be necessary. The schedule for soil sampling for a prospective study design should approximate that of an exponential function, with increasing increments of time between sampling times. This allows tracking of the pesticide's degradation, the identification of degradates, and the determination of half-lives for the pesticide and its degradates.

A typical soil-core sampling scheme could proceed as follows: initial sampling to the water table to obtain a pre-application sample, followed by samples on date of pesticide application, then 1-, 3-, 7-, 14-day and monthly post-application sampling. This schedule can be altered if there are valid data on degradation

half-lives. For example, if it is known that the pesticide is very persistent, then the early post-application samples (day 3, 7, 14) would not yield valuable information. On the other hand, if the pesticide has shown half-lives of less than 2 weeks, then more frequent samples near the date of application would define more accurately the residue half-lives. Additionally, this schedule needs to be flexible to allow for sample collection after significant rainfall and irrigation application. In conjunction with recharge, the sampling schedule also may depend on soil permeability. A more permeable, sandy soil may require more frequent sampling than a clay soil.

The required depth of sampling after pesticide application is not specific but must be deeper than the maximum depth of the post-application wetting front. The post-application wetting front is the depth to which rain or irrigation water has moved from the surface after pesticide application. The post-application wetting front is difficult to determine because little or no differences in soil-moisture content occur across the front. The pesticide front will lag behind the wetting front as a function of adsorption, degradation, and diffusion. At each sampling, an additional 2 feet of residue-free soil should be collected below the deepest depth of recorded pesticide residues. This assures that the maximum depth of pesticide migration has been identified. If the interval between sample collection and completed pesticide analysis is more than a few days, complete sets of soil cores from the surface to the maximum expected leaching depth should be taken unless a field-detectable tracer is utilized.

If immediate sample analysis is not available, the use of easily detectable conservative tracers is suggested. The tracer chosen should be more soluble than the chemical being studied and should be applied concurrently with the pesticide. Because of its greater solubility, the tracer will move downward through the soil profile ahead of the pesticide. As the soil cores are collected, a split of the sample can be analyzed onsite for the tracer. A better method would be a more frequent monitoring of soil water in soil-water sampling devices. This will be discussed in detail in the section on the "Use of Tracers for

Soil and Soil-Water Sample Scheduling." As long as the tracer can be detected in each sample, that sample also will be analyzed for the pesticide in question. When the tracer can no longer be detected, no deeper samples need to be taken. The use of tracers, therefore, can economize laboratory costs.

Compositing Soil-Core Samples

Several profiles of soil samples in a plot or field may be necessary for adequate representation. The additional samples can be analyzed individually or samples from the same depth can be mixed and a composite sample taken to represent that depth. For example, 5 to 20 individual sampling locations per sampling period would be adequate for a field of 4 acres or less. Equally adequate might be 20 samples from the same depth composited to 5 samples for analysis. The number of composite samples is dependent on the size of the field and its uniformity. For example, more samples probably would be necessary for each depth per sampling period from a field larger than 4 acres. Similarly, more samples may be required from a heterogeneous sandy loam site as compared to a uniformly sandy and flat field site.

An example of the benefits of compositing several soil-core samples from the same plot at a particular depth can be seen in table 1. The concentrations of two herbicides, atrazine and alachlor, in 20 individual soil cores and 5 composite samples are listed. The soil cores were obtained from a field planted to corn 3 weeks after the pesticides were applied by surface spray. The cores represent a depth from ground surface to 1 foot below ground surface. During the interval between application and sampling, 1.42 inches of precipitation were recorded at the field. A 200- by 40-foot plot was chosen within the field, and the sample coordinates were chosen by a random-number generator. When a soil core was collected, it was thoroughly mixed in a container that was cleaned with deionized water and rinsed with acetone to prevent cross contamination. Then two 100-gram samples of soil were taken from the mixture, one sample for a 5-core composite and one sample for a 20-core composite. The remainder of the sample was used in the individual-location sample analysis. The end

result was 20 individual core-location samples, 4 five-sample composites, and 1 twenty-sample composite.

Examination of table 1 reveals a significant variation in the concentrations of atrazine and alachlor in the samples taken randomly from the plot. The average concentrations of the 20 individual samples were 103 mg/kg (milligrams per kilogram) for atrazine and 135 mg/kg for alachlor. The 20-sample composite analyses yielded concentrations of 116 and 133 mg/kg, respectively. The averages of the four 5-sample composite analyses were 93.2 mg/kg for atrazine and 125 mg/kg for alachlor.

The average concentrations for the 20 samples provide the best measure of the pesticide concentrations in that plot. The single 20-sample composite provided a measure of average concentrations but no information on variability. Compositing reduces laboratory costs by decreasing the number of individual analyses and smooths the unavoidable spatial variability resulting from uneven pesticide application and small-scale variations in soil properties. Having several composites allows some measure of plot variability.

Soil Water

Because methods of analysis for pesticides in soil usually are less sensitive than methods available for the analysis of water, residue levels in soil water are critical in the characterization of leaching potential. Soil-water collection and analysis permit tracking of pesticide movement in the soil water after pesticide residues in the soil are no longer detectable by standard methods of analysis.

Methods of Collection

Many different soil-water samplers have been introduced in the last few decades; they vary in shape, size, and chemical and physical properties of their materials. The differences among the various samples and the problems involved in their use are reviewed by Hornby and others (1986) and Litaor (1988).

There are two basic types of samplers: (1) zero-tension lysimeters, which rely on gravity to move the soil water into the sampler, and (2)

Table 1. Comparison of individual soil-core analysis (TS) with composited soil-core analysis (TS-C) for atrazine and alachlor on a corn-producing silt-loam soil

[Concentrations are in milligrams per kilogram. Numbers in parentheses are computed concentrations]

Sample identification number	Atrazine	Alachlor	Sample identification number	Atrazine	Alachlor
TS-3	97.6	53.3	TS-1	81.5	13.8
TS-8	37.4	15.1	TS-9	111	61.5
TS-13	8.7	0.9	TS-14	170	153
TS-16	66.4	37.8	TS-17	149	200
TS-18	84.9	23.8	TS-19	311	314
Average of 5 samples	(59.0)	(26.2)	Average of 5 samples	(164)	(149)
Standard deviation	(36.1)	(20.2)	Standard deviation	(88.8)	(118)
TS-C-1	72.6	27.8	TS-C-2	96.2	87.2
TS-4	238	167	TS-2	59.8	486
TS-5	50.7	27.4	TS-10	70.9	22.5
TS-6	120	73.8	TS-12	108	74.9
TS-7	58.1	99.3	TS-15	63.5	277
TS-11	110	57.6	TS-20	57.4	548
Average of 5 samples	(116)	(85.0)	Average of 5 samples	(71.9)	(282)
Standard deviation	(75.2)	(52.6)	Standard deviation	(20.7)	(235)
TS-C-3	101	65.4	TS-C-4	103	320
TS-C-1	72.6	27.8	TS-C-5	116	133
TS-C-2	96.2	87.2	Composite of 20 samples		
TS-C-3	101	65.4	Average of 20 individual samples	(103)	(135)
TS-C-4	103	320	Standard deviation	(70.8)	(158)
			Average of four 5-sample composites	(93.2)	(125)
			Standard deviation	(14.0)	(132)

suction lysimeters, which rely on a negative atmospheric pressure to pull the water from the soil into the sampler. Most of the zero-tension samplers are difficult to install. However, the suction lysimeter, which basically is composed of an evacuated tube and ceramic cup, can be easily installed and used onsite.

Suction Lysimeters

The suction lysimeter is inexpensive, easily installed, and reliable in the extraction of soil water. The suction lysimeter's basic component is a porous ceramic cup through which the soil water is pulled by negative atmospheric pressure. The ceramic cup is placed on one end of a tube, which serves as a reservoir for the collected water and as an extension from the ground surface to the desired sampling depth. The upper end of the cup is sealed with a rubber stopper through which a flexible tube protrudes. The flexible tube can be connected to a vacuum pump, allowing the evacuation of air from within the lysimeter. The flexible tube then can be pinched closed to maintain the partial vacuum and allow soil water to be slowly drawn into the lysimeter.

