Guidance for Prospective Ground-Water Monitoring Studies

Environmental Fate and
Effects Division

Office of Pesticide Programs

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INTRODUCTION

The Environmental Protection Agency's (EPA) Office of Pesticide Programs (OPP) initiated a program of ground-water monitoring requirements in 1987 to better understand the impact of pesticide use on ground-water quality. OPP requested that pesticide registrants conduct these ground-water studies to support the registration of pesticides that were determined to have the potential to leach to ground water. This determination of the potential to leach to ground water was based on EPA's assessment of data to determine the mobility and persistence of the compound and EPA's evaluation of available field data and ground-water monitoring data.

Data generated from these studies have proven valuable to OPP scientists and risk managers in better understanding the potential for a pesticide to: (1) impact ground-water quality, (2) contaminate drinking water, and (3) reach ecologically important surface water systems, when used in accordance with label directions. Data from these studies have also proven to be very useful in developing predictive models of pesticide levels in vulnerable ground water (that is, where the ground water is shallow, unconfined, and there are no flow restrictive layers between the surface and the water table). Since development of the original Agency draft guidance for Prospective Ground-Water Monitoring Studies over a decade ago, studies have been conducted for over 50 pesticides. The recommendations in this guidance document represent the Agency's substantial experience accumulated over the last decade in developing and articulating effective procedures for collecting high quality data on pesticide movement into ground water. This document provides registrants with guidance on how to conduct Prospective Ground-Water Monitoring Studies, when to consult with EPA on what aspects of the study and how results should be reported to EPA.

1. OVERVIEW AND STUDY GOAL

Soils, hydrogeology, climate, agronomic practices, and chemical and biological processes vary significantly throughout pesticide-use environments. Predictions of pesticide persistence and mobility derived from core data requirements (e.g., laboratory studies) may not be sufficient to adequately characterize leaching that can occur under actual field conditions. For this reason, EPA requires Prospective Ground-Water Monitoring Studies for some pesticides. Simply stated, a Prospective Ground-Water Monitoring Study involves applying a pesticide and a mobile tracer compound under field conditions that can vary from “typical” to “high exposure”. The crop is grown in the field after the pesticide has been applied and the vadose and saturated zones under the field are monitored over time for residues of the pesticide and important degradates.

The goal of a Prospective Ground-Water Monitoring Study is to determine whether a pesticide will move to ground water under specific field conditions and to determine the concentration in ground water of an applied pesticide, its major degradates and other degradates of concern. EPA uses the results of Prospective Ground-Water Monitoring Studies to help answer questions such as: (1) Is there a high probability that the pesticide will leach in the pesticide use area? (2) Which uses present the greatest potential of the pesticide leaching to ground water? (3) What measures might be effective in mitigating the pesticide leaching?

When these studies are conducted for a new chemical prior to registration, the results can provide evidence not available from laboratory studies that natural factors cause a pesticide to degrade without contamination of water resources. Alternatively, they can provide evidence to indicate that ground-water contamination could result from use according to the pesticide label, and they can help to quantify the levels at which that can occur. These studies are also an important tool for understanding factors that influence the leaching of previously registered pesticides. The data from these studies are helpful in evaluating the effectiveness of a current management strategy (as stated on the product label) for a pesticide that has been shown to leach to ground water. The results of a Prospective Ground-Water Monitoring Study can also be used in exposure/risk assessments. For example, measured concentrations of a pesticide in ground water from a Prospective Ground-Water Monitoring Study can be used to estimate pesticide concentrations in drinking water drawn from shallow private wells.

The site approved by EPA for a Prospective Ground-Water Monitoring Study must have certain characteristics in order for the results to be useful in determining whether a pesticide will move to ground water under field conditions, and, in quantifying concentrations of pesticides and degradates in ground water over time. Depending on the objective of a particular study, the study site may be selected to represent an environment that is highly susceptible to leaching (e.g., sites with coarse-textured soils with low organic matter content and high sand content) or one that represents conditions under which the pesticide is most typically used.

In the past, the Agency had required both retrospective and prospective ground-water studies to be conducted. Today, EPA believes that prospective studies are preferable for purposes of understanding whether a pesticide or degradates move to ground water under actual field conditions and if so, at what concentrations. The prospective study has been designed so that factors that often confound the interpretation of retrospective monitoring studies are eliminated. For example, in the site selection process, sites with prior use of the pesticide or with point sources of contamination are not generally selected for study. Also, since the pesticide is applied according to a current or proposed label, concentrations observed during the study can be directly tied to labeled use.

Clearly, the first step in assessing the need for a prospective ground-water study is to assess the pesticide's potential to leach. That, coupled with a consideration of risk, may indicate that a ground water study is needed to refine the exposure assessment, which will be used to evaluate the pesticide's overall impact on ground-water quality, risk to ecosystems, and to human health via drinking water.

2. EVALUATING THE POTENTIAL TO LEACH

OPP scientists use several different methods and tools to evaluate a pesticide's potential to leach to ground water, and to characterize ground-water contamination. These are: the environmental fate assessment, evaluation of use and usage data, evaluation of monitoring data and modeling. This section briefly describes each of these important steps in OPP's analysis.

Conducting the Environmental Fate Assessment

As a condition of pesticide registration or reregistration, EPA requires that all pesticide registrants submit studies describing the chemical properties of the pesticide. These data indicate the likely modes of dissipation of the pesticide, give some measure of how rapidly this occurs, and identify major degradates. Modes of dissipation examined include: volatilization to air, accumulation in plants or fish, chemical degradation, biotic metabolism, adsorption to soil, leaching to ground water, and runoff into surface water. Each of these environmental fate studies provides information on one -- or both of two important pesticide properties -- persistence and mobility. These properties in particular affect a compound's potential to contaminate water resources. Persistence is a measure of the resistance of a pesticide to being chemically or biologically transformed. Mobility refers to the ability of a pesticide molecule to move through soil in the water. Leaching of a pesticide depends on both its persistence (most commonly described by a degradation half-life, $t_{1/2}$), and its mobility (most commonly described by partition coefficients, K_{oc} or K_d). These standard physical and chemical parameters are derived from a suite of studies specified in 40 CFR 158.290 and include:

- Hydrolysis,
- Photolysis in water and soil,
- Aerobic and anaerobic soil metabolism,
- Soil column leaching,
- Batch equilibrium, and
- Field dissipation.

The first three studies address the persistence of a pesticide, while the next two studies address its mobility. Other product chemistry data are also required (including solubility and vapor pressure) to determine the environmental fate of a pesticide. The field dissipation study (usually several studies done for each pesticide) tracks the dissipation of a pesticide from the surface soil layer, and the formation and dissipation of degradates. With the exception of the field dissipation study, all of the above studies are conducted in the laboratory. The prospective ground-water study, which focuses on the leaching route of dissipation through the vadose zone to the water table, is distinct from that of a field dissipation study--although it is theoretically possible that these two studies could be run concurrently at the same site.

Based on a review of available laboratory and field studies, EPA compiles an "Environmental Fate Assessment" of a pesticide that describes major routes of dissipation, identifies the rates of formation and decline of major degradates, and characterizes the potential for the pesticide (and major degradates) to affect ground or surface water quality via leaching or runoff. This assessment may also identify whether pesticide mobility or persistence is affected by pH, temperature, or other factors.

Evaluation of Registered or Proposed Uses

The way in which the pesticide is used can play a critical role in determining its impact on the environment. For example, pesticides which are exclusively used indoors pose little risk of direct ground-water contamination as a result of proper use. Some typical indoor uses are: baits, greenhouse uses, crack and crevice treatments, and use in food handling establishment. Some outdoor uses, like seed treatments and potato seed piece treatments, are agricultural uses, but the mass applied to the field is extremely low and not thought to pose a significant risk of ground-water contamination. Thus, a consideration of how the pesticide is or will be used is an important factor in assessing its potential to leach, and its overall potential impact on water quality.

Evaluation of Monitoring Data

In the field, many processes that cannot be simulated by the laboratory studies influence the fate of a pesticide. These processes can result in either less degradation or dissipation than would be predicted or in enhanced degradation or dissipation in the field. Prospective ground-water studies are specifically designed to look at the influence of real-world factors on pesticide concentrations in the vadose and saturated zones in a controlled setting.

When reviewing the data for some pesticides, EPA may have available monitoring data collected previously by academic institutions, the federal government, State agencies or pesticide registrants. Ground-water monitoring for pesticides has been conducted by federal agencies such as the USGS and USDA, State Agencies, academia, and pesticide registrants. Sources of these data include OPP's Pesticides in Ground Water Data Base (USEPA, 1992), reports submitted to EPA under FIFRA § 6(a)(2), the open literature and monitoring conducted by public water supply facilities in compliance with the Safe Drinking Water Act. OPP compiles and evaluates existing monitoring data, and examines the quality of the studies to determine the impacts of pesticides on ground-water quality. Monitoring data are useful in EPA's determination of the need for a prospective ground water study and may also be helpful in EPA's decision regarding preferred test sites. These data may highlight uses for which impacts appear to be lower, and, thereby help EPA to focus mitigation efforts and further prospective ground water studies on specific uses or geographical areas where impacts may be higher.

In general, while available monitoring data can be useful in the ways described above, monitoring data rarely negate the need for a well conducted and controlled prospective ground-water study in cases where all other aspects of EPA's assessment suggest the need for such testing.

Use of Modeling

SCI-GROW (Barrett, 1997) is an empirical model developed by OPP based on results of earlier prospective ground-water studies. This model requires limited input (K_{oc}, aerobic soil metabolism half-life and annual pesticide application rate) and provides a concentration expected in ground water under conditions similar to the prospective ground water studies the model is based on. When the use of SCI-GROW shows that a particular pesticide may leach into ground water at levels of concern, this is a very strong indication of the need for a prospective ground water study for the compound under review.

Mechanistic models such as the PRZM-3 (Carsel et al., 1997), CMLS (Nofziger and Hornsby, 1994), LEACHM (Hutson and Wagonet, 1992) may also be used to further characterize the potential of a pesticide to leach to ground water for purposes of making the decision on the need for a prospective ground water study. The RZWQM (DeCoursey et al.,1989), HYDRUS -1D (Simunek et al., 1998) and MACRO (Jarvis, 1994) are also being evaluated as tools to predict the leaching potential of pesticides.

3. CONSIDERATIONS OF RISK

Pesticides by their very nature are biological poisons. Some pesticides and pesticide degradates pose a high risk at very low concentrations, while others pose less risk at these same low concentrations. Although EPA is particularly concerned about the movement of the more highly toxic pesticides and degradates into ground water, contamination of ground water resources by any pesticide or toxic degradate is of concern to EPA. This is because: (1) clean ground water is an important natural resource; (2) preventing the spread of ground water contamination and cleaning up contaminated ground water is often difficult and costly; (3) ground water is linked to surface water, and surface water systems are vital ecological compartments; (4) over 88 million Americans rely on community water systems that derive drinking water from ground water and the cost of removal of pesticides by these water systems is very significant and (5) ground water from private wells is used for drinking water by over 27 million Americans and much of this water is not treated prior to use.

4. CASE STUDY

The following is an example of the assessment process that occurs before a ground-water study is required, for a (hypothetical) herbicide, Zapadoo, proposed for use on corn and soybeans, which are major agricultural crops.

Environmental Fate Assessment

The registration standard for Zapadoo required the full complement of environmental fate studies, and data submitted by the registrant are acceptable. Overall, Zapadoo is characterized as a potentially persistent pesticide (half-lives up to a few months) that can be mobile in a variety of soils. However, field dissipation studies suggest that Zapadoo degradation might be more rapid (i.e., within a few weeks) under some conditions in some soils.

The aerobic soil metabolism half-life was determined to be 35 to 70 days in studies done in several soils, and the anaerobic soil metabolism half-life averaged about 170 days. Based on these studies, it appears that Zapadoo could be persistent enough in the field for significant leaching to occur. However, at some field dissipation study sites, Zapadoo dissipated more rapidly (half-lives were less than three weeks at four of the eight study sites) than other soil-applied pesticides which have been found to contaminate ground water. Overall, at eight study sites, field dissipation half-lives for the upper six inches of soil ranged from eight to 46 days. From the field dissipation data, Zapadoo appears to degrade more rapidly in acidic soils in the southern part of its use range. However, it is not clear whether the enhanced dissipation in these soils was entirely due to more rapid degradation as opposed to soil leaching or other dissipation routes. Although residues were analyzed to a 3-foot depth at several of the field dissipation study sites, there were no consistent detections of Zapadoo or its major degradate, zap acid, below 18 inches at any of these sites. The minimum detection limit was 10 µg/L for both compounds (the maximum application rate for Zapadoo is 0.10 lb ai/A).

Zapadoo is fairly resistant to abiotic hydrolysis. Zapadoo was only slowly hydrolyzed in sterile water at pH 5 (half-life calculated to be 91 days by extrapolation from the data) and did not appreciably hydrolyze at pH 7 and 9 over the 30-day period of the study. Zapadoo is, however, very susceptible to photolysis, with an aqueous photolysis half-life measured to be 1 day and a soil photolysis half-life measured to be 7 days.

In general, the laboratory data show that Zapadoo is persistent in most soils with a degradation half-life of five to 10 weeks. Zap acid, the primary degradate, appears to persist for several months or longer in neutral or alkaline soils. However, zap acid has not been found to persist in the photolysis studies. No other degradates were found to accumulate at more than 5% of the applied parent compound. In the field, the accumulation of zap acid residues was highly variable, ranging from a maximum of 5% of the applied Zapadoo at one site to a maximum of 50% of the applied Zapadoo at another site.

Zapadoo partitions primarily into the soil water in most soils. In soil column leaching studies, it was mobile in a sand with 1.4% organic matter (5% to 10% leaching through the column) and moderately mobile in sandy loam (1.1% O.M.) and loamy sand (2.0% O.M.) soils (1% to 5% leaching through the column). In batch equilibrium studies, K_d (in this case equivalent to Freundlich adsorption constants) values ranged from 0.8 to 3.4 in five soils tested. The degree of adsorption was roughly proportional to soil organic matter content. The K_{oc} ranged from 34 to 72; the median K_{oc} was 47. The only K_d greater than 1.4 in four soils tested was for a soil with 12% organic matter. It should also be noted that Zapadoo solubility is considerably reduced in alkaline soils.