Installation

The suction lysimeter is installed by augering or pressing a borehole to a depth of 2 inches below the desired depth of the ceramic cup. Silica flour then is placed in the borehole to a depth of 2 to 3 inches, and the suction-lysimeter cup is placed firmly into this bed. Additional silica flour is placed in the annular space around the cup until it is covered by at least 2 inches. The use of silica flour packed around and beneath the porous ceramic cup during installation of the suction lysimeter maintains the hydraulic connection between the porous cup and the soil water. The enhanced hydraulic connection is due to the increased capillary rise created by the fine-grain silica flour. The use of a more coarse-grain material, such as sand or backfill, would decrease the capillary rise and weaken the hydraulic connection between the soil water and the porous ceramic cup (Brown, 1987). The installation of the suction lysimeter is completed by backfilling the remaining annular space to the ground surface with bentonite granules or powder. The use of bentonite

prevents movement of surface water down the sides of the suction lysimeter and into the porous ceramic cup.

The installation of the suction lysimeter should take place at least 2 weeks (longer if soil is dry) prior to an application of pesticides to the study plot. This allows time for the materials used to fill the annulus above and around the porous ceramic cup to equilibrate with the soil moisture. Also, an initial soil-water sample needs to be taken before pesticide application to determine background chemical concentrations.

A depth-increment system that will compliment the soil-core data is suggested when installing suction lysimeters (fig. 5). The ceramic cup of the suction lysimeter should be placed in the center of the soil-core interval. In this way, all soil-core analyses can be compared with soil-water analyses over the same approximate depth interval. For example, if soil cores are collected at 6-inch intervals to 2 feet, the ceramic cup should be placed at depths of 9, 15, and 21 inches. Successful operation of the suction lysimeter at a 3-inch depth is unlikely and should be omitted. If the soil cores continue with 1-foot intervals from 2 feet and deeper, the ceramic cups should be placed at 2.5 feet, 3.5 feet, and so forth.

Two suction lysimeters are suggested for each depth to provide composite samples representative of average leaching conditions and to provide additional leaching water for analysis. When there is little soil moisture, suction lysimeters yield small volumes of soil water. Because laboratory detection levels increase as the volume of sample decreases, large sample volumes are desired. Extraction of larger than needed sample volumes should be avoided because the soil surrounding the ceramic cup should not be excessively drained. Excessive draining in the vicinity of the suction lysimeter may result in convergence of unsaturated flow lines to the porous ceramic cup and enhance solute transport. Therefore, the optimum sample volume is the minimum required for laboratory analysis.

Operation

Suction lysimeters are used in conjunction with tensiometers. The tensiometer indicates

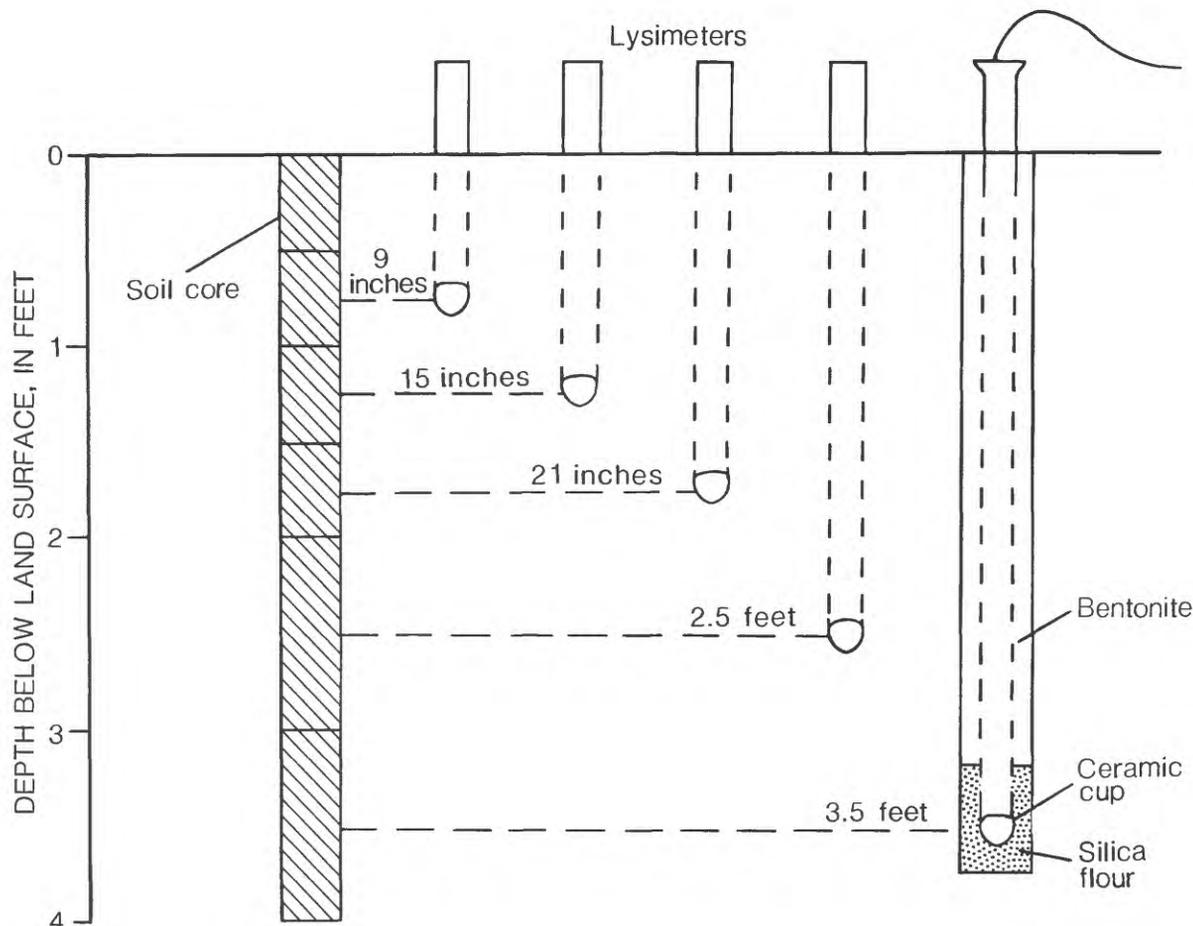


Figure 5. Installation of suction lysimeters in relation to soil-core sampling scheme.