Zap acid is even more mobile than Zapadoo, with K_{oc} values from batch equilibrium studies ranging from 4 to 17 in the same four soils in which Zapadoo sorption was studied. Zap acid was not confirmed to leach below 18 inches in field dissipation studies sampled to a 3-foot depth, but the soil analytical method could only detect residues exceeding about 20% of the applied pesticide, even if it was applied at the maximum rate and all retained in the upper six inches of soil.

Monitoring

Zapadoo parent was detected in ground water sampled in a small number (5) of studies reported in OPP's Pesticides in Ground Water Database. Three detections exceeded the pesticide's Health Advisory Level (HAL) of 7 µg/L, but the majority of the detections (75%) were below 1 µg/L. No data are available for zap acid in ground water. There are sufficient monitoring data to demonstrate that Zapadoo does leach to ground water after registered applications in some areas. However, some of the higher- level detections may have been due to chemical spills or other accidents. The monitoring data have not been collected in a sufficiently systematic way to determine under what conditions Zapadoo is most likely to reach ground water. A gross examination of the monitoring data implies that ground-water contamination may be more common in the northern part of the Zapadoo use area.

Modeling

Initially, evaluation of Zapadoo was performed with screening models SCI-GROW and CMLS. CMLS screening modeling demonstrates that Zapadoo has the characteristics (at least in the majority of use sites) of other pesticides with long-established uses that have been found to relatively commonly occur in ground water. This is especially true of zap acid, which is both more mobile and more persistent than Zapadoo parent. The zap acid soil half-life has not been directly measured, but it appears to be much longer than 6 months in at least some soils. SCI-GROW concentration estimates exceed the pesticide's Health Advisory Level (HAL) of 7 µg/L, with similar concentrations for zap acid.

PRZM II modeling was conducted at 10 representative use sites. A simulation of leached residues was compared with simulated Pikkleen residues, one of the most commonly detected corn and soybean pesticides in ground water. Twenty separate application years were simulated at each site. At one of the 10 sites, actual Pikkleen residues from an vadose zone and ground-water monitoring study were compared with PRZM II simulations of Pikkleen and Zapadoo. At this site, PRZM only roughly predicted the amount of Pikkleen leaching through the soil profile, with the uncertainty about how the chemical behavior of Pikkleen changes as it moves through the soil profile. At this, and most other sites, when aerobic metabolism half-lives and average Koc values were used, Zapadoo always leached to a depth of 3 or 6 feet more than Pikkleen (as a percentage of the application rate). However, if the Zapadoo degradation half-life is shorter (e.g., less than two weeks), then Zapadoo leaching is generally less than that of Pikkleen, and there is little likelihood of Zapadoo residues appearing in ground water in those areas. Zap acid, when formed in sufficient quantities, also may leach substantially at many use sites.

Data Evaluation

The weight-of-evidence of the environmental fate properties of the pesticide are enough to raise concern about its potential to contaminate ground water. Since the photolysis half-life for Zapadoo is so short, the foliar application for this chemical is considered less of a concern than the soil-incorporation method.

Modeling shows that there is a significant risk of Zapadoo residues leaching to ground water. Based on a comparison with actual monitoring data, there appears a potential for both Zapadoo and zap acid residues to impact the quality of ground water, and to exceed EPA's regulatory endpoint for drinking water in at least a portion of the use area. Moreover, zap acid has been found in tissues of laboratory animals in the studies used to calculate the MCL, and has also been found in the tissues of fish, which appear to be among the most sensitive non-target organisms. Ecotoxicity studies indicated that concentrations of 1 µg/L in water over a period of a few weeks are dangerous to trout (RQ of 12-30). This could pose a concern in areas where ground water discharges to surface water bodies. A more definitive analysis of the scenarios under which Zapadoo residues would leach significantly to ground water cannot be made at this time because of the uncertainty regarding the subsurface behavior of Zapadoo and zap acid. Such data could be obtained, however, with prospective ground water studies.

Given the large potential use area (corn and soybeans) at least two ground-water monitoring studies are recommended, one in a high-exposure area, and one in a more typical-use area. The studies should be conducted using the maximum label rate with application by soil-incorporation. EPA is requesting that a more sensitive analytical method be developed for analysis of Zapadoo and zap acid in water, down from the current 0.5 µg/L minimum detection limit to 0.1 µg/L.

This case study illustrates the complex analysis that is involved in determining the environmental fate of a pesticide and in evaluating its potential to contaminate ground-water resources as a result of normal agricultural use. The uncertainty in the analysis is heightened in the case of chemicals that have never been used before, as no ground-water monitoring data exist. This is often the case as well for degradation products of registered pesticides. In these cases, scientists must rely exclusively on the environmental fate assessment to determine the likelihood of leaching, and predictions of models to estimate the concentrations that might occur. Prospective ground water studies can provide EPA risk assessors and risk managers particularly valuable information in these circumstances.

5. STUDY COMPONENTS

The major design components for prospective ground-water monitoring studies and guidance on how to carry out these studies are explained in detail in subsequent chapters of this document. This guidance is intended to be performance-based, rather than a definitive description of how to install wells and how to collect samples. The goal is to provide the study director with adequate flexibility in selecting equipment and methods needed to provide high quality results, while at the same time standardizing the study design.

The study director must understand that this flexibility also allows the installation of more sampling devices and collection of more samples than stipulated to meet the goal of the study. For example, if OPP approves a site where the hydrology is more complex and the depth to ground water is greater than average, it is expected that more site instrumentation will be needed and that the term of the study is likely to be longer in order to determine the concentrations of the pesticide and major degradates in ground water resulting from application of a pesticide according to its label.
Included in this guidance are chapter describing the following activities:

- Site Selection,
- Site Characterization and Conceptual Model,
- Monitoring Plan Design,
- Site Characterization and Monitoring Plan Design Reports,
- Monitoring Plan Implementation, and
- Reporting

6. STUDY RESULTS

As specific stages of a prospective ground-water study are completed, results should be reported to EPA. These different reports require varying levels of effort and detail, and are described more fully in the guidance. The reports are:

- Site Selection Report: Maps, tables, and a brief interpretive text. OPP will select the study site from the set of candidate sites proposed by the registrant.

- Site Characterization and Monitoring Plan Design Reports: Site-specific data and more detailed interpretation. Proposed monitoring plan, including maps. The Site Characterization and Monitoring Plan Design Reports must be submitted to and approved by EPA before the Monitoring Plan Implementation phase of a ground-water study can begin.

! Quarterly Progress Reports: Brief data summary relying on summary tables and graphs. New data for the quarter is highlighted. Any deviations from protocol, equipment failures, or other complications are identified. Typically, reviews of these quarterly reports will not prompt any action, unless results of analysis or irregularities in the performance of the study warrant further action.

! Termination Report: Brief letter report indicating study results and rationale for termination with accompanying data summary.

! Final Report: The final report will consist of a final review of study results, and appendices containing the earlier submissions. This final report will serve as a comprehensive primary reference for the study.

The following chapters describe in more detail the components of a prospective ground water study.

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CHAPTER 2

SITE SELECTION

Careful selection of ground-water monitoring study sites is critical in ensuring that study results are useful to aid risk assessors and regulatory managers in pesticide regulatory decisions. The soils, hydrogeology, and climate at the study site (or sites) must be accurately described or characterized in order to properly instrument the site and to interpret the results of the study. Also, the range of soils, hydrogeology, and climatic characteristics represented by the use site must be established to properly interpret the data collected. The characteristics of candidate sites will depend on the specific use and the conditions the study is intended to explore (e.g.,"high exposure" or "typical use," irrigated or dryland sites). For example, a site may be selected which has a combination of environmental characteristics typically associated with ground-water quality problems. Another aspect to consider in site selection is that the conditions are such that the study can be conducted within a reasonable and predictable time frame. Ultimately, the success of the site selection will be performance based. The study should be able to clearly track the applied tracer through the vadose zone to the saturated zone and track any downward movement of pesticide residues.

OPP recommends that the registrant consider a number of sites in the preliminary site selection process. The following four-step process for the selection of field sites is suggested. These steps are described in detail in the following sections:

- STUDY SCOPE
- A SET OF CANDIDATE SITES
- COOPERATOR INTERVIEW
- PRELIMINARY SITE CHARACTERIZATION

All proposed sites that meet the criteria discussed in this chapter should be suitable for study. Sites should be ranked according to soil type, hydrogeologic characteristics and other relevant factors, and this information should be submitted to EPA in tabular form. Pesticide application and data collection cannot begin before the study site is approved in writing by EPA. Therefore, in the interest of saving time and resources, the study director should take special care during site selection to identify candidate sites. Full site characterization activities (Chapter 3) may begin following EPA approval of the study site(s).

1. STUDY SCOPE

Definition

The first step in selecting a study site is for the registrant to describe where and how the pesticide will be or is used. Included in the preliminary assessment should be usage (application rates, number of applications, maximum application) information for all use sites, stratified by geographic area (region, state, and county). The registrant should also provide information on the pesticide formulation, relevant agronomic practices (e.g., application timing or irrigation requirements), mode of action, environmental fate characteristics of the pesticide or soil properties that affect the mobility or persistence of a pesticide in the field.

Since a pesticide use area may have some locations with a greater probability for ground-water contamination than others, the registrant should assess the ground-water "vulnerability" throughout the use area. Ground-water vulnerability depends on many factors, and can be characterized using overlay (GIS) and indexing methods (Leaching Potential) (Kellog et al., 1992; Diaz-Diaz et al., 1998), process-based methods (modeling), or statistical methods. The assessment can be as simple as county-scale ranking, or as sophisticated as layered GIS data layer maps (Burkart et al., 1994) or vulnerability surfaces. Appropriate State Agencies may be contacted to determine whether areas highly susceptible to ground-water contamination have already been identified in the usage areas. The registrant should use any of these methods to: 1) describe the overall vulnerability of the pesticide use area to ground-water contamination; 2) identify the vulnerability associated with a "typical use site"; 3) identify sites throughout the use area that are most vulnerable to ground-water contamination; and 4) characterize the vulnerability of the sites they propose to study.

Based on this information, EPA will determine the uses for which the monitoring study is required, the number of studies for each use, the implementation schedule, and the conditions of the study (application method, soil type, geographic area). More than one study site may be needed because of major differences between uses (e.g. rice or corn), or if use occurs in very different geographic areas (e.g., CA and NY). A careful definition of study scope will assure that the answers to regulatory questions such as these are obtained:

- Will the pesticide leach at any location in the pesticide use area? Will fate properties be important or influence study results (e.g., soil pH and pesticide hydrolysis)?

- Which uses pose the greatest risk of leaching?

- Is there a high risk that leaching will occur in a specific geographic area or for a specific use; if so, what measures can mitigate this risk?

It is important to design individual prospective ground-water studies to answer questions particular to the pesticide in question. The chemical properties of a pesticide may require that the registrant evaluate leaching potential for application to different soil types, for different application methods, formulations or for applications at different label rates. If a single study is performed on a site representing high vulnerability for leaching within a pesticide's use area, and pesticide residues are not found in the ground water, it can be assumed that this chemical is not likely to leach unless subsequent monitoring data show otherwise. On the other hand, studies performed on a highly vulnerable site and at a less vulnerable site that may be more "typical" of the pesticide's use would provide some basis for extrapolation of leaching potential between these different scenarios, perhaps through the use of computer models.

This preliminary assessment is intended to identify acceptable sites that are candidates for extensive site characterization activities. The regional assessment of candidate areas should yield a list of areas where vulnerable and relatively homogeneous sites might be found. Study sites that are approximately 2 to 5 acres are then identified within these candidate regions.

Compounds of Interest and Analytical Methods

All pesticides and major pesticide degradates in the study and the conservative tracer compound to be used on the site are considered compounds of interest. A major degradate is one accounting for $\geq$ 10% of the applied at any time during the laboratory studies, or one that has been identified as of potential toxicological, environmental or ecological concern. The test pesticide should be applied using the method of application stated on the product label. The application should be made at the highest recommended label rates for the crop used in the study.

A comprehensive description of the methods (USEPA, 1992) selected for the analysis of all compounds of interest must be provided. Information on the analytical procedures to be used for both water and soil samples, and on the method detection limits (MDL) (USEPA, 1992) must also be reported. Any background information and references that might assist EPA in the evaluation of the nature, accuracy, and selectiveness of all proposed analytical methods should also be included. If no standard analytical method is available for the compounds of interest, methods must be developed, validated, and approved by EPA before beginning the prospective study.

Since the enactment of the Food Quality Protection Act of 1996 (FQPA), the Agency is required to conduct an assessment of human exposure from all routes (aggregate exposure). This requires a consideration of exposure from chemicals with similar modes of action, including degradates (common mode). Therefore, to obtain an indication of the human health risk associated with a pesticide in ground water, the cumulative exposure of multiple chemicals must be determined. When selecting an analytical method for a specific pesticide, several factors should be considered. The MDL and practical quantitation limit (PQL) should be appropriate for the objectives of the analysis. MDL refers to the minimum concentration of the compound of interest that can be measured and reported with a specified confidence (99% probability) that the concentration is above zero (USEPA, 1992). The registrants must provide or develop an analytical method for water for the parent pesticide and its degradates that has an MDL of 1% of the label application rate, or 0.1 µg/L, whichever is lower. PQL refers to the lowest concentration at which the laboratory can confidently quantify the concentration of the compound of interest. The study authors must report all samples with concentrations above the MDL as detections, including those below the PQL in which the concentration cannot be quantified. In addition, the study authors must provide sample equations to demonstrate how the PQL was calculated.

Analytical methods used should also be selective for the compound of interest, and free of any interference problems from other substances likely to be present in the sample. If less selective methods are used (e.g., ELISA (immunoassay) methods, gas chromatography (GC) with electron capture detection or nitrogen/phosphorous detection for sample screening), all detections should be confirmed using a different method (e.g., a second GC column with a different polarity). The procedure used to analyze significant degradates identified in the Subdivision N Environmental Fate studies must also be reported.

2. A SET OF CANDIDATE SITES

The second step in the site selection process is a regional assessment of sites within the pesticide use area and identification of candidate sites. The characteristics of candidate sites will depend on the specific use and the conditions the study is intended to explore ("high exposure" or "typical use," irrigated or dryland, etc.).

A regional assessment for candidate sites involves several steps. It is important to first investigate certain general factors including pesticide use, vulnerability of the use area, soil type, general hydrologeology including aquifer type and depth, and climate. This reconnaissance work can be done easily using spatially distributed data such as a GIS display. Once an area is found that appears to meet these factors, the next step is to look for individual fields that might be appropriate for the study. At this time, it is important to focus on specific site characteristics including aquifer characteristics and other criteria listed below.

With few exceptions, all candidate sites for a prospective ground water study must meet the following criteria (ordered by expected significance):

! Unconfined aquifer,

! Less than 30-foot depth to the water table,

! No flow restrictive layers between the surface and water table,

! Single Soil Series Mapping Unit

! Less than or equal to 2% topographic slope (generally level),

! Two to five acres in area, and

! Sufficient distance from drainage features to ensure stable hydraulic gradient conditions.

Unconfined Aquifer

Prospective ground-water monitoring studies are designed to monitor the downward movement of pesticides toward the water table. The ground-water quality of shallow, unconfined aquifers in areas where recharge is rapid is most likely to be affected by pesticide use. The impact of pesticide use under these conditions is manifested reasonably quickly. Under different conditions, for example, where the aquifer is deep or recharge is not rapid, it may take several years for the impact of a pesticide to be seen in ground water. Therefore, the time it takes for a pesticide to leach from its point of application to ground water -- its travel time -- can be quite variable and highly dependant upon transport pathways. It is therefore important to consider the “travel time” of the tracer or pesticide residues to reach ground water when selecting a site. Travel time will most likely increase with increasing depth. Thus, the longer time period that the study maybe required to run. Registrants should therefore consider travel time while the site selection process is occurring.

Unconfined aquifers are defined here as those where the water table forms the upper boundary and where no significant low-permeability layers overlie that boundary. The water table is defined as the top of the saturated zone, where the fluid pressure is approximately equal to atmospheric pressure (Freeze and Cherry, 1979).

Shallow Aquifer

Depth to the uppermost aquifer material is an important variable in determining the occurrence of agricultural chemicals. Kolpin et al. (1993) stated that the greater the depth to the top of the aquifer, the smaller the frequency of herbicide detection. In Mehnert et al. (1995), study results showed that the occurrence of agricultural chemicals was higher when the well depth was less than 30 feet. Therefore, to determine the potential for a pesticide to leach during the time frame in which the study occurs, shallow is defined here to be an average depth to ground water of less than or equal to 30 feet and the depth to the water table suggests a recharge zone. While no specific depth is considered “too shallow”, sites with shallow water tables may actually have an upward flux rather than downward flux. So care should also be used as not to pick a site that may be too shallow. Sites with drain tiles, drainage ditches, etc. may also need to be considered for some pesticide uses.

No Flow Restrictive Layers

Sites with soil layers that may restrict the downward movement of water must be avoided. Often the definition of restrictive zones is limited to those layers such as clays and hard pans that restrict downward water movement. These are soil layers that normally have low hydraulic conductivity values (less than 0.5 cm per hour (Soil Survey Staff, 1992). Soil particle size distribution (texture), soil structure, and pore size distribution are factors the significantly influence the leaching of pesticides through the soil profile to ground water (USEPA, 1990). However, soil layers with highly contrasting soil textures may also inhibit water flow (e.g., sandy loam overlying a coarse sand or fine gravel) and should not be considered. Sites should be carefully evaluated for soil properties that may inhibit water flow.

Single Soil Series Mapping Unit

Single soil series mapping units in the field are desirable to best define the conditions represented by multiple samples collected over the extent of the field. While no field is truly homogeneous, sites can be selected to minimize site variability and sampling designs can be used to better understand pesticide fate. The site should have uniform soil characteristics in three dimensions: aerially or spatially (same series) and vertically (similar properties from the soil surface to the water table). It is likely to be easier to ensure that soils are uniform spatially, than that they do not vary with depth.

The study director should at least ensure that each 2- to 5-acre study site be a single soil mapping unit as defined by the National Resource Conservation Service (NRCS) (formerly Soil Conservation Service or SCS). The mapping unit should be a consociation, which is a delineated unit dominated by a single soil series and similar soils. In general, at least three-quarters of the mapping unit consists of the named soil series and similar soils (from a hydrologic standpoint). The total amount of dissimilar inclusions are generally less than 15 percent if the soil properties are more limiting and 25 percent in not limiting. (Soil Division Staff, 1993).

Once a particular study area has been identified, specific soil mapping units containing the soil series on the candidate site can be found by consulting county soil surveys published by NCRS. Refinement of NCRS maps may be necessary to achieve the level of detail necessary for site selection and characterization. The soils maps should be evaluated and refined as needed by a qualified soil scientist.

In addition to being relatively homogenous over the candidate study site, the soil physical properties must be consistent with the conditions the study is intended to evaluate. For instance, soils appropriate for high-exposure ground-water monitoring studies must be among the most vulnerable soils allowed on the product label for a particular use. Two types of soils are appropriate in these situations:

! Coarse-textured soils with low organic matter content: These soils are characterized by high sand content, low silt and clay content, and low organic matter (less than 2%) in the uppermost soil horizons; or

! Structured soils with high hydraulic conductivity.

Sites that do not consist of either of these types of soils would be removed from further consideration.

The selection of a "typical use" study site would be carried out in a similar fashion, but the main selection criteria would favor a site representative of the most common conditions to which the pesticide will be applied, which might not reflect the highest vulnerability to leaching. A determination of the areas with the greatest use cannot be the sole criterion in the selection of a study site. "Typical-use" studies will only be requested if there is a question as to whether the pesticide will leach under those conditions.

Low Topographic Slope

The site must be as level as possible to minimize runoff or run on. The topographic gradient of proposed study sites should not exceed 2%. In addition to slope, the shape of the land surface should also be considered. For example, concave land surfaces will encourage infiltration and convex land surfaces would tend to encourage runoff, and should therefore be avoided.

Stable Hydraulic Gradient

It is recommend that study sites not be located within the radius of influence of irrigation or production wells. Sites also should not be located near surface-water bodies or tides that control the direction of ground-water flow. The Agency has a concern that surficial water bodies could cause extreme fluctuations in the direction of ground water-flow. Whatever information that might be gained concerning the leaching potential of a pesticide would be obscured by the effects of outside influences on the height of the water table and direction of ground-water flow. Further information on local conditions may be obtained from area reconnaissance and an investigation of wells and surface drainage features on surrounding properties.

3. COOPERATOR INTERVIEW

The third step in the site selection process is to interview farmers ("cooperators") to investigate the history of pesticide use at each site and to secure permission to use individual fields as study sites. Once the registrant has narrowed the search for appropriate study sites to the county or soil-series level, individual candidate sites can be identified. Individual farmers must be contacted about past agricultural practices and the long-term availability of the site for extended monitoring.

No Prior History of Test Pesticide Use

The history of the site must be known in order to identify use of the test pesticide, degradates, tracer, or other compounds which could interfere with analytical procedures or interpretation of the study results. Therefore, the registrant must demonstrate that there has been no use of the test pesticide on the test site during the previous five-year period. For pesticides with extremely long half-lives (greater than six months), study directors should investigate a longer prior use history.

Pesticide use information should be verified using the cooperator's written records. In addition, the study director should be thorough in inquiring if any pesticide spills, pesticide storage near wells, or other point sources have occurred at or near the site. It is incumbent upon the study director to fully investigate the site and report results before the commencement of the monitoring study. Sites where such potential point sources occur should be eliminated from further consideration at this stage.

Long-Term Availability of Study Site

Ground-water monitoring studies are typically conducted over a 2 - 3 year period. The length of the required monitoring period is determined by several factors, the most important of which is the pattern of movement of both the pesticide and tracer through the soil column, as determined by the analysis of pore-liquid and well-water samples. The site owner should be made aware that time estimates are imperfect, and that study conditions may require the site to be available for more than 3 years. Sites that are not available for this length of time should be eliminated from further consideration at this stage.

4. PRELIMINARY SITE CHARACTERIZATION

The fourth step in the site selection process is to undertake a reconnaissance of candidate sites. The final result should be a set of proposed study sites. Once a set of candidate fields has been identified and access is secured, preliminary characterization should be carried out. This investigation includes estimations of soil characteristics and variability, a description of site hydrogeology, identification of topographic and surface features that could impact the study, and site access considerations. Utilizing benchmark soil series as established by the NRCS will provide the registrant the additional soils data. Because these Benchmark series fall within a specified range of criteria and is available in GIS coverage, the spatial distribution of the soil and the range of properties could be characterized to identify how vulnerable the site actually is and how it fits within the entire use area.

Information about pesticides used on and near the site should be gathered to ensure that contamination of the aquifer has not occurred. In addition, it is important to ensure that no chemicals were applied that would be difficult to analytically separate from the test compound. The results of these investigations should be submitted to the Agency in the form of tables presenting the characteristics of the candidate sites, maps indicating locations of candidate sites, a description of which sites are most preferred, and why. The presence of compounds that interfere analytically with the test pesticide will result in rejection of the site.

Ranking of the various sites should be based on how likely each site would be to meet study guidelines after full characterization. A small number of soil samples should be collected for analysis from each candidate site, with the intent of determining the texture, organic matter, and permeability of the uppermost soil layers. Local water table depth should be determined by consulting the local NCRS office, examining existing wells on the site, or by installing piezometers. The natural configuration of the land surface should also be considered; sites containing depressions or low-lying areas that could facilitate ponding should be avoided. Any additional information that can be collected during this phase of the characterization should further the goal of ensuring that a chosen site will be accepted after a more resource-intensive, full site characterization.

Upon receiving the preliminary site characterization data from the registrant, EPA will give conditional acceptance of sites that appear to be consistent with study guidelines. Full site-characterization can then commence.

Absence of Dominant Fracture Flow

The hydraulic gradient, the configuration of the piezometric (or potentiometric) surface, and textural variations in the aquifer media are typically used to estimate the average direction and velocity of ground-water flow. This technique is not appropriate for the determination of ground-water flow and velocity in karst or highly fractured regions. For this reason, areas where prevalent ground-water flow occurs along karst or fracture-flow features are generally unacceptable for highly vulnerable study sites, unless significant use of the pesticide is anticipated in such an environment. Special monitoring techniques should be planned for such situations.

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CHAPTER 3

SITE CHARACTERIZATION AND CONCEPTUAL MODEL

Interpretation of the results of a prospective ground-water monitoring study largely depends upon whether the hydrogeology of the study site is adequately understood. To achieve this understanding, it is necessary to fully characterize the site. Site characterization data are necessary to more accurately assess site vulnerability, thereby placing into context results of the study relative to conditions throughout the pesticide use area.

Site characterization includes a description of topography at the site and in the vicinity, soil characteristics, and vadose and saturated zone hydrogeology. Not measured onsite, but also fundamental, are the description of agronomic practices (including irrigation and tillage) and climate (rainfall frequency, amount, and seasonal distribution). This information is needed before monitoring equipment is installed. Information collected in this phase of the study may be used as input parameters for computer models.

A conceptual model should be developed to understand how the site characteristics may affect the fate of the test pesticide. This model involves the analysis and interpretation of data collected during site characterization for soils, the vadose zone, and the saturated zone. Various methods exist to compile, analyze, and present these data in both graphical and tabular form. Visual displays of data are usually the most convenient and useful for presenting site characterization data. Once the flow system is understood, and the conceptual model is developed, a monitoring plan can be designed that is suited to the study site (Chapter 4).

Site characterization activities are divided into four steps. These steps are described in detail in the following sections:

EXISTING LOCAL DATA AND BASE MAP

SOIL AND VADOSE ZONE INVESTIGATION

SATURATED ZONE INVESTIGATION

CONCEPTUAL MODEL

Products of site characterization are: 1) a summary of existing local data; 2) a detailed base map; 3) site- specific characterization data; and 4) a conceptual hydrogeologic model of the site. All these data and the conceptual model must be summarized and described in the Site Characterization Report (Chapter 5).

1. EXISTING LOCAL DATA AND BASE MAP

The first step in the site characterization process is to gather all available information about the geology, topography, soils, hydrology, climate, and agricultural practices that could affect the fate and transport of the pesticide at the study site. These data are used to characterize the local hydrogeologic and agricultural conditions, and relate site-specific conditions to the regional framework. The base map of the study site provides a spatial reference for all site characterization information and monitoring results.

Compile Existing Local Data

A description of the regional hydrogeology is important background information for developing the conceptual model of flow and transport at the study site. An understanding of the hydrogeologic framework is typically needed to interpret the results of monitoring and to understand field observations.

Soil is a primary factor in regulating whether rainwater runs off or infiltrates. Data obtained from soil surveys are used to create maps of soil classes, where average values of soil properties are estimated within a defined region of a mapping unit (Webster, 1985; Cambardella et al., 1994). Thus, a first cut of possible study site locations can be determined in part with a published USDA Soil Conservation Survey. Site-specific soil characterization and delineation in addition to the Soil Survey will normally be necessary.

The timing and intensity of rainfall has a strong impact on the transport of pesticide residues off a field due to leaching or runoff. NOAA has a nationwide system of weather stations that measures rainfall and computes statistics (averages, return frequencies). During the course of a prospective ground-water study, an onsite weather station is strongly recommended to at least measure rainfall amount and intensity, soil and air temperature and pan evaporation. Historical rainfall at or near the study site should be determined to ensure that water input during the study is in line with historical data. A water balance should be developed which provides an estimate of the net historical recharge at the site.

Develop a Base Map

An accurate base map of each study site should be developed to provide a spatial reference for site characterization observations and for subsequent monitoring data. The base map should fully represent the significant features of the study site and the surrounding area; particularly those that may affect ground and surface water flow systems. It is strongly recommended that all base maps include:

! The location of the test site by latitude and longitude (and by township range, and section). The use of more exact methods, such as a Global Positioning System (GPS) or standard survey methods should also be considered,

! The location of nearby roads, surface water bodies, fences, and municipal boundaries,

! The location of nearby wells (including identification of irrigation source), canals, and drainage systems,

! The date the base map was developed and the sources of base map information,

! The organization and individual responsible for the base map,

! The area and slope of the control plot and test plot,

! Ground surface elevations and topographic features in the vicinity of the study site, and

! Map scale, map title, county name, and complete legend including topographic contour interval, explanation of map symbols, and north arrow.