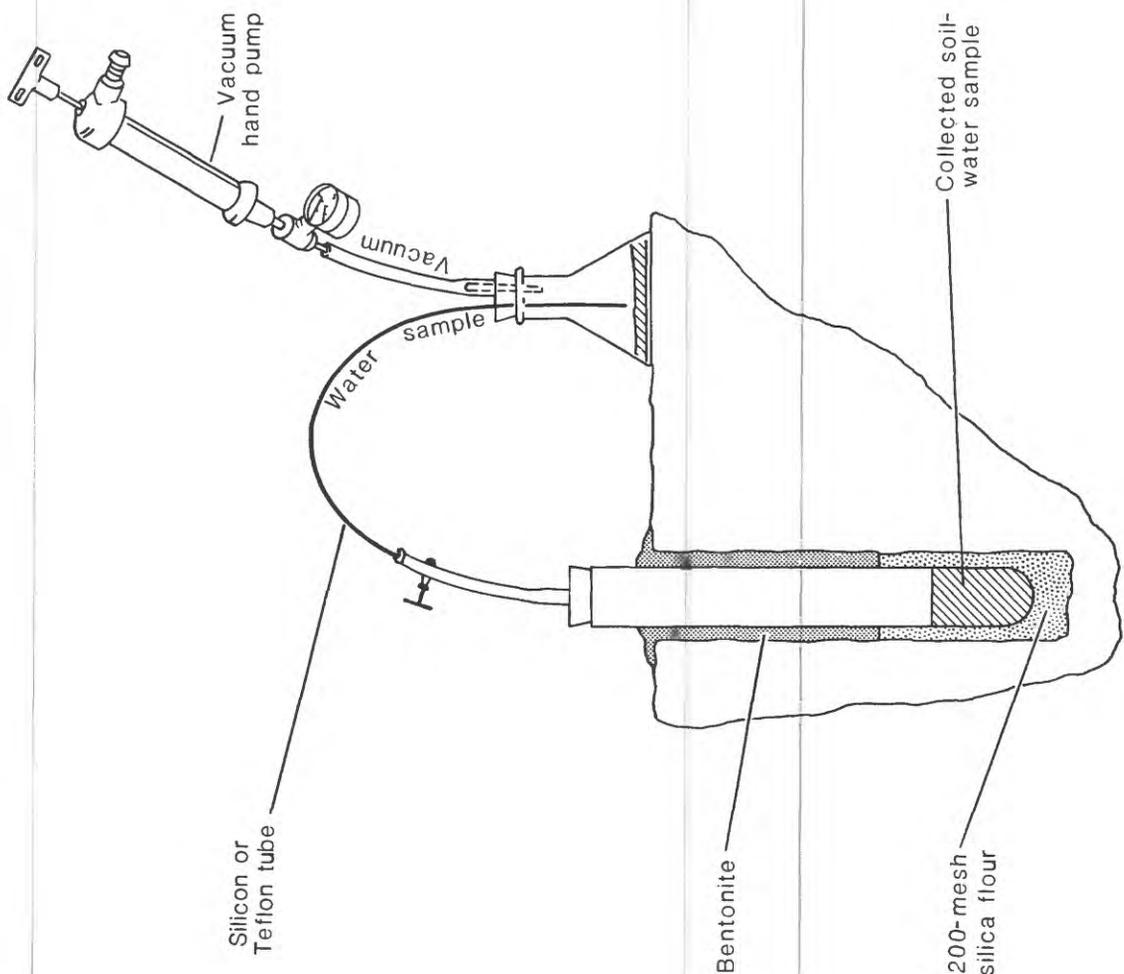
approximately how much water is available within the soil for sampling and how long and how large a suction should be maintained to obtain the sample. For example, if the tensiometer reading indicates a soil-moisture content greater than field capacity, the suction lysimeter can be sampled within hours after the application of suction. Tensiometer readings showing soil-moisture content much less than field capacity indicate less water is available for sampling, and several days may have to lapse between application of suction and sampling.

The amount of vacuum placed on each suction lysimeter will depend on the soil type and the amount of soil water present. Typical suction values applied are 60 to 70 centibars. To extract water the vacuum placed on the suction lysimeter needs to be greater than the in-situ soil-water tension. If vacuum in the suction lysimeter decreases to less than the in-situ

tension, soil water will move out of the porous cup back to the soil matrix. Addition of water to the suction-lysimeter tube to replace the extracted sample volume is questionable. The additional water will dilute the concentrations of any chemical dissolved in the soil water. If enough water was added, the hydraulic gradient in the immediate vicinity of the ceramic cup could be reversed, transporting the dissolved constituents away from the sampler.

Soil water in a shallow suction lysimeter (6 foot or less) can be collected with the suction from a small vacuum pump (fig. 6). A clean silicon or Teflon¹ tube is inserted into the lysimeter through either the suction tube or the opened lysimeter (remove rubber stopper) to the

¹ The use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.



A.



B.

Figure 6. (A) suction-lysimeter installation and (B) lysimeter installed onsite.

bottom of the ceramic cup. To avoid catching the end of the tubing on the lip of the ceramic cup, a length of glass tubing can be attached to the longer silicon or Teflon tubing. The glass acts as a weight, keeping the flexible tubing straight and allows complete removal of the sample into a reusable glass flask. The addition of the glass tubing necessitates the removal of the rubber stopper and the evacuation tube. Care should be taken when loosening the stopper to prevent sucking soil or dust into the lysimeter. The stopper and the top of the lysimeter pipe should be cleaned with a brush and wiped clean with a towel before opening.

Pressure-suction lysimeters are used for depths greater than 6 feet. These lysimeters are approximately 2 feet long and have two tubing lines attached. The one line is used to evacuate or pressurize the lysimeter. The other line extends to the bottom of the ceramic cup to allow extraction of a sample when the lysimeter is pressurized. Care should be taken to keep the tubing ends free of dust and dirt.

Soil-Water Sample Scheduling

The frequency of sampling soil water depends on the permeability of the soil. Permeable soils require frequent sampling because recharge water (with solute) percolates rapidly through permeable soil. A sampling schedule similar to that for the soil-core samples would be flexible enough to account for pesticide-mobility characteristics, soil characteristics, and recharge. This allows a comparison between soil and soil-water analyses at each sampling interval.

Use of Tracers for Soil and Soil-Water Sample Scheduling

The use of conservative (one that does not degrade or sorb to soil particles) organic or inorganic tracers is suggested to improve estimates of probable leaching rates and to economize the analysis of samples. The tracer should be very soluble so that it moves easily through the soil with the water. Suction lysimeters are used to quickly monitor the absence or presence of the tracer onsite. One of the most common inorganic tracers is potassium chloride. Potassium chloride can be detected by the titration method (Black, 1965) or with a

conductivity meter. The suction lysimeter can be evacuated, and a small sample of water collected for tracer analysis. If no tracer is detected, the remaining sample volume in the suction lysimeter is allowed to return to the soil. This is accomplished by eliminating the negative pressure within the suction lysimeter. Soil and soil-water samples should be collected down to and at least one depth interval below the deepest detection of the tracer. Not only does the use of tracers help determine sampling times and depths, but it also provides additional information on solute transport.

Ground Water

Well Siting

The direction of shallow ground-water flow must be known to properly site monitoring wells. The discussion that follows is applicable to both the prospective and retrospective studies. If the lateral direction of shallow ground-water flow can be determined from existing wells near the study plot, then the design and placement of monitoring wells can proceed. If there are no preexisting wells or data to determine the direction of ground-water flow, the following approach is suggested.

Initially, the surface topography around the study plot should be noted, and the surface altitudes determined from topographic maps. Shallow ground-water flow can be visualized on a preliminary basis as a subdued replica of the topography. Shallow ground water generally will flow from an area of the highest ground-surface altitude towards an area of the lowest ground-surface altitude. This generalization can be used to describe the slope of the water table and to plan the location of a minimum of three monitoring wells that will be used to define more accurately the lateral direction of shallow ground-water flow.

It is suggested that an initial monitoring well be located in the upgradient part of the study plot, as indicated by preliminary evaluation of the direction of shallow ground-water flow; that is, at a relatively high ground-surface altitude. The second and third wells should be located downgradient from the first in such positions as to form an equilateral triangle. Preferably, the triangular area would

enclose the primary area of interest in the study.

After these wells are installed and an altitude of the measuring point on the top of the well casing has been established, water-level altitudes can be obtained. The altitudes of ground water in these wells can be used to establish the direction of ground-water flow more accurately. If additional wells are necessary to improve definition of the flow direction, these initial results can be used to determine the location for such wells.

The wells can also be used for monitoring water-level changes and ground-water chemistry. At each well location, a minimum of two wells should be constructed. The first well should have the top of its screen placed just below the water table. This placement permits sampling of the top of the water-table aquifer, which should have the largest concentrations of pesticides if leaching has been vertical. A second well at the same location should have the top of its screen placed at least 10 feet below the first. Water samples from the second well can be used to verify a vertical gradient in solute concentrations, and the well can act as a backup sampling point in the event there is a large decline in the water table. If pesticides are found in the water-table aquifer, it may become necessary to drill additional wells to define the extent of pesticide movement.

Well Construction

There are many drilling techniques available for well construction: solid-stem augering, hollow-stem augering; cable-tool drilling; direct-circulation mud-rotary drilling; reverse-circulation mud-rotary drilling; and air-rotary drilling. Barcelona and others (1983) or Shuter and Teasdale (1989) and Hackett (1987) provide more detailed discussions of each drilling technique. The effects of drilling fluids on ground-water chemistry is examined by Brobst and Buszka (1986).