Detailed information on site topography is needed to identify areas within a field where leaching is more likely to occur. Although the study site has a low overall slope, small-scale natural variations in slope occur within a field that direct the flow of water to runoff, run on, or pond. Identification of these areas is important for developing a conceptual model of the site, and in interpreting results of monitoring. We strongly recommend surveying the study site and adjacent areas to provide elevation data at a one foot or less contour interval depending on the slope of the site.

Base maps are used to record the locations of all pertinent study features and sampling sites including the location of soil cores, infiltration tests, piezometers, monitoring wells, lysimeters, drinking and irrigation wells, buried drainage tiles, the weather station, pesticide mixing and loading areas, pesticide storage facilities, disposal areas, and buildings. In addition, the location of a control area hydrologically upgradient of the study site should be identified and located on the base map, as well as a site for the test pit excavation. The Site Characterization Report should include this base map.

Information Sources

Sources of information on soils, geology, hydrology, topography and climate include: local experts, USDA agricultural extension service, the United States Geologic Survey (USGS) and state geologic surveys, USDA NRCS soil surveys, and the National Oceanic and Atmospheric Administration (NOAA) climatic databases. Information on pertinent surficial features obtained from aerial photogrammetric surveys may also be of use in base map development. State transportation departments, environmental protection departments, and county planning departments often maintain such information for land areas under their jurisdiction. Private companies may also be a source for aerial photogrammetric information in some areas.

2. SOIL AND VADOSE ZONE INVESTIGATION

Soil structure and variations in soil texture, surficial geology, hydrology, and the effect of years of agricultural practices (tillage, irrigation, drainage structures) influence how much precipitation will infiltrate or runoff from a field. If site characterization is inadequate, these real-world complexities will limit the interpretation of the monitoring data obtained from a field study. Thus, characterization of the subsurface is fundamental and necessitates substantial sampling, particularly between the soil surface and the saturated zone. The following sections group the investigation into two categories: an exploratory coring program in which sampling and testing occur throughout the study site, and a test pit excavation, located adjacent to or near the study site. The sections below describe parameters that should be characterized during the coring and test pit investigations. There is significant flexibility in which methods can be used to measure the parameters for site characterization. The emphasis is on performance-based methods as dictated by site specific conditions. Techniques are to be approved by the EPA prior to use.

Exploratory Coring Program and Field Testing

All site characterization programs must include an exploratory coring program to directly investigate and characterize the vadose zone. The purpose of the exploratory coring program is to obtain information about selected soil properties which reflect a soil's capacity to hold and transmit water, to bind or retain a pesticide, and to degrade or transform a pesticide; or those factors which considered together affect a pesticide's mobility and persistence at a specific study site. The soil coring program is also a means to assess the vertical and horizontal homogeneity of these parameters across a study site. Data collected from exploratory coring is used to develop an initial conceptual model of subsurface conditions at the test site. In this phase of the study, soil heterogeneities or barriers to leaching not discovered in preliminary site selection will be identified.

Continuous soil cores from at least 8 locations throughout the study site from the surface to the water table, as well as 1 continuous core from a control area upgradient of the study site will be collected. A detailed drilling log must be prepared by a trained soil scientist or geologist to describe the texture, color, structure, and moisture content of the soils as they are collected over the complete core by split spoon samplers or similar means. Methods for collecting split barrel (or split spoon) and thin-walled tube (shelby tube) samples can be found in the open literature. Such a log should give special attention to confining layers, abrupt changes in texture or color, and other features needed to characterize the physical and chemical properties of the vadose and saturated zones. In addition, observations of the depth to the water table, and blow count and sample recovery in individual split spoons, should be recorded.

Soil sub-samples must be taken from each core for laboratory analysis. Special attention is to be paid to the top six feet of the soil column to allow comparison with NRCS soil surveys, which describe soils to a depth of six feet. The top six feet of the core are to be divided into six-inch intervals or by soil diagnostic horizon, which ever is less. Emphasis is placed on the surface six feet because soil texture, porosity, structure, and organic matter content have a large influence on the persistence and mobility of the applied pesticide.

Below the top 6 feet of the soil core, sub-samples are to be collected every four feet, except when a visible change in soil properties (color, texture, structure) is observed. In this case, at least two sub-samples are to be taken from the 4-foot interval to characterize the difference between the two soil types. Each sample should be described in the field by an experienced geologist and/or soil scientist. In addition, all soil sub-samples must be analyzed for the following information:

- soil texture class, particle density, bulk density, porosity, fraction sand, fraction silt and fraction clay,
- organic matter content or organic carbon content,
- field capacity (1/3 bar) and wilting point (15 bar),
- saturated hydraulic conductivity,
- hydraulic conductivity vs. soil water content and matric potential,
- field soil water content, residual water content and saturated water content,
- matric potential vs. soil water content (water characteristic function)
- Munsell color (specify moisture condition, i.e., wet or dry), and

! pH and cation exchange capacity or anion exchange capacity (if appropriate).

These samples are not to be composited**.** Compositing of samples precludes obtaining information about the variability of these important parameters across the field. Standard methods for the parameters listed above are available from ASTM and are described in Mason (1983), Klute et al. (1986), Jury et al. (1991) and Wilson et al. (1995).

The compounds of interest must also be analyzed from soil collected in each horizon to ensure there has been no prior use of these compounds at the study site. If the test compound has not been registered, this need not be done.

Number and Locations of Soil Cores

Given that the study will be conducted in a field that is approximately two to five acres in size, a minimum of eight soil cores are needed to characterize the vadose zone. A greater number of cores will likely increase the reliability of interpretations of subsurface conditions.

There are a number of ways of determining where these soil cores should be collected. The most important factor to consider is that core locations be distributed throughout the field in such a manner that a strong conceptual model can be developed. This can be accomplished by locating the cores randomly, along a grid, or stratifying them according to some predetermined criterion. The grid may be oriented perpendicular or parallel to the ground-water flow field. The field may be segmented into sectors, gridded, and cores randomly located in each sector. If piezometers will be installed at core locations, these locations must be located at or near the corners of the study site.

Coring methods should be selected based on consideration of the anticipated textures of the vadose and saturated zones, the anticipated borehole depth, stability of the borehole, and ease of collection of samples for analysis. Drilling methods appropriate for these considerations are described in the ASTM standards manual.

Field Testing

The description or prediction of processes which influence pesticide dissipation, specifically leaching, in the field requires an understanding of infiltration, recharge, and internal drainage (water redistribution). Thus there is a need to characterize soil hydraulic properties, such as soil water content, matric potential vs. soil water content (water characteristic function) relationships and hydraulic conductivity. Because soils in a field are typically heterogeneous, solute transport is controlled by properties which vary both spatially and temporally, and these are also often scale dependant. Therefore, it is important that these parameters are measured in the field.

In these two to five acre study sites, we recommend that the saturated and unsaturated hydraulic conductivity be measured at a minimum of six locations dispersed across the study site (and indicated on the site base map) to take into account field variability of soils. If significant variability in hydraulic conductivity is evident, then measurements should be made in additional locations to further define the range of variability across the site. In general, measurements are made for at least two depth horizons at each measurement location - one at the soil surface and for each soil horizon below the surface to a depth of six feet. The soil water content should also be measured at these sites from the surface to the water table. These data will be correlated with the water characteristic function determined in the lab and the matric potential will be estimated for these locations. The matric potential indicates the direction of water movement in the vadose zone. The field determined soil water content will also be correlated with the hydraulic conductivity and compared to the lab results from the soil cores. This will provide insight into how well the results of the lab tests represent actual conditions in the field.

Preservation and Transportation of Formation Samples

ASTM provides guidance for preserving and transporting soil samples for analysis. Although some flexibility in these procedures might be necessary due to the practical considerations in sampling a farm field, certain procedures must be followed in every case. The field personnel must follow all relevant OSHA hazardous materials regulations concerning the shipping of dry ice. These samples should be sent by overnight mail the day they are collected, or kept frozen until they arrive at the laboratory.

Quality Assurance and Quality Control Procedures

Procedures for ensuring the quality of all soil samples and the data derived from those samples are an integral part of the exploratory coring program. Mason (1983) and Barth et al. (1989) present details on quality assurance for soil and formation sampling activities. Good laboratory practices relevant to field investigations should be followed.

All soil core logs and subsurface descriptions recorded during the drilling operation should be included in the Site Characterization Report. State or local regulations concerning the permitting and/or documentation of exploratory coring activities should be followed. Chain-of-custody forms must be prepared and archived for all subsurface samples, and subsurface samples that are not destroyed by analytical procedures must be retained as reference samples for the duration of each study.

Test Pit Excavation

Test pit excavations are particularly useful in characterizing the lateral extent or thickness of low-permeability layers noted during soil survey and exploratory boring activities or in identifying dominant patterns at a site (Mason, 1983). Soil structure or other features that may result in significant preferential flow should be noted and reported. Such features are not atypical, and are not usually a basis for rejection of a potential study site. The excavation should be located adjacent to or near the area of the site where the compounds of interest are to be applied and monitored. Test pits shall not be located within the active monitoring areas. The locations of the test pits should be indicated on the base map. The walls of the test pits should be described using methodology and nomenclature which is consistent with the Soil Survey Manual (Soil Survey Div. Staff, 1993), Soil Taxonomy (Soil Survey Staff, 1975), and Keys to Soil Taxonomy (Soil Survey Staff, 1992). Photographs of pit walls could also be considered.

Field workers should take care when entering a test pit to characterize soil properties. Occupational Safety and Health Administration standards state that test pits should not be excavated to deeper than five feet unless a shoring system (e.g. trench box or trench shield) is installed to support the pit walls. However, since the stability of pits five feet deep and shallower can also vary with soil texture and moisture, safety precautions should be considered in these scenarios as well. Proper abandonment procedures for test pits must be undertaken and documented in the First Quarterly Report.

Abandonment of Soil Core Holes

Characterization of the shallow saturated zone requires the installation of at least four piezometers. Some of the cores drilled for soil characterization may be converted into piezometers. The holes created by soil coring that are not converted to piezometers must be properly abandoned prior to the application of the compounds of interest. Guidance on proper abandonment of soil coring locations may be found in Aller et al. (1990) and American Water Works Association (1984). Boring abandonment procedures should also comply with any state or local regulations for agricultural fields.

3. SATURATED ZONE INVESTIGATION

A limited investigation of the saturated flow regime must be conducted for each study site. This information is needed to develop the conceptual model and to interpret monitoring data. The following sections describe the recommended procedures for characterizing the ground-water flow characteristics of the aquifer. These procedures include collecting hydraulic head data and conducting pumping tests and/or slug tests. The data derived from these activities are then used to estimate the direction of ground-water flow, the hydraulic conductivity of the aquifer, and the ground-water velocity at the study site.

Hydraulic Head

Piezometers must be installed at the site to measure the hydraulic head. Piezometers can be placed in the same borehole where the exploratory soil cores were collected to save resources. At least four piezometers should be installed at the corners of the study site to establish the water-table surface. These piezometers should remain in place for the duration of the study so that these simple measurements can continue to be made. Since suitable sites for ground-water monitoring studies must exhibit low topographic relief, small errors in surface elevation measurements can seriously impact the interpretation of subsurface conditions. Therefore, care should be taken to measure and record elevation data accurately. A small cut or indelible mark should be placed on the piezometer well casing for use as a measuring point (MP), and this point must be surveyed relative to the local U.S. Geodetic Vertical Datum. The location and height of this point should be measured to an accuracy of plus or minus 0.01 foot.

Procedures for measuring depth to water in monitoring wells are detailed in ASTM Standards. Initial measurements of water levels should not be collected until after the piezometer or well has had time to stabilize from the effects of construction and development activities. Piezometer locations should be specified on the base map, and initial water level data should be presented on a map in the Site Characterization and Monitoring Plan Report.

Direction of Ground-Water Flow and Hydraulic Gradient

A map of the potentiometric surface of the surficial aquifer must be prepared for each study site. This map should use the site base map for location information and should include the locations of piezometric head measuring points. Contour lines representing equal hydraulic head should be constructed. Methods for constructing water-table maps and estimating hydraulic gradient and ground water flow direction from these maps are provided in Freeze and Cherry (1979).

Hydraulic Conductivity

The hydraulic conductivity of an aquifer controls the rate at which ground water flows under a given hydraulic gradient. The velocity of the ground water can be used to approximate how long it will take the conservative tracer and pesticide to travel beyond the test site boundaries.

Hydraulic conductivity is typically measured in the field by means of slug tests or pumping tests. Slug tests should be conducted at locations where the soil cores indicate very low hydraulic conductivity aquifer materials. A pumping test under these conditions is usually not possible because the yield of the aquifer is too small to collect sufficient data to analyze using typical methods. Slug tests sample a very small region around the well and the results only represent the aquifer properties in that region. Therefore, they are of limited value and one must be done at every well. Pumping tests should be used when the hydraulic conductivity values are large enough to collect sufficient data to analyze using typical methods. Pumping tests sample a much larger region of the aquifer and give a more representative hydraulic conductivity value for the aquifer. Also, fewer pumping tests would have to be conducted because they do sample a much larger portion of the aquifer. Methods for conducting and analyzing slug tests and pumping tests are provided in Freeze and Cherry (1979), Walton (1987) and Fetter (1988). The results and interpretations of all slug tests and pumping tests should be included in the Site Characterization Report.

Background Water Quality

Basic data must be collected to establish the background quality of ground water, irrigation water and precipitation at the study site. Analyses should be done for major ions, temperature, electrical conductivity and pH. Additionally, water should be analyzed for the test compound (to ensure that there are no residues, and to check the analytical method) and the tracer compound (typically bromide).

If the irrigation source is a well within a quarter mile of the test plot, the study director must determine if pumping this well has any effect on the water table below the test site. This can be accomplished by using a data logger probe in the monitoring well nearest the irrigation well, and monitoring any drawdown of the depth to water when the irrigation well pump is turned on.

4. CONCEPTUAL MODEL

Site characterization data are analyzed and interpreted to produce a three-dimensional representation of the characteristics of the study site. The site-specific conceptual model must include graphical displays of interpreted hydrogeologic characteristics that illustrate the relationship between soil and hydrogeologic features. The conceptual model should be discussed with reference to graphs, figures, and maps and the data collected during site characterization. The discussion should integrate site hydrogeology, surface hydrology, and historical climatic data. The minimum graphical tools and analyses needed to develop the model are described in the following sections.

Soils and the Vadose Zone

The results of the soil analyses including preliminary surface investigations and NRCS information, exploratory coring program, and test pit excavation must be analyzed and integrated. At a minimum, the following are needed to interpret these data:

! At least two stratigraphic cross sections (or fence diagrams) for each study site, one parallel to the direction of ground-water flow and one perpendicular to ground-water flow,

! A detailed map of surface soils (1:100 to 1:1,000),

! Graphs or tables of particle-size distribution vs. depth for each core,

! Graphs or tables of matric potential head vs. depth and soil water content,

! Graphs or tables of hydraulic conductivity vs. soil water content,

! Graphs or tables of organic matter content vs. depth for each core,

! Tables and/or graphs that display ranges of hydraulic conductivity,

! Ranges of bulk density and hydraulic conductivity values for significant subsurface horizons,

! An estimate of the amount of water needed for the tracer to reach ground water in two years and

! An estimate of travel time needed for the tracer and/or pesticide to reach ground water.

A brief discussion of the above information should identify areas in the study site (at the surface or at depth) where variations in topography, soil texture, or other factors could cause differences in recharge. All data analysis techniques and the results of those techniques should be documented in the Site Characterization Report.

Saturated Zone and Water Quality

The results of saturated zone investigations and background water quality analyses are used to interpret the subsurface hydrogeology of the site. At a minimum, the following are needed to interpret these data:

! Contour map of the water table surface indicating the direction of ground-water flow,

! Analyses of slug tests and/or pump tests

! Estimate of hydraulic gradient and flow velocity of the aquifer,

! Comparison of the spatial distribution of hydraulic conductivity using data obtained from laboratory and field investigations,

! Graphical display of water quality data from the onsite wells, the irrigation source and precipitation and

! Sample chromatogram from an analysis of the test compound(s) in onsite water.

These and other data analysis techniques and the results of those techniques should be documented in the Site Characterization Report. The discussion accompanying these data must address water table fluctuations based on the collection of local historical data. Regional recharge and discharge areas should also be discussed, including nearby features such as irrigation wells and canals that could influence the flow system. The discussion should also include a description of the variations in hydraulic conductivity, the presence of confining layers, and the overall aquifer flow system at the site using historical data where necessary. Any interferences identified when analyzing the water collected at the site must also be discussed.

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CHAPTER 4

MONITORING PLAN DESIGN

Once the site has been characterized, the variability of soil properties and the groundwater flow system are understood, and a conceptual model developed, a monitoring plan can be designed that is suited to the study site. The number of wells and other sampling devices required to provide a high degree of statistical certainty in the study results would likely prevent the cooperating farmer from growing a crop on the field using standard agronomic practices, and would make the study prohibitively expensive. However, with a good conceptual model and a reasonable number of sampling locations, monitoring data will be adequate to answer regulatory questions. The clear advantages of testing a pesticide in the field under conditions that as closely as possible resemble those in which it will actually be used, as discussed in chapter 1, outweigh any disadvantages. Additional tools such as lysimeters and computer models can provide useful data to augment the field data obtained. It IS strongly recommended that studies must be conducted under FIFRA GLP, as described in 40CFR160. Written standard operating procedures (SOP) must be developed and maintained by the study director.

The compounds of interest (Chapter 2) will be monitored in surface soils, the vadose zone, and the saturated zone. A conservative tracer will be used to follow water movement through the system and weather will be monitored throughout the study. Aspects to consider, and minimum data collection needs, are described in the following sections:

- SETTING UP
- SOIL MONITORING PLAN
- PORE-LIQUID MONITORING PLAN
- GROUND-WATER MONITORING PLAN

Design decisions should be integrated into one Monitoring Plan Design Report for the Prospective Ground-Water Monitoring Study.

1. SETTING UP

<u>Agricultural Management Practices</u>

Standard agricultural practices for the target crop and the intended use of the test pesticide should be followed while conducting the Prospective Ground-Water Monitoring Study. All pesticides, fertilizers, and farming, maintenance, and sampling equipment must be stored away from the study site so as to eliminate the possibility of contamination.

Irrigation

Irrigation must be scheduled at regular intervals, as well as applied at critical periods in the growing season, to meet the target water input. The initial irrigation event must be scheduled to occur within three days after the pesticide application, unless sufficient precipitation occurs during this time. Following the first irrigation event, dates must be established when additional water will be applied to the field if monthly targets of total applied water are not reached as a result of natural precipitation. The schedule must be flexible enough to ensure that adequate water is applied to meet the needs of the crop, particularly in critical moisture periods such as the period of tasseling through silking for corn, or during fruit development for orchard crops. The Monitoring Plan Design Report must indicate the irrigation method, rate, schedule, and duration. Actual dates of irrigation events must be documented and reported in the Final Report.

Initial Post-Pesticide Application Irrigation Event

The relationship between rainfall timing and intensity and herbicide leaching has been reported by a number of researchers (Isensee et al, 1990; McLay et al., 1991, Shipitalo et al., 1990; Sigua et al., 1993;1995). Since rainfall is both spatially and temporally variable, it is necessary to supplement rainfall so that a study can be conducted within a reasonable time period. Therefore, it is recommended that an initial irrigation be applied to the study area within three days after the pesticide application.

Rainfall amount, intensity, and frequency is related to geographic location. The method proposed by Weiss (1962) and discussed in Schwab et al. (1981) is suggested as a way to determine how much irrigation needs to be applied within three days of the pesticide application for a given location. Weiss (1962) developed an equation (1) to determine rainfall amount (I) for a given location by linearizing the return period and duration values:

$$I = 0.0256(C - A)x + 0.000256((D - C) - (B - A))xy + 0.01(B - A)y + A \qquad (1)$$

where I= rainfall amount in inches, x = return period variate, y = duration variate, A= 2-year, 1-hour rainfall amount, B = 2-year, 24-hour rainfall amount, C = 100-year, 1-hour rainfall amount and D = 100-year, 24-hour rainfall amount. Variables A, B, C, and D are obtained from rainfall frequency maps for 1- and 24-hour duration storms and for return periods of 2 and 100 years (Hershfield, 1961).

The recommended amount of water, I, to be added should be determined for a 1-hr duration storm with a 10 year return period. When I is less than 2 inches, 2 inches of irrigation should be applied. The water should also be applied at a rate so that no runoff occurs.

Irrigation After Initial Event

The intent of the Prospective Ground-Water Monitoring Study is to evaluate a pesticide's potential to contaminate ground water and to provide an idea as to the concentrations that could be seen in ground water through normal agricultural activities. It is therefore necessary that enough water be added to the site so that recharge reaches the ground water. Due to the stochastic nature of precipitation, to rely strictly on precipitation may result in the study having to be conducted for many years. Thus irrigation can be applied to reduce the length of time that a study may need to run.

The amount of irrigation water applied should, at a minimum, be sufficient to obtain a normal crop yield, and at most, should be sufficient to transport the tracer to the water table within two years. Information on crop water requirements and irrigation scheduling can be obtained from local farmers and the Agricultural Extension Service. Monthly precipitation and evaporation records for the previous 25 - 30 years should be obtained from the nearest source, usually a NOAA weather station. The data on precipitation and crop water consumption requirements along with soil hydraulic properties are the basis for the calculation of irrigation targets for the study. For a "high exposure" study, irrigation must be applied to ensure that 130% of the baseline total applied moisture is achieved at the site for the growing season. For a "typical" site, irrigation must be applied to reach a target of 120% of the baseline total applied moisture.

Mixing and Loading Area

The location of pesticide mixing and loading activities should be identified on the base map. Ideally these activities should take place down gradient and downslope from the site to minimize the possibility of point-source contamination. Other activities that could take place in this area include calibration of the sprayer equipment with water, sampling of the application (tank) mixture, and sampling equipment cleaning.

Control Plot

To establish background ground-water quality, at least one well must be placed hydraulically up gradient of the field where the test pesticide will be applied. Control plots should be planted and maintained the same as the treated field. Control wells must sampled on the same schedule as monitoring wells in the treated field. The control area and control well location(s) must be identified on the base map.

Decontamination Area

Prior to sampling soils or ground water, equipment must be cleaned to minimize the likelihood of cross-contamination. This must be done far enough away from the study site so that activities and onsite disposal of rinsate will not affect study results. The decontamination area must be identified on the base map.

Weather Station

Onsite climatic monitoring is essential in evaluating pesticide leaching relative to the timing and magnitude of precipitation. Precipitation data are also needed to determine the required amount of monthly irrigation. Daily rainfall amount and intensity, pan evaporation, and temperature data are also key input parameters for several computer simulation models. A variety of automated weather stations and data logging equipment are commercially available that record daily precipitation, pan evaporation, wind speed, solar radiation, minimum and maximum air temperature, and soil temperature. Special care must be taken to protect parts of the weather station that can easily be damaged by birds and other animals, such as rain gauges and evaporation pans.

Application of Pesticide and Tracer

Pesticide

Decisions about pesticide application rates are made when the study scope is defined. Application method, calibration procedures, amount applied, and the number of applications must be documented for the test pesticide and reported in the Site Characterization and Monitoring Plan. The tank mixture should be sampled and the concentration confirmed. The pesticide application rate must be verified using pan samplers, shallow soil samples, application cards or other insitu collection devices. Nominal and actual application rates must be reported.

Tracer

A conservative tracer must be applied along with the test pesticide to provide information on the direction and rate of movement of water through the vadose and saturated zones.

When selecting a tracer, the chemistry of the compound should be considered along with potential sources of background interference, achievable detection limits, and potential losses due to adsorption, volatilization, and plant uptake. Bromide and chloride have typically been used to trace the movement of soil water in agricultural studies. Other tracers may be acceptable if approved by EPA.

Appropriate tracer application rates should be determined prior to initiation of the study, taking into consideration analytical methods and limits of detection and quantification, and concentrations in background water samples. Analytical methods, calibration procedures, amount of tracer applied, and application frequency must be documented and reported in the Monitoring Plan Design and Final Reports.

2. SOIL MONITORING PLAN

The primary purpose of soil sampling in these studies is to verify pesticide application rate, and not to track the movement of the test compound through the subsurface. Experience with prospective studies over the past 10 years indicates little correlation between pesticide detections in soil cores and detections in ground water. Some subsurface soil samples are collected early in the study to identify residues that remain in top meter of the soil column, above the uppermost lysimeters. Deeper vertical transport will be tracked using suction lysimeters and wells and not soil cores. Soil samples are to be analyzed for residues of the test pesticide, degradates, and tracer compounds. The soil moisture content must be measured for each sample collected.

Soil Sampling Methods and Instrumentation

Soil samples to verify the application rate must be collected using methods that ensures that pesticide-free soil does not dilute the samples to which the pesticide has been applied. When the pesticide is applied as a spray, soil samples for application verification must be collected from the surface soil without adding deeper pesticide-free soil. In this case, a sampler such as the box sampler will allow the collection of a wide (30 cm) and shallow (8 cm) sample. If the pesticide is soil incorporated, the initial soil samples should be collected to the depth of the disturbed zone. If a banded application is used, soil samples should be collected in the band to the depth of the disturbed zone. To avoid discarding any of the applied pesticide, surface plant residue should not be removed from these samples.

Number and Location of Soil Cores

A sufficient number of soil samples should be collected from a study site to qualitatively demonstrate the variability in pesticide application rates across the study site. The distribution of soil sampling locations across each study site should be dictated by the method of pesticide application and the degree of soil homogeneity on the site. For example, the collection of a minimum of 15 individual soil cores is required at each sampling period for a 2- to 5-acre study site with relatively homogeneous soil conditions. Sites that exhibit marked soil heterogeneities will require a greater number of soil samples.

Soil Sampling Timing and Frequency

In general, soil samples should only be collected during the first month of the study. Soil cores collected during the first two soil sampling rounds (pre-application and immediately post-application) should only sample surface soil. Shallow soil cores (0 - 10 cm) must be collected during rounds 3 and 4. Slightly deeper cores (0 - 100 cm) may be collected following the initial irrigation event, or earlier if a precipitation event occurs. Analysis of soil samples for pesticide and tracer residues must be continued until at least three consecutive (normally monthly) samples show no residues above the minimum detection (not quantitation) limit.

3. PORE-LIQUID MONITORING PLAN

Tracer and pesticide residues in pore liquid are monitored to provide an indication of the movement of water and the test pesticide through the vadose zone. Pore-liquid samples, collected with soil-solution samplers, suction lysimeters, or other devices, qualitatively track the downward transport of pesticide residues. Analytical methods for pesticides in soils commonly have higher minimum detection limits than those in water, typically more than an order of magnitude. Thus, pore liquid samples can be used to better track the movement of pesticide residues or tracer in vadose zone media with a greater power of detection than in soil samples.

Soil Water Content Measurements

The amount of water in soil, or the soil water content, is an important component of a site's overall water balance. It is also important for providing water to plants and for transporting solutes. Evaporation of water from the soil, transpiration by plants, movement of water, and the transport of solutes in soil are functionally related to the soil water content. Soil water, therefore, is a dynamic property which varies both spatially and temporally.

Soil water content throughout the site should be measured at lease monthly. Soil moisture measurements are required for modeling flow and for onsite water management; for example, to determine when irrigation is needed. Soil water content must be determined for soil samples collected for pesticide and tracer residue analysis because these parameters must be reported on a dry weight basis.

Instrumentation

A number of direct and indirect methods are available to measure soil water content (Gardner, 1986; Topp, 1993). The gravimetric method--a direct, destructive procedure--is a standard technique commonly used to collect reference data on soil water content. Indirect methods include: electrical conductivity, capacitance and resistance, neutron thermalization, and gamma ray and neutron attenuation. Of these methods, the three that appear to have the greatest use and utility are: gravimetric soil-water content; Time Domain Reflectometry (TDR), an electrical capacitance method; and neutron probe (neutron thermalization). Techniques such as TDR or frequency domain capacitors have the advantage of real-time readouts and no radioactive source.

Tensiometers or other suitable methods should be used to determine the availability of pore water for sample collection (Cassel and Klute, 1986; Rawlins and Campbell, 1986). Stannard (1990) provides a summary of the theory, design, installation, and use of vacuum-gauge, manometer, and pressure-transducer tensiometers in field investigations. The types of tensiometers used at each study site, and their locations, should be documented and reported in the first quarterly report.