The selection of a drilling method should be based on the type of well needed and the earth materials in which it is drilled. The following considerations should be made:

1. The ability of the method to penetrate all anticipated earth materials, at a desired

rate, and to construct a borehole of desired diameter for well installation and for the placement of a gravel or sand pack and necessary formation-sealing material, such as bentonite or cement.

2. Identification of lithology for development of a geologic log of all formations and materials penetrated, including physical characteristics and visual description of color, texture, and other properties.
3. Collection of samples of aquifer fluids during drilling and prior to well construction, while at the same time minimizing potential for cross-contamination.
4. Collection of "undisturbed" soil samples from the center line or sidewall of the borehole (this objective often requires that the drilling be halted while soil samples are collected from the bottom of the incomplete borehole).
- 5a. Completion of a monitoring well in the borehole during the initial construction process; that is, constructing a well as the borehole is drilled or constructing a well in the borehole immediately after the drilling tools are removed.

or

- 5b. Completion of a monitoring well in the borehole following a time lapse for interpretation of geologic or geophysical data from the borehole. Geophysical logging of the borehole is desirable in most situations.

The use of a hollow-stem, continuous-flight auger is generally appropriate for drilling wells to monitor shallow water-table aquifers. The hollow-stem auger is capable of drilling as much as 150 feet into unconsolidated material. The augering procedure normally uses no drilling fluids, thereby minimizing the potential of contamination of geologic materials by the drilling process (Shuter and Teasdale, 1989). Soil-core samples can be obtained during the drilling process by inserting a Shelby tube or a split-spoon (split-barrel) sampler inside the hollow stem, lowering the assembly to the

bottom of the hole, and driving the sampling tube into the undisturbed profile (Shuter and Teasdale, 1989). The core samples can be used in the lithologic description of materials penetrated. Once the borehole has been drilled to the desired depth, a small-diameter well casing with a well screen can be inserted inside the hollow stem. With the use of a well swab to prevent sand-plug formation in place, the hollow-stem auger can be pulled out of the borehole leaving the well casing below the water table. The well casing then can be grouted. Details of a procedure for placement of a well casing below the water table using a well swab to prevent sand-plug formation in a hollow-stem auger are provided by Perry and Hart (1985). In most cases, the hollow-stem auger will produce a sufficiently deep borehole for a small-scale ground-water study designed to detect the leaching of pesticides from normal agricultural use. Where deeper wells are needed or where consolidated formations are encountered, other drilling techniques may be required. Shuter and Teasdale (1989) describe a variety of drilling techniques.

After the first hole has been drilled from the ground surface to the desired depth, the soil cores from this site may be used for lithologic identification. For any other wells drilled on the same plot, the first 18 inches of earth can be removed with a shovel, reducing the possibility of soil from these upper zones from contaminating the lower drilling depths. This is desirable for retrospective studies, as the first 18 inches of soil often contain the larger concentrations of pesticides.

To properly define the movement of pollutants vertically and laterally, "it is essential to collect depth-discrete water level data" (Hallberg and others, 1984). The water-table aquifer or uppermost aquifer provides the starting point for determining the vertical movement of a pesticide in the saturated zone. This data can be obtained from "well clusters" or "piezometer nests," which are groups of two or more wells with short screens located very near each other and which penetrate different depths of the aquifer; that is, each well is screened at a different depth to obtain two-dimensional sampling of the aquifer at each well cluster. Ideally, at each cluster there should be a well near the surface of the

water table, a second well screened below this, and if necessary, a third well screened even lower. There should be at least three well clusters spatially distributed across the study area. Each well in the cluster should be individually cased. This construction procedure is suggested in lieu of the construction of a multiple-screen well because the integrity of the individual seals for a multiple-screened well may be suspect.

A 2-inch well diameter accommodates most sampling devices. There are several casing-material choices. The following materials were ranked (in the order listed) by the U.S. Geological Survey as to their inertness and suitability as casing materials: glass, Teflon, stainless steel, polyvinyl chloride (PVC), black pipe, and fiberglass (Imbrigiotta and others, 1988). A combination of materials for well casing is suggested, specifically, "a Teflon or stainless-steel screen and casing in the water bearing zone and PVC casing for the remainder of the hole" (Imbrigiotta and others, 1988). This procedure is suggested for both volatile and nonvolatile pesticides of expected small concentrations in a noncorrosive environment; that is, a pH greater than 5.0, no iron precipitation, and small concentrations of organic solvents. No organic-based solvents or sealers should be used in well construction because of the possibility of contamination. Casing joints should be threaded and screwed together, not glued together. Local and State requirements for materials used in the construction of monitoring wells should be checked.

After completion of the borehole, the well casing and screen are lowered into the hollow-stem auger to the depth of interest, and the auger is withdrawn. Generally, unconsolidated material below the water table will collapse around the casing and screen. If aquifer material is smaller than the well-screen slots, it may be necessary to place a coarser material around the screen before auger withdrawal. If the borehole remains open after augers are removed, quartz sand or pea gravel should be filled in around the screen to several inches above the screened interval. Gibb and Barcelona (1984) suggest a 1-foot layer of fine Ottawa or silica sand be placed above a pea-gravel screen pack. Above this, a layer of

bentonite pellets should be placed in the annular space to prevent movement of water down the borehole. The bentonite pellets, upon expansion, should provide a seal to prevent downward migration of bentonite slurry and neat-cement seals. The slurry may be followed by bentonite powder up to within 2 to 3 feet of ground surface. A final cement-grout cap should be placed to a depth of the probable deepest frost (Porter and Trautmann, in press); this protects the well from frost heaving. It is important to keep any use of cement away from the screened interval because grout in contact with well water may cause pH changes in the well water and thereby affect the pesticide persistency in that well water.

Using backfill material removed from the well borehole during drilling to fill the annulus is not suggested because the material could introduce pesticide residues into the borehole from the surface. The effects of the materials used to fill the annular space between well casing and well bore are expected to be more important than the well-casing material because of the relatively greater surface-area contact of solutes with aquifer solids than with well-casing materials (Keith and others, 1983).

Sample Scheduling

Once the wells are in place, ground-water samples can be collected for water-quality determinations. At a minimum, all wells should be sampled once a month for 2 years and after periods of major recharge (major storms, snowmelt, or irrigation). It is possible that leaching pesticides may appear in very shallow ground water beneath the field within the first period of major recharge following pesticide application. Sampling over an extended period of several years may be necessary to get a range of natural climatic conditions and to give chemical residues additional time to migrate downward. If no irrigation is practiced and the first year of the study receives less-than-normal rainfall, then a second year may be necessary to locate residues that do not leach in the first year.

Assuming a retrospective study plot has had several years of seasonal pesticide use, pesticides may be detected in well samples at any time of the year. However, the two optimal

times for sampling beneath and just downgradient of the study plot are shortly after pesticide application in late spring and early summer and during the winter-spring snowmelt.

Sample Collection

Before a well is sampled, it must be purged of its standing water or storage water until the well yields representative aquifer water upon pumping. Storage water is water that does not come into contact with the flowing ground water (Wilson and Rouse, 1983). It is necessary to purge the well because water standing in the casing has the opportunity to interact with the well-casing material and exchange with atmospheric gases.

In the past, the most common method used to obtain a representative aquifer sample was to flush the well by pumping a specified number of well volumes of water. This procedure is now considered outdated. It is suggested that each time a well is sampled the specific conductance, pH, and temperature of the water be allowed to stabilize before taking a sample that is considered representative of the aquifer (Hardy and others, 1989).

Onsite measurement of chemical constituents is best accomplished with an in-line, closed measurement cell (Wilson and Rouse, 1983). When the values of specific conductance, pH, and water temperature are observed to vary less than 5 percent, 0.1 standard unit, and 0.2 °C, respectively, during pumping, the well may be presumed to have been adequately flushed for representative sampling. When in-line measurement cells are not practical, conductivity and standard pH meters and thermometers are used. All containers used for measurements should be rinsed three times with representative well water.