Location and Frequency of Sampling

Soil water content measurements should be collected near the suction lysimeters and wells. Soil water content should be measured when lysimeters are sampled to at least a depth of one meter.

Pore Liquid Sampling

Because water in the vadose zone is held at negative matric potentials, water will not flow freely into sampling devices. Suction, in excess of the soil matric potential, must be applied to induce the flow of water into sampling devices. Therefore, suction lysimeters or other pore-liquid samplers are required. There is an extensive body of literature on the function and limitations of different devices and techniques for extracting water from soil using a pressure differential. Reliable, documented methods must be used to collect samples of pore water for analysis of the applied chemical, degradation products, tracers and other species of interest.

Instrumentation

The operation and effectiveness of suction lysimeters have been described by Morrison (1983); Everett, Wilson and Hoylman (1984); and Everett and McMillon (1985). The function and limitations of various suction sampler designs are presented in Wilson (1990). Vacuum samplers can be used to obtain pore-liquid samples from up to 6 feet below the ground surface. Pressure-vacuum lysimeters are recommended for water sample collection to a depth of 50 feet (Parizek and Lane, 1970). Limitations are discussed by Litaor (1988).

The porous sampling membrane of suction lysimeters can be constructed from a number of materials. Testing has shown that sampling membranes constructed of PTFE (Teflon) cannot sustain a sufficient vacuum to collect samples under high matric potentials. Prior to installation, however, laboratory studies should be conducted to assess the degree of sorption exhibited by the compounds of interest onto the ceramic membranes.

Depth and Number of Lysimeters

A minimum of eight clusters of four lysimeters each must be installed within the boundaries of the treated study site. The lysimeters at each cluster should be installed at four different depths (e.g. 3, 6 , 10, and 15 feet) to provide the greatest coverage of the vadose zone.

Time of Emplacement

Lysimeters must be in place a minimum of 2 weeks, and preferably one month, prior to the application of the test pesticide to the study site. In most cases, this will allow materials in the lysimeter to seal the annular space and to equilibrate with soil-moisture conditions. In some instances, a longer period of time may be necessary to achieve reliable and consistent samples from suction lysimeters. It should be noted that Litaor (1988) generally recommended that solution sampler systems be installed one year before sampling begins so that the samplers can equilibrate with the surrounding soil. Suction lysimeters must therefore be tested for operational effectiveness prior to the field application of the compounds of interest.

Sampling Frequency

Tensiometers should be regularly monitored to assess the availability of soil water for collection, and to determine the level of suction required to draw water from soil pores. Samples must be collected from lysimeters prior to pesticide application and frequently in the early part of the study. Soil pore water sampling activities should be coordinated with the collection of ground-water samples. A typical sampling scheme is as follows:

ROUND	TIMING	DEPTH
Sample 1	Pre-application	3, 6, 9, 15 feet (ALL DEPTHS)
Sample 2	7 days after application	3, 6 feet
Sample 3	14 days after application	3, 6, 9 feet
Sample 4	1 month after application	3, 6, 9 feet
Sample 5	2 months after application	3, 6, 9 feet
Sample 6	3 months after application	3, 6, 9, 15 feet
Sample 7 - ?	continue monthly sampling	3, 6, 9, 15 feet (ALL DEPTHS)

Samples must be drawn from lysimeters at each sampling period and analyzed individually. In the event that an insufficient volume of water is collected from a lysimeter, samples from two lysimeters located at the same depth increment may be composited. Criteria for termination of sampling is presented in Chapter 6. Approval for termination of monitoring must be received from EPA in writing.

4. GROUND-WATER MONITORING PLAN

The purpose of monitoring tracer and pesticide residues in ground water is to provide an indication of the movement of water, the test pesticide and its degradates through the vadose zone to ground water. Ground-water samples must be collected and analyzed for all compounds of interest (Chapter 2).

Monitoring Well Design

The success of a ground-water monitoring program for a prospective monitoring study depends in part on the proper installation of monitoring wells. Installation of these wells by licensed professional monitoring well installers, according to published standards specifically related to the construction of monitoring wells, should ensure that the wells will provide representative ground-water samples. Auger, direct push and other acceptable methods of well installation may be used provided the wells are installed and constructed to ensure reliable sampling of groundwater and well materials do not affect sample quality. Local and state monitoring well construction, instillation and location requirements should be taken into account in planning well design and planning. Well abandonment at the completion of the study must be done in accordance with local and state regulations.

Number, Emplacement, and Screen Lengths of Wells Within a Cluster

Groundwater monitoring wells may be installed as clusters or as multilevel sampling wells. At each well location at least two levels must be sampled. The magnitude of seasonal fluctuations in the water table should be determined prior to monitoring well installation. The shallowest well at each location must be placed to intercept the shallowest occurrence of groundwater. This generally means that it will be screened across the water table. The top of the second well screen should be placed at the bottom of the shallow well screen.

In order to avoid excessive dilution of a pesticide residue or tracer and to focus on a discrete portion of the aquifer, screen lengths must be no longer than 1.5 meters. If the depth to the water table does not fluctuate drastically, each cluster should monitor the top 3 meters of the aquifer. Where the water table fluxuates due to seasonal, tidal or other influences a greater thickness of the aquifer must be screened.

Number and Location of Monitoring Well Clusters

Monitoring wells should be located up gradient of the treated field in the control plot, within the treated field and down gradient of the treated field. A minimum of eight monitoring well locations should be spatially distributed within the treated field. State and local requirements for groundwater monitoring should be included in planning.

The locations of wells should be randomly distributed within the field. They may be placed at randomly chosen nodes on a regular grid to simplify data analysis and to reduce interference with agronomic practices such as planting, pesticide applications, and irrigation. Alternatively, the field may be divided into sectors and more wells located in selected sectors based upon the site characterization data and the conceptual model. Factors that might induce differential rates of infiltration and solute transport through the soil and subsoil include soil texture and structure, surface topography (shape and gradient), and hydraulic conductivity. Monitoring wells should be placed in areas of high infiltration and in "low-lying areas" (e.g., micro-relief areas with a concave shape) or in areas that have ponding of surface water.

Time of Emplacement

Wells should be installed a minimum of 2 weeks prior to pesticide application. Time should be allowed for development and stabilization of the wells prior to use. They should be in place to allow background sampling of groundwater for site characterization prior to pesticide application.

Sampling Frequency

Ground-water samples must be collected more frequently in the early part of the study and coordinated with the collection of soil and pore liquid samples and irrigation events. One pre-application sample must also be collected from all wells. Ground-water samples must be collected 14 days after the initial application, and at least once a month after that time from all monitoring wells. Additional samples may be collected before 14 days if there is reason to believe the compounds of interest may move rapidly. Some researchers have indicated that pesticides may leach to very shallow ground water beneath agricultural fields shortly after major recharge events. Based on analytical results of soil and pore water sampling, additional ground-water sampling events may be scheduled. Criteria for termination of sampling is presented in Chapter 6. Approval for termination of monitoring must be received from EPA in writing. A typical sampling scheme is:

ROUND	TIMING
Sample 1	Pre-application
Sample 2	14 days after application
Sample 3	1 month after application
Sample 4	2 months after application
Sample 5	3 months after application
Sample 6 - ?	continue monthly sampling

Instrumentation

The study director should ensure that all sample collection equipment will not alter the quality of ground-water samples during transfer or collection activities. A wide range of sampling devices suitable for sampling nonvolatile organic chemicals in ground water is available, but only a few are suitable for volatile organic compounds. For instance, most pumps and bailers are not suitable for the collection of volatiles. Also, certain types of sampling equipment may not be appropriate in any situation: i.e., peristaltic pumps generally cannot sample as deep as 30 feet. Sampler parts must be constructed of materials that will not contaminate or alter sample integrity. Typically teflon or stainless steel are preferred (USEPA, 1986b). In addition, pesticides may adsorb to certain types of tubing such as silicone rubber, Nalgene 180, Tygon R-3603, and low-density polyethylene. Teflon or stainless steel bailers should alleviate this problem in most situations. Dedicated sampling pumps are recommended to avoid cross-contamination. If these will not be used, then decontamination procedures which are appropriate for the situation must be used.

Sampling Methods

Before any well is sampled, the static water levels must be obtained. Water levels must also be measured in each piezometer during the sampling round. This information will be used to construct a water table map for each sampling period. Wells must be purged before sampling. Samples must be drawn from each monitoring well during each sampling period and analyzed individually. The first ground-water samples from each round should be drawn from the furthest up gradient well clusters. Sampling should then progress down gradient. Sampling for subsequent events should remain in the same order unless analytical results indicate contamination of up gradient wells. In this case, sampling should progress from the well displaying the lowest pesticide residues to the well displaying the greatest pesticide residues.

Integrated Sampling Schedule

Once design decisions have been made about how and when to sample soil, pore liquid, and ground water, these decisions should be integrated into one monitoring plan for the ground-water monitoring study. An example of a coordinated monitoring schedule is given below:

ROUND	TIMING	MEDIA SAMPLED
Sample 1	Pre-application	Soil (0 - 3 inches), ALL Soil Water, ALL Monitoring Wells.
Sample 2	Immediately post-application	Soil (0 - 3 inches)
Sample 3	1 day after application	Soil (0 - 1 foot),
Sample 4	3 days after application, (irrigate)	Soil (0 - 1 foot),
Sample 5	7 days after application	Soil (0 - 1 foot), Soil Water (3, 6 feet)
Sample 6	14 days after application	Soil (0 - 1 foot), Soil Water (3, 6, 9), ALL Monitoring Wells
Sample 7	1 month after application (irrigate)	Soil (0 - 2 feet), Soil Water (3, 6, 9), ALL Monitoring Wells
Sample 8	2 months after application (irrigate)	ALL Soil Water, ALL Monitoring Wells
Samples 9 - ?	3 months after application - study termination (irrigate)	ALL Soil Water, ALL Monitoring Well

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CHAPTER 5

SITE CHARACTERIZATION AND MONITORING PLAN DESIGN REPORTS

Reports summarizing the site characterization process and the development of monitoring plans for each study site must be submitted to EPA for approval prior to the installation of the monitoring system. The Monitoring Plan Design Report should be prepared simultaneously with the Site Characterization Report. Although both reports must be submitted before the implementation phase of the study can begin, they do not have to be submitted together. Final approval of monitoring plans will be provided after review. Required elements of both of these reports are described below. All reports and supporting data should be submitted in an editable electronic format and as many hard copies as required by Registration Division or Special Review and Reregistration Division.

1. SITE CHARACTERIZATION REPORT

The Site Characterization Report should be completed after the site characterization process. The required elements of this report have been described in detail in Chapter 3. They will be briefly summarized here and include:

- A summary of regional conditions,

- A site base map,

- Description of surficial soil characteristics,

- Description of field testing methods and results in the vadose zone (saturated and unsaturated hydraulic conductivity, soil water content)

- Description of historical water needs of crop and net recharge at the site,

- Descriptions and results of test pit excavations,

- Description of the design, implementation, and results of the exploratory boring program,

- Results of shallow saturated zone investigations,

- Description of the irrigation, groundwater and precipitation water quality,

! Development of a conceptual model of the site, and

! Any additional information that may impact the design, performance, or conclusions of the study.

Summary of Regional Conditions

Regional hydrogeology and agriculture should be described to provide a framework for interpreting the site-specific data collected during the site characterization process. A description and map depicting the site location with respect to geographic features, regional topography, dominant soil types, major aquifers (including those used for drinking water), regional water table depths and direction of ground-water flow, regional irrigation trends, and other regional agricultural practices should be included. Maps and figures to illustrate the regional conditions are encouraged.

Site Base Map

An accurate base map of each study site displaying the information collected during the site characterization process must be included in the Site Characterization Report. The required elements of a site base map are listed in Chapter 3, Section 1.

Surficial Soil Characteristics

The results of detailed soil investigations conducted by a qualified soil scientist should be presented. A map depicting the soil series present at each study site should accompany a description of the characteristics of the soils present on each site. A site-specific soil profile describing the various soil horizons typical at each study site should be included. Soil profile descriptions should follow the conventions established by the U.S. Department of Agriculture.

Field Testing Methods and Results

The procedures used to determine the hydraulic conductivity, matric potential head and soil water content of each test site should be reported. A map indicating the locations of test sites should be presented along with the results of the tests.

Historical Water Needs and Net Recharge

The data used to establish a baseline value for the average historical water needs of the crop and net recharge at the site should be summarized. If historical weather data is derived from readily available sources, such as the nearest NOAA weather station, the average of the monthly precipitation and evaporation data should be summarized in a concise table, and the data source cited. If these data were derived from a local source near the study site, the summary table should be accompanied by a more detailed description of the data source, as well as the name of a contact who is willing to discuss and verify the data. If historical irrigation records are available, these should be described in text and summary tables. If such data are not available, the method used to estimate irrigation requirements should be described in detail. Copies of the historical irrigation records or calculations used to estimate irrigation needs should be included as an appendix to the Site Characterization Report.

Test Pit Excavation

Test pit investigation results should be reported. All excavations should be located on a site map, and sketches and descriptions of significant features in the test pit walls should be included in the report.

Exploratory Boring Program

The design of an exploratory boring program is described in Chapter 3, Section 2. Documentation of all exploratory borings is critical to the characterization of subsurface conditions at each study site. This documentation should include a reference to the boring methods and subsurface sample collection methods used, copies of all drilling logs, reference to the preservation and transportation procedures for soil samples, a summary of the methods used to analyze soil sample properties, and the physical and chemical characteristics of all soil samples. Quality assurance procedures ensuring the integrity of soil samples and the data derived from those samples should also be reported.

Saturated Zone Investigations

The procedures used to gather information on the hydraulic characteristics of the shallow saturated zone must be reported. Contour maps illustrating the potentiometric surface of the shallow aquifer at each study site should be constructed, and estimates of the hydraulic gradient at each site should be reported. Any information on water-table fluctuations associated with each study site should be reported, along with estimates of the magnitude and potential impacts of the fluctuations on the study. Hydraulic conductivity estimates obtained at each study site must be reported, and the methods used to determine these estimates must be described. The range of hydraulic conductivity values obtained from different locations across the site, the results of pump testing, if used, and the results of laboratory permeability tests should be compared to obtain an estimate of the variability in hydraulic conductivity at the site.