When a well has been drilled and developed, a pumping test or a slug test may be conducted to provide hydrologic information to determine the rate and period of time each well should be pumped prior to the collection of a sample. Small 2-inch wells should not be pumped to the point of dryness. A pumping rate slow enough to be continuous over long periods of time is necessary. Overpumping can cause excessive

silt and clay fines to be drawn into the well, and dewatering of the gravel pack may cause water-chemistry changes through aeration (Barcelona and others, 1985).

Pumps used to purge and sample wells vary. Table 2 outlines pump choices for sampling and purging of small-diameter shallow wells (Barcelona and others, 1985). The sampling pump selected should be constructed so that only relatively nonreacting materials, such as stainless steel, Teflon, or Viton, contact the ground water. Syringe-type pumps and gas-lift or suction-lift type pumps are not suggested for ground-water sampling. It is advised that small, shallow wells be purged slowly. The peristaltic pump has a pumping rate of 0.2 to 1 gallon per minute, which can be adjusted to a flow rate slow enough so as not to pump the well dry during purging.

Imbrigiotta and others (1988) compared the ability of seven different samplers to recover purgeable organic compounds from ground water. The results of their study, conducted with each of the seven samplers at three different sites, indicated that the peristaltic (suction-lift) pump and the syringe pumps were the least effective samplers at collecting purgeable organic compounds in ground water. The point-source bailer (Teflon or stainless steel), bladder pumps, helical rotor submersible pumps, and gear-driven submersible pumps are all constructed to allow the ground-water sample to contact surfaces of stainless steel, Teflon, Viton-type materials only.

In the choices of sampling devices, sample-tubing choice is critical. Teflon and polypropylene and linear polyethylene are suggested. Any tubing constructed of materials containing plasticizers and stabilizers should be avoided.

A combination of pumps may be used for evacuation and for sampling. A large well may be evacuated with a suction-lift pump but sampled with another type of pump. If a Teflon bladder-type pump is used, it is important that there is enough water to completely cover the pump to prevent the introduction of air into the water sample. Sampling devices should minimize the introduction of air and gas bubbles into the sample (Schuller and others, 1981; Gibb

and Barcelona, 1984). For wells without enough water to cover the bladder-type pump, a Teflon or stainless-steel bailer resembling a long, narrow bucket may be used. All sampling devices should be flushed three times with at least 1 quart of representative well water before a sample is collected.

Sample Transport

Once the sample is obtained onsite, it must be transported to the laboratory for its appropriate analysis with minimal alteration or contamination. Samples should be carefully placed in appropriate containers with onsite information recorded and the sample identified. The containers should be packed to prevent sample loss or sample modification by environmental conditions during shipping.

Containers

Soil, soil-water, and ground-water samples should be placed in appropriately sized wide- or narrow-mouth glass bottles that have been cleaned in the following manner. They should be washed with detergent (nonphosphate type) and hot water, rinsed with tap water, then distilled water, air dried, and then oven dried at 105 °C. Finally, the bottles should be solvent rinsed with n-hexane and allowed to air dry. Care should be taken to chill the sample immediately and to shield it from direct sunlight.

Records

All samples need to have collection records, with a map to show the location of the sampling site. The following information should be written in waterproof ink for each sample in a log book or on a well schedule and on a tag secured to the bottle:

1. Depth to water if measured;
2. Pumping time before sampling;
3. Sampling point and depth;
4. Sample identification number;
5. Time and date;
6. Tracer concentration; and
7. Name of sampler.

Table 2. Summary of characteristics of pumping devices available for sampling small-diameter ground-water monitoring wells

[Modified from Barcelona and others, 1985. <, less than]

Pumping device	Minimum well diameter (inches)	Approximate maximum sampling depth (feet)	Typical sample delivery at maximum depth (gallons per minute)	Flow-control ability	Materials ¹ (sampling device only)	Potential for chemical alteration	Ease of operating, cleaning, and maintenance	Approximate cost for complete system ²
Bailers	0.5	Unlimited	Variable	Not applicable	Any	Slight to moderate	Easy	<\$100-\$200
Bladder pumps	1.5	400	0.5	Good	Stainless 316, Teflon, Viton, PVC, silicone	Minimum to slight	Easy	\$1,500-\$4,000
Gear-driven submersible pumps	2.0	200	.5	Poor	Stainless 304, Teflon, Viton	Minimum to slight	Easy	\$1,200-\$2,000
Helical rotor submersible	2.0	125	.3	Poor	Stainless 304, EP DM, Teflon	Slight to moderate	Moderately difficult	\$3,500

¹ Materials dependent on manufacturer and specification of optional materials.

² Costs are dependent on materials specified for devices and selection of accessory equipment and are based on 1989 prices.

Packing and Shipping

The following sample-packing and shipping procedures are suggested to ensure against breakage of and temperature increases in the samples:

1. Samples should be shipped in styrofoam-insulated boxes or styrofoam coolers.
2. The individual glass sample containers should be wrapped in foam or plastic bubble to separate the sample bottles during shipping to prevent breakage.
3. Frozen-gel packs can be placed in each cooler but should not be in direct contact with any of the glass sample containers. Because the frozen-gel pack maintains a temperature of less than 0 °C for several hours, it could freeze the liquid samples inside of the glass containers and cause the containers to crack.
4. To help maintain the frozen-gel-pack temperature and keep the cooler temperatures around 4 °C, ice sealed in plastic bags can be added. The ice should be bagged to prevent seepage during transport.
5. Sample delivery should be made within 24 hours of sample collection and packing. Either priority mail or other overnight mail service should be used. It is recommended that the samples be extracted within 14 days after reaching the laboratory.

QUALITY ASSURANCE AND CONTROL

Variability in analytical results occur even under rigorously controlled onsite and laboratory conditions. For example, errors can be introduced into sample results through: (1) Selection of a sampling location or method that produces a sample that fails to represent the conditions of interest; (2) improper use of instruments; (3) contamination of the sample; and (4) inappropriate methods of analysis. These errors can be so small that they cannot be measured, or so large that their presence is obvious. Quality-assurance programs are used

to detect and control errors and to maintain and document the reliability of results. Quality assurance is the term used to describe programs and the sets of procedures, including (but not limited to) quality-control procedures, which are necessary to assure data reliability. The term includes both practices employed by sources outside of an analytical laboratory (onsite conditions) and practices used by a laboratory to assure the quality of laboratory data. Quality control is the term used to describe the routine procedures used to regulate measurements and produce data of satisfactory quality (Friedman and Erdmann, 1982). Additional U.S. Geological Survey quality-assurance methods and practices are described in manuals by the Office of Water Data Coordination (1977).

Five types of samples can be submitted for quality-assurance testing: (1) blind split samples; (2) spiked samples; (3) standard reference samples; (4) distilled-water blank samples; and (5) filter blank samples (Blanchard, 1987). Blind split samples are exact duplicates, either a water sample that has been churned and split or a soil sample that has been homogenized and split. Each duplicate is given a different coded number and submitted to the analytical laboratory as a unique sample (Wershaw and others, 1987). Spiked samples result from the addition of a known amount of one or more of the compounds of interest to the sample prior to analysis. Analysis yields accuracy data (from a synthetic matrix) or recovery data (from an authentic matrix) (Wershaw and others, 1987). Standard reference samples are a mixture of compounds of interest prepared in a suitable solvent and diluted to approximate environmental concentrations. Distilled-water blanks are sent as samples for analysis to check the possibility of cross contamination at the laboratory. Filter blank samples are distilled water passed through any filtering device. A pair of blank samples can be used for quality assurance for each sampling crew and distilled-water reservoir (Blanchard, 1987).

SUMMARY

This report contains some guidelines for designing and conducting unsaturated- and saturated-zone studies that involve pesticide leaching. These guidelines include:

1. Design of prospective and retrospective studies;
2. Methods of obtaining hydrologic and geologic information;
3. Methods and schedules for sampling of soil, soil water, and ground water;
4. Quality assurance and control; and
5. Methods of laboratory analysis available.

Onsite leaching studies can be categorized into two groups--prospective and retrospective studies. A prospective study tracks the movement and fate of pesticides in soil, soil water, and ground water from the time of application to a predetermined level of dissipation or length of time in an individual field or plot. The dissipation can be monitored by collecting temporal and areal soil-core data, suction-lysimeter data, and data from wells specifically installed for the study. The major objective of this type of study typically is to define the depth of leaching of the pesticide and the half-life of parent compounds and degradates. A retrospective study is appropriate for pesticides currently being used, for which there is a known or suspected potential for leaching. This type of study may be initiated because of documented ground-water contamination. The primary objective of a retrospective study is to determine the degree that a particular pesticide has leached to ground water in specific fields characteristic of a certain crop use and associated agricultural practices. The retrospective study focuses on the water-table aquifer but also characterizes the leaching pattern in the unsaturated soil profile.

Field information is needed in both study types. This information includes climatic data, hydrogeologic properties, and soil properties.

Climatic information includes daily measurements of rainfall, evaporation, radiation, wind, temperature, and barometric pressure. Irrigation scheduling is also important when applicable.

Hydrogeologic information includes a determination of the stratigraphy, depth to ground water, aquifer composition and permeability, and direction of ground-water

flow. Preliminary information for most areas is available from existing publications of government agencies and academic institutions. Site-specific information requires onsite exploratory drilling and geophysical logging and the installation of wells for monitoring water levels and the extracting of ground-water samples.

Soil properties of interest are soil classification, particle-size distribution, bulk density, percentage of organic material, permeability, and percentage of soil moisture. Particle-size distribution analyses must be performed in a laboratory. Bulk density can be measured in the laboratory or onsite by means of a gamma-radiation probe. Percentage of organic material in the soil must be measured in the laboratory. Soil permeability is one of the most important factors to be determined in a leaching experiment. It can be estimated from soil particle-size distribution, or measured in the laboratory or onsite with permeameters. Soil moisture can be measured in the laboratory or onsite with tensiometers or neutron-moisture meters. Available water for each soil type is the difference between the field capacity and the wilting point.

Soil cores can be obtained by using hand-coring tools or truck-mounted coring rigs. Shallow cores are best collected by hand or by light-weight coring rigs to prevent soil compaction. Precautions must be taken to prevent contamination of the sample during coring. Soil-core sampling schedules should take into account soil lithology, water availability, and chemical properties of the pesticide. Advantages of compositing samples include decreasing laboratory costs (fewer samples) and smoothing the unavoidable variability of chemical-concentration data.

Soil-water sampling can be accomplished by the use of suction lysimeters. The ceramic cup is placed at a depth that coincides with soil-core sampling. The sampling schedule should follow that of the soil cores. Compositing of soil-water samples provides additional volume during dry-soil conditions. The use of conservative tracers on study plots or fields helps determine sampling times and depths and aids in pesticide analysis.

Ground-water sampling involves proper well siting, well construction, and sample scheduling and collection. Wells should be clustered to provide two-dimensional information on ground-water flow direction and gradient. Information on lithology and aquifer composition is also gathered during drilling. Proper well construction is necessary to prevent contamination of the borehole during the drilling process. Proper location of the well screen, selection of casing material, and well packing and sealing are also important factors in well construction.

Proper methods of sample collection, storage, and shipping to analytical laboratories should be used to minimize the potential of contamination, degradation, or loss of the water sample. A quality-assurance program is required to detect and control sampling and analytical errors and to maintain and document reliability of results.

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APPENDIX I.--LABORATORY PROCEDURES FOR ANALYSIS OF SOIL SAMPLES

Laboratory analyses of pesticide-residue concentrations generally are separated into two groups--water samples and soil samples. This grouping is a result of the different chemical techniques needed to extract the residue from the sample. These techniques vary according to the method used to quantify the concentration and the accuracy desired. Quantification methods range from high-pressure liquid chromatography with mass spectrometry, to gas chromatography with flame-ionization detectors, to onsite methods, including immunoassay techniques.

Standard laboratory techniques for most pesticide-residue analyses of water samples are available (Minear and Keith, 1984). However, procedures for soil samples are not as common. Soil-sample extraction procedures for five pesticides, as developed by John Tessarri at the Colorado State University Physiology Laboratory, are listed in this Appendix. Documentation of the analytical results of the extraction procedures by using immunoassay techniques are available (Bushway and others, 1988; E.M. Thurman, U.S. Geological Survey, written commun., 1989).

A. Extraction and Analysis of Atrazine

1. SAMPLE SIZE USED FOR ANALYSIS

A 50-gram sample of soil is used for this method.

2. DETECTION LEVEL

Using a 50-gram sample, 50 grams per milliliter = 50 milligrams per microliter X 3 microliter = 150 milligrams atrazine

$$\frac{(100 \text{ picograms per microliter}) (3 \text{ microliters})}{150 \text{ milligrams}} = 2.0 \text{ parts per billion (theoretical) .}$$

3. SAMPLE PREPARATION

Obtain representative soil samples from U.S. Geological Survey. These samples will be used as controls and for spiking purposes. Sieve soil through a 2-millimeter sieve. Soil samples are not dried or ground before analysis.

4. EXTRACTION

- a. Place 50 grams of soil in a 150-milliliter French square bottle and add 100 milliliters of acetonitrile (ACN).
- b. Extract soil-ACN solution using a polytron for 5 minutes at slow speed. Rinse polytron rotor into soil-ACN solution with a few milliliters of acetone, let settle.
- c. Filter the supernatant through Whatman No. 42 filter paper in a Buchner funnel under vacuum and collect filtrate. Polytron soil with another 50 milliliter of ACN for 5 minutes. Add contents of French square bottle to the Buchner funnel and collect filtrate. Rinse French square bottle with three 50-milliliter volumes of ACN, adding each rinsate to the Buchner funnel. Collect filtrate. Gravity filter the resulting filtrate through Whatman No. 1 filter paper. Collect this filtrate in a 1,000-milliliter boiling flask. Rinse the filter paper with three small volumes of ACN.
- d. Reduce the volume of the ACN-soil extract to a few milliliters using a rotoevaporator.

- e. Transfer extract concentrate to a macro-Florisil column, rinse the boiling flask with three small volumes of elution solvent (5-percent ethyl ether in hexane) and transfer to Florisil column. Transfer remaining elution solvent to the Florisil column (total elution solvent volume = 200 milliliters).
- f. Collect elution from Florisil column in a 500-milliliter boiling flask and reduce elution volume to a few milliliters using a rotoevaporator. Transfer elution concentrate to a 13-milliliter graduated tube using hexane rinses. Reduce extract volumes further to 0.5 milliliter and redilute in hexane, ending with a 1-milliliter final volume.
- g. Analyze the final solution by gas chromatography with a nitrogen-phosphorus detector.

5. GAS-CHROMATOGRAPHIC ANALYSIS

Gas chromatograph with a nitrogen-phosphorus detector (HP 5890A) and a DB 5- to 30-meter megabore column.

The chromatographic temperature program is as follows:

$T_o = 180\text{ }^\circ\text{C}$	$T_1 = 200\text{ }^\circ\text{C}$	$T_f = 250\text{ }^\circ\text{C}$
$t_o = 4.0\text{ minutes}$	$t_1 = 4\text{ minutes}$	$t_f = 3\text{ minutes}$
$R_o = 30\text{ }^\circ\text{C per minute}$	$R_1 = 30\text{ }^\circ\text{C per minute}$	$R_f = 0$
$InL = 270\text{ }^\circ\text{C}$	$Det = 280\text{ }^\circ\text{C}$	Carrier flow = 25 cubic centimeter per minute.

6. SPIKING STANDARDS AND CONCENTRATIONS USED:

Standards used for spiking should be in acetone.

LOW SPIKE:

atrazine standard 100 nanograms per milliliter $\xrightarrow{1.0\text{ milliliter}}$ 100 nanograms in 50 grams of soil = 2 parts per billion.