Background Water Quality

Basic data must be collected to establish the background quality of ground water, irrigation water and precipitation at the study site. Analyses should be done for major ions, temperature, electrical conductivity and pH. Additionally, water should be analyzed for the test compound (to ensure that there are no residues, and to check the analytical method) and the tracer compound (typically bromide).

Conceptual Model

Information required for each study site is presented in Chapter 3, Section 4 and includes:

! A topographic map of the site,

! A detailed map of surface soils (1:100 to 1:1,000),

! Graphs or tables of particle-size distribution vs. depth,

! Graphs or tables of matric potential head vs. depth and soil water content,

! Graphs or tables of hydraulic conductivity vs. soil water content,

! Graphs or tables of organic matter content vs. depth for each core,

! An estimate of the amount of water needed for the tracer to reach ground water in two years and

! An estimate of travel time needed for the tracer and/or pesticide to reach ground water.

! Graphs or tables of infiltration rates and saturated and unsaturated hydraulic conductivity measured across each study site, and

! Contour maps of site hydraulic conductivity, soil water content, matric potential head and hydraulic head. The latter map should illustrate the direction of ground-water flow and give estimates of the hydraulic gradient.

Geologic cross-sections should be constructed from soil core information collected during site characterization. At least two cross-sections should be prepared for each study site that depict significant stratigraphic and hydrogeologic features. One cross-section should be oriented parallel to the direction of ground-water flow; the other should be perpendicular to the flow direction. The following information should be included on each cross-section:

! Orientation of the section across the site,

! Description of all stratigraphic units,

! Structural features,

! Zones of high and low hydraulic conductivity,

! Location of each borehole intersecting or projected into the section, with the total depth of the borehole and the depth to the water table indicated,

! Indication of the rate and direction of ground-water flow.

2. MONITORING PLAN DESIGN REPORT (PROTOCOL)

In contrast to the level of site-specific detail required in a Site Characterization Report, extensive detail in the Monitoring Plan Design Report should only be provided for chemical-specific information, or when elements of the proposed study design vary from the recommendations provided in the remaining chapters of this Guidance Document. Study directors are discouraged from submitting "draft protocols." If the design requirements spelled out in this guidance document are met, then timely approval of the Monitoring Plan Design Report will allow the experimental phase of the study to begin on schedule. Most subsequent changes to the study design can be addressed in a series of memoranda, rather than by submitting a series of draft reports.

If the study director believes that some aspect of the Monitoring Plan Design cannot be consistent with the guidelines in this document, a detailed description and justification must be submitted. This situation may be caused by the conditions of the study site or chemical characteristics of the pesticide or degradates.

The Monitoring Plan Design Report must clearly detail how the pesticide application, sampling, and analysis will provide the data necessary to evaluate the leaching potential of the pesticide and its degradates under the site-specific study conditions. The following chemical-specific data must be provided:

! Application rates,

! Compounds to be analyzed, including degradates,

! Analytical methods,

! Application method,

! Equipment calibration methods, and

! Method used to confirm the application rate.

The above information should be provided in summary form, with reference to readily available standard operating procedures. Field personnel must document referenced procedures in official field notebooks to comply with Good Laboratory Practice requirements.

The design of the proposed monitoring program for each study site should also be fully described in the Monitoring Plan Design Report. The following information, detailed in Chapter 4, must be provided in the Monitoring Plan Design Report:

! The number of monitoring wells and suction lysimeters that will be installed,

! A diagram showing proposed well and lysimeter locations,

! A description of the proposed pore-liquid sampler design,

! A schematic diagram of the proposed well construction details,

! Intended method, rate, schedule, and duration of irrigation,

! Proposed experimental start and finish dates, and

! Soil, pore-liquid, soil water content, matric potential and ground-water sampling schedules.

The Monitoring Plan Design Report must also detail the field procedures that will be used to instrument the site, conduct the sampling, and abandon the site at the conclusion of the study. These required elements are described in Chapter 4. These procedures should be described in summary form, with reference to readily available standard operating procedures.

CHAPTER 6

MONITORING PLAN IMPLEMENTATION

Once the Monitoring Plan Design has been approved, work on instrumentation can begin. At this stage all design decisions have been made. What remains is to install monitoring devices, apply the pesticide and tracer, to collect samples, and to send them off for analysis. This chapter describes factors to be considered in the field during instrumentation, application, sample collection, and sample handling.

EPA anticipates that field-scale ground-water monitoring studies will be conducted over a minimum of a 3-year period. This period includes 1 year for site selection, site characterization, the development of a monitoring plan, and the installation of the monitoring system, and 2 years for post-application monitoring. Additional time will likely be required for the preparation of the final study report. The duration of these studies may vary depending on the results obtained. Termination of monitoring at study sites requires EPA approval. Generally, conditions appropriate for termination of the study include:

! The tracer has peaked in concentration in all monitoring wells at the site, and has shown a marked decline for at least three months and

! Residues of the pesticide (parent and degradates of concern) have completely degraded and dissipated in the entire profile (vadose and, if applicable, saturated zone). This is generally defined as no detections for three consecutive sampling times over an interval of at least two months.

or

! Pesticide residues have clearly peaked (parent and degradates of concern) in ground water beneath the treated field (for each of the well clusters) or concentrations have leveled off for an extended period (usually about 4 to 8 months) while significant pesticide residues and tracer substance no longer remain in the vadose zone.

Sampling of pore liquid and ground water must continue until the patterns of transport and decline have been established for the test pesticide and its degradates. No study will be terminated before the questions for which the study was designed have been reasonably answered. The registrant may suspend sample analysis with EPA approval (but not continued sample collection) if they believe these criteria have been met while awaiting formal response from EPA as to whether the Agency agrees that the criteria for study termination have been met.

This chapter is divided into the following sections:

APPLICATION OF PESTICIDE AND TRACER

IRRIGATION

SOIL MONITORING

PORE LIQUID MONITORING

GROUND-WATER MONITORING

SAMPLE HANDLING AND TRACKING

1. APPLICATION OF PESTICIDE AND TRACER

The field crew should document that the application of the test pesticide and tracer corresponds to the rates and methods defined in the Monitoring Plan Design Report. Background concentrations of the tracer in the vadose and saturated zones need to be established ahead of time and the application rate should be sufficient that breakthrough of the tracer into shallow ground water can be clearly detected with the analytical method used. Application methods, calibration procedures, amount applied, and the date and time of each application must be documented carefully in the field notebook and reported in the First Quarterly and Final Report. The tracer identified in the Monitoring Plan Design Report should be applied the same day as the test pesticide.

Field notes should record the climatic conditions on the day of application, including wind speed, temperature and precipitation. It is particularly important to document in detail soil water content and temperature conditions on the day of application and for following days. The field crew must take detailed notes (supported by photographs when appropriate) on the amount, type, and positioning of plant residues or organic amendments relative to the planting rows (if applicable), surface roughness, row spacing, ridge height and depth and method of plowing, crop stage and vigor, weed composition and cover, and other factors which may significantly influence pesticide dissipation especially in the critical first few hours and days after application. Application should not take place on a day when conditions could cause pesticide loss due to spray drift or runoff, or if conditions are inconsistent with label directions. All entries to the field notebook throughout the study be consistent with FIFRA Good Laboratory Practices (GLP).

2. IRRIGATION

Detailed guidance on how to determine the amount of irrigation water needed throughout the course of the study is provided in Chapter 4. The cooperating farmer tending the study field must be familiarized with the schedule and method of irrigation identified in Monitoring Plan Design. With the exception of the irrigation event during the first week after pesticide application, times when irrigation is needed will not necessarily correspond to days field personnel are scheduled to conduct sampling. Soil water content determinations up to a one meter depth should always be made prior to any irrigation event as well as for all sampling events (normally several in the first month after application and once a month thereafter). The Study Director should keep in close communication with the cooperating farmer to ensure that monthly irrigation targets are being met, and that records of the dates and amounts of irrigation are being kept.

3. SOIL MONITORING

Soil sampling is important for verification of field application rate. For at least the month after application (normally including samples taken 0, 1, 3, 7, 14, and 30 days post-treatment) samples should not be composited before analysis in order to establish spatial variability of the application. Analysis of soil samples for pesticide and tracer residues must be continued until at least three consecutive (normally monthly) samples show no residues above the minimum detection (not quantitation) limit.

For soil monitoring, permanent equipment will not be installed in the field. Therefore, the first step in the field procedure is decontamination of sampling equipment, followed by sample collection and handling. Careful attention to avoid cross contamination of samples is important, especially in the early sampling intervals when pesticide residues on the field are highest. The field crew must carefully document procedures in the field notebook, noting any problems or deviations from the Monitoring Plan Design.

Decontamination of Sampling Equipment

Decontamination minimizes the likelihood that pesticide or tracer residues will be introduced into deeper soil horizons during sampling. A decontamination area should be designated in a location downgradient of the study plot. Soil-sampling equipment must be cleaned prior to sample collection at each sampling interval. Field-blank water samples must be taken with each sampling round to test the effectiveness of the soil-equipment decontamination methods. All rinsate used in the decontamination process must be disposed of away from the study site.

Field personnel can take additional precautions beyond equipment decontamination to prevent sample cross-contamination. For example, each person collecting samples should wear a clean pair of gloves during collection of each soil core. Decontaminated sampling equipment should never come in contact with the ground until the actual sample collection. Decontaminated sampling equipment should be placed in a clean plastic bag between uses to avoid accidental contact with contaminated soil or water.

Soil Sample Collection and Handling

The primary concern at the time of soil sampling is that representative samples be collected, being careful not to cross-contaminate samples from different depths or cores. Surface plant residue must be included with shallow soil samples to account for pesticide residues clinging to this material. When collecting successive samples for a deeper core, the top portion of each core should be carefully scraped to remove soil from the previous depth increment. The locations of sampling cores should be carefully measured and recorded in the field notebook, to avoid re-sampling in a location previously disturbed by coring. After sampling, core holes should be refilled with pesticide-residue free soil according to State and local regulations.

4. PORE-LIQUID MONITORING

The primary purpose of pore-liquid monitoring is to track the movement of dissolved pesticide and tracer toward the water table. The movement of the tracer through the soil column indicates that recharge has occurred. Monitoring pesticide residues gives an indication of the relative rate of transport of the pesticide.

Instrumentation

The proper installation of soil water content monitoring devices is described in manufacturer's materials and in USEPA (1986b), ASTM (1994), Nielsen and Johnson (1990), Everett, Wilson, and Hoylman (1984), and Morrison (1983). All lysimeters must be cleaned and leak tested before installation in the field to ensure that they will be able to hold sufficient vacuum to draw a soil-water sample. Testing of lysimeters prior to installation is of special practical importance, since any lysimeter that does not function properly during the study will require that a replacement be installed. Recommended methods for pre-installation cleaning and leak testing of pore-water samplers are described in USEPA (1986b). In some instances, the manufacturer of the sampling device may recommend other cleaning procedures that are appropriate for the specific device.

The maximum suction that can be applied to a lysimeter before contact with soil-water is broken is the bubbling pressure (or air entry pressure). If a suction greater than the bubbling pressure is applied to a lysimeter, only air will be drawn into the collection cup. If the bubbling pressure for a lysimeter is not provided by the manufacturer, this value should be determined before lysimeters are installed in the field. This can be done by saturating the collection cup with water, immersing the cup in water, and applying pressure to the lysimeter. The bubbling pressure is the pressure at which air escapes from the ceramic cup into the surrounding water.

Pressure-vacuum lysimeters offer some advantages over suction lysimeters. For example, the maximum operating depth of pressure-vacuum lysimeters is 15 meters, as opposed to 6 meters for suction lysimeters. Also, pressure-vacuum lysimeters collected samples through tubing which is part of the sample equipment, thus tubing is not reused eliminating this as a potential source of contamination. Good hydraulic contact between the porous segment of the sampler and the unsaturated media is needed to minimize leakage along the annulus of the borehole. This may be accomplished by packing silica flour around and beneath the porous segment of suction samplers. The use of other materials, such as sand or soil backfill will not provide as strong a hydraulic connection and may necessitate equipment replacement. Bentonite powder should be used to form a tight seal in the annular space immediately above the porous component of the sampler to prevent contamination from the surface. The supervising scientist must record problems encountered during installation or deviations from procedures and describe them in the First Quarterly Report and in the Final Report.

Decontamination

Sample collection tubing in a pressure-vacuum lysimeter is a dedicated part of the sampling device, and need not be decontaminated. Other types of lysimeters, for example suction lysimeters, have sampling tubing that is attached at the time of sampling and must be decontaminated if it is used for multiple lysimeters. In all cases, sampling tubing should not be allowed to come in contact with the ground and should be handled with clean gloves during sample collection. Any rinsate should be disposed of away from the study area.

Sample Collection

The following procedures pertain to the collection of samples from pressure-vacuum lysimeters. Methods for the collection of pore-water samples are generally provided by the equipment manufacturer and are summarized in ASTM (1994), Nielsen and Johnson (1990), and USEPA (1986a).

Pore-water samples should be collected from suction lysimeters by maintaining a constant level of suction on the porous cup of the lysimeter for at least 24 hours. The suction induces the flow of water from the surrounding unsaturated media into the sampler. To collect a sample, pressure is applied to the second line and water is forced from the porous cup through the discharge tubing into the collection bottle.

The appropriate amount of suction for each lysimeter depends upon the type of soil and the ambient soil moisture at the time of sampling. The suction placed on the lysimeter must be greater than the suction naturally occurring in the soil in order to induce flow into the collection container and to prevent backflow from the porous sampling cup to the soil matrix. The pressure applied to the lysimeter to force sample water from the collection cup to the surface must not exceed the bubbling pressure of the lysimeter, or the collected sample will be forced from the ceramic cup back into the surrounding soil.

The following should be included in the field notes for each lysimeter sampled:

- Amount of suction applied,
- Date and time that suction was applied,
- Remaining suction at time of sampling,
- Date and time of sampling,
- Pressure applied for sampling and
- Volume of sample collected

If the volume of available pore liquid or ground water is not sufficient for both pesticide and tracer analyses, pesticide analyses should be given first priority. If sample volume allows, duplicate and field-spike samples should be collected.