HIGH SPIKE:

atrazine standard 1,000 nanograms per milliliter $\xrightarrow{1.0\text{ milliliter}}$ 1,000 nanograms in 50 grams of soil = 20 parts per billion.

B. Simultaneous Extraction and Analysis of Atrazine and Alachlor

1. SAMPLE SIZE USED FOR ANALYSIS

A 50-gram sample of soil is used for this method.

2. DETECTION LEVEL

Using a 50-gram soil sample:

a. Atrazine

(50 grams per milliliter Fv) = 50 milligrams per microliter X 3 microliters = 150 milligrams.

$$\frac{(100 \text{ picograms per microliter}) (3 \text{ microliters})}{150 \text{ milligrams}} = 2 \text{ parts per billion (theoretical) .}$$

b. Alachlor

(50 grams per milliliter Fv) = 50 milligrams per microliter X 3 microliters = 150 milligrams.

$$\frac{(200 \text{ picograms per microliter}) (3 \text{ microliters})}{150 \text{ milligrams}} = 4.0 \text{ parts per billion(theoretical)}$$

3. SAMPLE PREPARATION

Obtain representative soil samples. Virgin soil samples will be used as controls and for spiking purposes. Sieve soil through a 2-millimeter sieve. Soil samples are not dried or ground before analysis.

4. EXTRACTION

- a. Place 50 grams of soil in a 150-milliliter French square bottle and add 100 milliliters of acetonitril (ACN).
- b. Extract soil-ACN solution using a polytron for 5 minutes at slow speed. Rinse polytron rotor into soil-ACN solution with a few milliliters of acetone. Let settle.
- c. Filter the supernatant through Whatman No. 42 filter paper in a Buchner funnel under vacuum and collect filtrate. Polytron soil with another 50 milliliters of ACN for 5 minutes. Rinse French square bottle and the Buchner funnel using 150 milliliters of ACN and collect filtrate. Gravity filter the resulting filtrate through Whatman No. 1 filter paper. Rinse the filter paper with three small volumes of ACN. Collect this filtrate in a 1,000-milliliter boiling flask.
- d. Reduce the volume of the ACN-soil extract to 2 milliliters using a rotoevaporator.
- e. Transfer extract concentrate to a macro-Florisil column; rinse the boiling flask with three small volumes of elution solvent (5-percent ethyl ether in hexane) and transfer to Florisil column. Transfer remaining elution solvent to the Florisil column. (Total elution solvent volume = 200 milliliters.)
- f. Collect elution from Florisil column in a 500-milliliter boiling flask and reduce elution volume to a few milliliters using a rotoevaporator. Transfer elution concentrate to a 13-milliliter graduated tube using hexane rinse. Reduce extract volumes further to 0.5 milliliter and redilute in hexane, ending with a 1-milliliter final volume.
- g. Analyze the final solution by gas chromatography with a nitrogen-phosphorus detector.

5. GAS-CHROMATOGRAPHIC ANALYSIS

Gas chromatograph with a nitrogen-phosphorus detector (HP 5890A) and a DB 5- to 30-meter megabore column.

The chromatographic temperature program is as follows:

$$T_0 = 180 \text{ }^{\circ}\text{C}$$

$$T_1 = 200 \text{ }^{\circ}\text{C}$$

$$T_f = 250 \text{ }^{\circ}\text{C}$$

$$t_0 = 5.5 \text{ minutes}$$

$$t_1 = 8 \text{ minutes}$$

$$t_f = 6 \text{ minutes}$$

$R_0 = 30\text{ }^\circ\text{C per minute}$ $R_1 = 30\text{ }^\circ\text{C per minute}$ $R_f = 0$
 $\text{InL} = 270\text{ }^\circ\text{C}$ $\text{Det} = 280\text{ }^\circ\text{C}$ $\text{Carrier flow} = 25\text{ cubic centimeter per minute.}$

6. SPIKING STANDARDS AND CONCENTRATIONS USED:

Standards used for spiking should be in acetone.

Spiking Level

1 milliliter of atrazine (100 nanograms per milliliter) in 50 grams soil = 2.0 parts per billion.

1 milliliter of alachlor (200 nanograms per milliliter) in 50 grams of soil = 4.0 parts per billion.

C. Extraction and Analysis of 2,4-D

1. SAMPLE SIZE USED FOR ANALYSIS

25-gram sample of soil is used for this method.

2. DETECTION LEVEL

Using a 25-gram sample: (25 grams per milliliter Fv) = 25 milligrams per microliter = 125 milligrams.

$$\frac{(100\text{ picograms per microliter}) (5\text{ microliters})}{125\text{ milligrams}} = 4.0\text{ parts per billion .}$$

3. SAMPLE PREPARATION

Obtain representative soil samples. Virgin soil samples will be used as controls and for spiking purposes. Sieve soil through a 2-millimeter sieve. Soil samples are not dried or ground before analysis.

4. EXTRACTION

- a. The soil sample is thawed, and 25 grams are placed in a 200-milliliter centrifuge bottle.
- b. 50 milliliters of a 2-percent KOH solution are added and mixed with the soil by swirling.
- c. The centrifuge bottle is covered with a watch glass and placed in a 60 °C water bath for 45 minutes. Bottles then are removed and allowed to cool.
- d. The soil solution then is homogenized with a polytron homogenizer for 5 minutes at a moderate speed followed by centrifugation to produce a soil-free supernate.
- e. This supernate is decanted into a 250-milliliter separatory funnel; the remaining soil plug is resuspended in an additional 25 milliliters of 2-percent KOH and again centrifuged. Supernate from second centrifugation is combined with that of the first.
- f. The combined supernates are extracted with 50 milliliters of diethyl ether (shaken for 1 minute, then allowed to separate). The aqueous phase is transferred to a second 250-milliliter separatory funnel, and the ether phase is discarded.

- g. The pH of the aqueous phase is adjusted to less than or equal to 3.0 using concentrated sulfuric acid.
- h. The pH-adjusted aqueous phase is extracted twice with 50 milliliters diethyl ether, following which the aqueous phase is discarded.
- i. The ether extracts are combined and passed through a reservoir column containing 3 inches of acidified sodium sulfate beneath a glass wool plug (see "Special Materials" for acidified sodium sulfate preparation). The dehydrated ether extract is collected in a 250-milliliter boiling flask.
- j. Reduce the volume of the dehydrated ether extract to a few milliliters by rotary evaporation at 30 °C and transfer with hexane rinses to a 13-milliliter test tube. A small amount of acidified sodium sulfate may be required in the bottom of the boiling flask if residual water is present.
- k. Extract volume is reduced further under nitrogen to 0.5 milliliter.

5. DERIVATIZATION

- a. To the 0.5-milliliter extract add, dropwise, diazoethane derivatizing agent until the yellow color persists (see "Special Materials" for diazoethane preparation). Allow to stand at room temperature for 15 minutes and then bubble nitrogen through the extract until yellow color disappears.
- b. Transfer the derivatized extract to a macro-florisil reservoir column and elute first with a 10-percent diethyl ether and hexane mix and second with a 15-percent mix. The fraction is collected and discarded, while the 15-percent fraction is collected and saved in a 250-milliliter boiling flask.
- c. Reduce the 15-percent fraction volume to a few milliliters by rotary evaporation (30 °C) and transfer to a 13-milliliter test tube. Further reduce this volume under nitrogen to 0.2 milliliter, redilute to 4 milliliters in hexane, again concentrate to less than 1 milliliter, and adjust to a final volume of 1 milliliter with hexane.

6. GAS-CHROMATOGRAPHIC ANALYSIS

- a. Using gas chromatograph with an electron-capture detector and a 1.5-percent OV-17 per 1.95-percent OV-210 column.

The operating parameters are:

column temperature:	175 °C
inlet temperature:	234 °C
transfer temperature:	274 °C
detector temperature:	282 °C .

7. SPIKING-STANDARD CONCENTRATION:

(50 nanograms of 2,4-D acid per milliliter of acetone) (2 milliliters) —————>

100 nanograms of 2,4-D acid per 25 grams of soil = 4 parts per billion.

8. SPECIAL MATERIALS

a. Acidified sodium sulfate

- Place a known mass of anhydrous sodium sulfate in a 1,000-milliliter boiling flask and add pesticide-grade acetone until sodium sulfate is slightly covered.
- To the slurry add 0.5 milliliter of concentrated sulfuric acid per 100 grams sodium sulfate and mix by gently swirling.
- Dry the sodium sulfate by rotary evaporation, transfer to a beaker, cover with aluminum foil, and bake in a 100 °C oven overnight (store in oven when not in use).
- Check acidity by mixing 1 gram of the oven-dried acidified sodium sulfate with 5 milliliters of water; pH should be less than or equal to 4.0.

b. Diazoethane

- In a 125-milliliter Erlenmeyer flask, dissolve 2.3 grams of KOH in 2.3 milliliters of benzene extracted water. Allow solution to cool by placing in a freezer.
- Add to this solution 25 milliliters hexane and return to the freezer for 15 minutes.
- In a glovebox, gradually, in small portions, add 1.6 grams of N-ethyl-N'-nitro-N-guanidine to the hexane and KOH solution. Gently swirl to mix each addition.
- Decant the hexane layer into a glass vial and close with a Teflon-lined cap.
- Store in a freezer (maximum shelf life approximately 1 week).

D. Extraction and Analysis of Trifluralin

1. SAMPLE SIZE USED FOR ANALYSIS

A 50-gram sample of soil is used for this method.

2. DETECTION LEVEL

Using a 50-gram sample, (50 grams per milliliter Fv) = 50 milligrams per microliter X 5 microliters = 250 milligrams.

$$\frac{(50 \text{ picograms per microliter}) (5 \text{ microliters})}{250 \text{ milligrams}} = 1.0 \text{ part per billion .}$$

3. SAMPLE PREPARATION

Obtain representative soil samples. These samples will be used as controls and for spiking purposes. Sieve soil through a 2-millimeter sieve. Soil samples are not dried or ground before analysis.

4. EXTRACTION

- a. Place 50 grams of soil in a 150-milliliter French square bottle and add 100 milliliters of acetonitrile (ACN).
- b. Extract soil-ACN solution using a polytron for 5 minutes at slow speed. Rinse polytron rotor into soil-ACN solution with a few milliliters of acetone. Let settle.

- c. Filter the supernatant through Whatman No. 42 filter paper in a Buchner funnel under vacuum and collect filtrate. Add 50 milliliters of ACN and polytron for another 5 minutes. Pour contents into funnel and with another 150 milliliters of ACN rinse the French square bottle and the contents of the Buchner funnel. Collect filtrate.
- d. Gravity filter the resulting filtrate through Whatman No. 1 filter paper. Rinse the filter paper and the vacuum flask with three small volumes of ACN. Collect the filtrate in a 1,000-milliliter boiling flask.
- e. Add the ACN-soil extract to 500 milliliters of 2-percent Na_2SO_4 solution in a 2-liter separatory funnel. Add 100 milliliters of hexane and shake for 2 minutes. Save the bottom aqueous layer for two further extractions of 50 milliliters of hexane each. After each extraction, the hexane layer is collected in a 500-milliliter boiling flask. The separatory funnel is rinsed with about 10 milliliters of hexane after the final extraction.
- f. Reduce the volume of hexane extract to a few milliliters using a rotoevaporator.
- g. Transfer the extract concentrate to a Florisil column; rinse the boiling flask with three small volumes of elution solvent (12-percent ethyl ether in hexane) and transfer to Florisil column. Transfer remaining elution solvent to the column (total elution volume = 200 milliliters).
- h. Collect elution from Florisil column in a 500-milliliter boiling flask and reduce elution volume to a few milliliters using a rotoevaporator. Transfer the elution concentrate to a 13-milliliter graduated tube using hexane rinses. Reduce extract volume further to 0.1 milliliter and redilute in hexane to a final volume of 1 milliliter.
- i. Analyze the final solution by gas chromatography with an electron-capture detector.

5. GAS-CHROMATOGRAPHIC ANALYSIS

Using gas chromatograph with an electron-capture detector and a DC-200 column (6 feet X 0.25 inch outside diameter). The operating parameters are:

column temperature:	180 °C
inlet temperature:	270 °C
transfer temperature:	280 °C
Carrier flow (nitrogen):	76 cubic centimeters per minute.

6. SPIKING STANDARDS AND CONCENTRATIONS USED:

Standards used for spiking should be in acetone.

LOW SPIKE:

50 nanograms per milliliter standard, 1 milliliter in 50 grams of soil

50 nanograms per 50 grams = 1 part per billion.

HIGH SPIKE:

500 nanograms per milliliter standard, 0.5 milliliter in 50 grams of soil

250 nanograms per 50 grams = 5 parts per billion.

E. Extraction and Analysis of Metolachlor

1. SAMPLE SIZE USED FOR ANALYSIS

A 50-gram sample of soil is used for this method.

2. DETECTION LEVEL

Using a 50-gram soil sample, (50 grams per milliliter Fv) = 50 milligrams per microliter X 3 microliters = 150 milligrams.

$$\frac{(100 \text{ picograms per liter}) (3 \text{ microliters})}{150 \text{ milligrams}} = 2.0 \text{ parts per billion (theoretical) .}$$

3. SAMPLE PREPARATION

Obtain representative soil samples. Virgin soil samples will be used as controls and for spiking purposes. Sieve soil through a 2-millimeter sieve. Soil samples are not dried or ground before analysis.

4. EXTRACTION

- a. Place 50 grams of soil in a 150-milliliter French square bottle and add 100 milliliters of acetonitrile (ACN).
- b. Extract soil-ACN solution using a polytron for 5 minutes at slow speed. Rinse polytron rotor into soil-ACN solution with a few milliliters of ACN.
- c. Filter the soil-ACN solution through Whatman No. 42 filter paper in a Buchner funnel under vacuum and collect filtrate. Rinse French square bottle with 50 milliliters of ACN two times and add rinsate to the Buchner funnel and collect filtrate. Rinse contents of the Buchner funnel with two 50-milliliter volumes of ACN and collect filtrate.
- d. Reduce the volume of ACN-soil extract to 2 milliliters using a rotoevaporator.
- e. Transfer extract concentrate to a Florisil column¹; rinse the boiling flask with three small volumes of elution solvent (60-percent ethyl ether in hexane) and transfer to Florisil column. Transfer remaining elution solvent to the Florisil column (total elution solvent volume = 200 milliliters).
- f. Collect elution from Florisil column in a 500-milliliter boiling flask and reduce elution volume to a few milliliters using a rotoevaporator. Transfer elution concentrate to a 13-milliliter graduated tube using hexane rinses. Reduce extract volumes further to 0.2 milliliter and redilute in hexane to 3 milliliters. Repeat this dry-down procedure two more times ending with a 1-milliliter final volume.
- g. Analyze the final solution by gas chromatography with a nitrogen-phosphorus detector.

¹ Sodium sulfate may require prewashing with 20-percent ethyl ether in hexane to eliminate interfering contaminants.

5. GAS-CHROMATOGRAPHIC ANALYSIS

Using gas chromatograph with a nitrogen-phosphorus detector and a Supelco SPB-608 capillary column.

The operating parameters are:

column temperature:	175 °C
inlet temperature:	170 °C
detector temperature:	220 °C.

6. SPIKING STANDARDS AND CONCENTRATIONS USED:

Standards used for spiking should be in acetone.

LOW SPIKE:

Metolachlor standard, 100 nanograms per milliliter $\xrightarrow{1.0 \text{ milliliter}}$ 100 nanograms in 50 grams of soil = 2.0 parts per billion.

HIGH SPIKE:

Metolachlor standard, 1,000 nanograms per milliliter $\xrightarrow{1.0 \text{ milliliter}}$ 1,000 nanograms in 50 grams of soil = 20 parts per billion.