Any problems or variations in procedures in the Monitoring Plan Design Report must be described in the Quarterly Reports and in the Final Report. Reasonable effort must be made to follow the prescribed sampling program. Adjustments may have to be made during periods of bad weather but samples should still be collected according to the prescribed intensity (i.e., still at an average frequency of once every month unless a deviation from the protocol is approved by the Agency) and at times closest to the scheduled date that are feasible.

5. GROUND-WATER MONITORING

As with the soil pore-water sampling devices, monitoring well design decisions have been made and described in the Monitoring Plan Design Report. Problems or variances from these procedures must be documented and discussed as they arise in each Quarterly Report and in the Final Report.

Instrumentation

The ability to collect representative ground water samples depends on the proper installation of monitoring wells. Most States require that a permit be filed prior to the installation of monitoring wells and that well construction records be returned to the State within a specific time following the emplacement of monitoring wells. States may also have specific monitoring-well construction requirements that must be followed.

Wells must be installed by licensed drillers familiar with all relevant State and local requirements.

All information pertaining to work performed during the well construction should be recorded in detail in a bound project notebook using waterproof ink. Field-book entries for each monitoring well must be sufficiently detailed to allow the preparation of a detailed well log. The following minimum information should be provided on every well log:

- Well number and permit number,
- Well location,
- Well depth,
- Elevation of the top of the casing,
- Depth to the water table,
- Well construction details including: materials; length and diameter of the casing, screen, and surface casing,
- Well annulus construction details including: depth, thickness, and materials selected for the filter pack, plug, and surface pad,
- Geologist's field observations of soil characteristics from continuous split-spoon samples including: soil texture, color, moisture, and structure,
- Geotechnical information, such as blow counts necessary to advance the split spoon and sample recovery and
- Names of the drilling contractor and supervising geologist.

Any deviations must be recorded and described in the First Quarterly Report and in the Final Report.

Well Development

Well development procedures must be undertaken once a monitoring well has been installed and sufficient time has passed to allow the annular seal to cure. The purpose of developing a monitoring well is to improve the hydraulic characteristics of the filter pack by removing fine-grained materials from the pack, and causing coarser materials to settle around and stabilize the screen. Once this is accomplished, the monitoring well can be used to collect representative ground-water samples.

Removal of fine materials may be more difficult if the surrounding soil itself is fine-textured, or if the soil water is naturally turbid. In these cases, indicator parameters such as pH and conductivity should be monitored during development (Driscoll, 1986). Development should continue until parameters stabilize or the turbidity of the discharge water is less than 5 nephelometric turbidity units (NTU), as recommended in USEPA (1986b). If the parameters do not stabilize, this is an indication that the development method is not effective and an alternate method is needed. Information recorded during the development of each well must include: date of development and development method, volume of water removed, and a log of parameters monitored.

Decontamination

Unless dedicated pumps are used for sampling, all ground-water sampling equipment must be cleaned before use, and between wells. Non-dedicated sampling equipment should be washed with a nonphosphate detergent, rinsed with tap water then distilled water, and finally rinsed with a pesticide-grade acetone (or hexane or methyl alcohol) to aid in drying and to remove any organic residue (Barcelona at al., 1985). Other options are given in Driscoll (1986). All solvents used in decontamination activities must be disposed of in accordance with State or local regulations.

If a single pump will be used to purge multiple wells or collect ground-water samples, tubing should be dedicated to individual monitoring wells. Any nondedicated equipment must be designed so that it can be disassembled for cleaning at the decontamination area before a different well is sampled. Tubing removed from a well after each purging or sampling event should be rinsed with deionized water before placing in a clean storage container and sealed. Field blanks should be collected from sampling equipment between wells to test the effectiveness of decontamination. Bailers should be filled once and then decanted into sample collection bottles. If nondedicated pumps are used for sample collection, spectrographic-grade water should be pumped through equipment after decontamination and a sample collected for analysis.

Some States have developed guidelines for decontamination protocols (Mickam et al., 1989). State regulatory agencies should be consulted to obtain current information on standard decontamination practices for saturated and vadose zone monitoring programs. These standards should be used to supplement the guidelines outlined in this document.

The water purged from the wells should be discharged away from all well clusters. Field personnel can take precautions beyond decontamination of sampling equipment to ensure that cross-contamination between wells does not occur. Decontaminated equipment should be handled using rubber laboratory gloves, and should not be placed directly on the ground. It is best to store equipment in clean sealed containers after decontamination (e.g., plastic bags or coolers) for relocation to the well site. If bailers are used for purging and sampling wells, bailer cords should be discarded after a single use.

Sample Collection

Prior to sampling any of the monitoring wells at a study site, field conditions should be described in the field notebook. This includes observations of weather and soil surface conditions, and the height of the water table in all wells and piezometers.

In order to collect a ground-water sample from a monitoring well that is representative of the water in the surrounding aquifer, standing water must be removed from the well casing, screen, and surrounding filter pack. This procedure is called purging. The volume of water purged, the rate at which it is withdrawn, and the location of the sampling intake all determine how representative the sample is to the water in the aquifer. Typically parameters such as dissolved oxygen, specific conductivity, oxidation-reduction potential, turbidity and pH are continuously monitored throughout purging. When these parameters stabilize, the well is considered purged (Driscoll, 1986). Alternatively, a specific number of well casing volumes can be removed. Low-flow purging is a method that is recommended to minimize the disturbance of the formation and sample volumes withdrawn from the aquifer. In low-flow purging, the flow rate is adjusted to minimize drawdown in the aquifer. Meters used to monitor pH, temperature, and specific conductance should be calibrated before each use.

Bailers should be gently lowered into the water column to a measured depth just below the water table. Samples for volatile pesticides should be headspace-free. Only a bladder pump is suitable for sampling for volatile pesticides.

Ground-water samples should be collected in containers that will not interact with the sample. Ground-water samples must not be composited, but placed directly into sample collection bottles. The techniques used need to be validated for providing a representative sample in which the analytes are stable under the conditions of transport and subsequent storage before analysis.

If the volume of available pore liquid or ground water is not sufficient for both pesticide and tracer analyses the pesticide analyses should be given first priority. The analytical procedures described in the Monitoring Plan Design must be used and documented. Duplicate samples and field spike samples must be collected.

6. SAMPLE HANDLING AND TRACKING

Water and soil samples must be placed directly into coolers after collection. To ensure against breakage and temperature fluctuations in the samples, the following sample packing and shipping procedures must be followed:

- ! Samples must be shipped in insulated boxes or coolers. Devices are available to automatically monitor and record temperature while the samples are in transit.

- ! Individual glass sample containers should be wrapped either in plastic bubble wrap, placed in Styrofoam holders, or somehow packaged to separate the sample bottles during shipping.

- ! Gel-Cold packs or other materials to maintain stable temperatures can be placed in each cooler, but should not be in direct contact with any of the glass sample containers. To help maintain the Gel-Cold pack temperature and keep the temperature of the coolers around 4 °C, ice sealed in plastic bags may be added. The ice must be bagged to prevent seepage during transport. Soil samples should be packed in a container at or below 0 °C as soon as possible after collection. If dry ice is used to preserve soil samples during shipment, field personnel must follow all hazardous substance labeling requirements.

- ! It is important that all sample tracking paperwork be included with the shipment and that the chest be sealed according to chain-of-custody procedures.

All samples must be stored after collection according to GLP-compliant procedures and the stability must be validated by a storage stability study. Coordination with the laboratory concerning frequency and number of samples is important for sample preservation and to ensure that sample holding times are not exceeded. The laboratory should therefore be notified prior to sample collection to ensure that samples will be processed and analyzed quickly.

The sample tracking procedure described in the Monitoring Plan Design portion of the Study Protocol must be followed. A number should be assigned to each sample collected. That number should be marked on the sample container and recorded on the tracking form and in the project notebook. Weather conditions or field comments should also be recorded on the tracking form or in the field notebook. A three-part label should be used that includes numbered descriptive information to be placed on the sample container. In general, sample labels should be placed in duplicate on the sample container and must include:

- ! Date and time of collection,

- pH, temperature, and specific conductance,
- Identification of sample location,
- Analytes, and
- Signature of field technician.

If samples are shipped to a laboratory, samples must be shipped in such a way as to avoid breakage of sample containers and maintain sample integrity.

Measures to Reduce Sample Analysis Burden

Normally, all soil core, soil pore-liquid, and ground-water samples collected must be analyzed for all pesticide residues and for tracer. On a case-by-case basis, certain procedures for reducing analytical burden of these studies may be considered by EPA, such as the following:

- Use of relatively cheap and rapid analytical methods that may have a potential for false positives for initial screening of samples which are considered unlikely to contain residues of the pesticide provided that the false negative rate is documented to be extremely low and that all detections and a percentage of non-detects are reanalyzed by a chemical-specific analytical method.

- Initial analysis (in chronological sequence) of deeper soil pore-liquid samples and of ground-water samples taken in the initial weeks and months may be for tracer only (with a percentage always analyzed for pesticide residues) and followed by pesticide residue analysis only if tracer is detected or other evidence that sufficient recharge may have occurred at the study site for the pesticide residues to appear at that depth. However, in no case will this sort of tiered analysis approach be approved for analysis of the soil cores or the shallowest (usually 1 meter depth) lysimeter pore liquid samples in each cluster in the field.

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CHAPTER 7

REPORTING

Quarterly status reports for each prospective ground-water monitoring study must be submitted following the application of the compounds of interest. Required elements of these status reports are described in Section 1. These status reports are required to allow adjustment to the study design, if necessary, and for the determination of when the stated goals of the study have been fulfilled. However, in the interest of efficiency, quarterly reports will not be formally reviewed unless the results presented warrant further action.

The monitoring plan implementation phase of a prospective ground-water study may end once the EPA approves a Study Termination Report submitted by the registrant. While ground-water sampling in a prospective study would ideally be completed two years after the application of the test chemical, the appropriate termination point of a study is a function of site-specific and chemical-specific characteristics. Section 2 describes milestones in the ground-water study that should occur before the Study Director considers submitting a Study Termination Report.

At the conclusion of each study, a Final Study Report must also be submitted to EPA. Required elements of this report are described in Section 3. As this document should be able to stand alone as a full report on the small-scale prospective study, it will include information already presented in previous submissions. This report is the vehicle in which the registrant can provide interpretation of the study results, suggest further mitigation measures, and extrapolate the results through modeling, or comparison to other available data. All information referenced to sampling locations should conform to EPA's minimum data elements standards. All reports and supporting data should be submitted in an editable electronic format and as one hard copy.

1. QUARTERLY REPORTS

Quarterly status reports must be submitted to EPA beginning with the first quarter following the application of the compounds of interest to each study site. The required elements of these reports include:

! A summary of the activities at the site during the quarter,

! Mass balance for the conservative tracer and total pesticide residues at each cluster,

! Protocol deviations from the approved monitoring plan, and

- ! Results of all chemical analyses for samples (including quality control samples) collected during the quarter.

These report elements are described further in the following sections. The submittal of additional information that may impact the design, conduct, or findings of the study is encouraged.

Summary of Site Activities

The summary of site activities should include all activities related to agronomic practices, monitoring, and irrigation. The application dates for fertilizers or other compounds applied to the study area should be reported along with information on other agronomic practices conducted during the quarter. Similarly, the dates of sample collection must be reported along with information on weather conditions during the quarter. If irrigation water was applied to the study site during the quarter, then the dates and amounts of water applied must be reported, and compared to the targets set in the Irrigation Plan. The results of field measurements such as soil water content and matric potential should be reported along with a water budget indicating the amount of net recharge to the site.

Mass Balance

A mass balance for the conservative tracer and total pesticide residues should be reported for each cluster. The mass balance at each lysimeter and well should be approximated.

Protocol Deviations

Any deviations from the protocol established and approved as part of the Monitoring Plan Design must be reported for each quarter. Reporting of deviations should include a discussion of the proposed and approved procedures, a description of the revised procedures that were implemented during the quarter, the reasons for the revisions, and the anticipated effects on the study.

Analytical Results

The results of all chemical analyses (i.e., analyses for the test pesticide, degradates, and tracer) conducted on samples must be reported in tabular format. MDLs and the results of quality control analyses should also be reported. Comments and a brief discussion of the analytical results for the quarter may be included.

2. STUDY TERMINATION REPORT

The sampling program of a prospective ground-water monitoring study would ideally last two years. However, in reality the duration of a successful study is a function of how long it takes for applied water to recharge to ground water and of how long it takes for the pesticide and its degradates to leave the vadose zone by degradation and/or dissipation. This time frame is a function of the soil type, properties of the pesticide, and the amount of net recharge at the site.

In order to consider proposing an end to the sampling phase of a prospective study, the study director should assess whether the following criteria have been met:

- The tracer has peaked in concentration in all monitoring wells at the site, and has shown a marked decline for at least three months and

- Residues of the pesticide (parent and degradates of concern) have completely degraded and dissipated in the entire profile (vadose and, if applicable, saturated zone). This is generally defined as no detections for three consecutive sampling times over an interval of at least two months.

or

- Pesticide residues have clearly peaked (parent and degradates of concern) in ground water beneath the treated field (for each of the well clusters) or concentrations have leveled off for an extended period (usually about 4 to 8 months) while significant pesticide residues and tracer substance no longer remain in the vadose zone.

The Study Termination Report should detail the fact that the above conditions have been met, give a brief summary of study results, and propose a date for the termination of the sampling phase of the monitoring study. Sample collection must continue until EPA reviews the Study Termination Report and concurs that sampling can end. No study will be terminated before the questions for which the study was designed have been reasonably answered.

3. FINAL REPORT

A Final Report must be submitted to EPA at the conclusion of each study. This report must include

- Documentation of the application of the compounds of interest, climatic monitoring, and irrigation practices;

- Documentation of all sampling and sample analyses activities;

- Results of all chemical analyses and discussion of findings; and

- Documentation of quality assurance activities.

These report elements are described in more detail in the following sections. The submittal of additional information that may impact the interpretation of study results is encouraged.

Field Practices

The agricultural practices conducted during the course of the study should be summarized in the Final Report. Information on the application methods, rates, and dates for the compounds of interest should be reported. The results of climatic monitoring at each study site should be reported along with information on the irrigation methods used, and irrigation rates, dates, and duration.

Sampling Activities

Information collected during each sampling episode should be reported, including

- Static water levels in monitoring wells and piezometers,

- Weather conditions and field comments,

- Tensiometer readings and the amount of suction used to collect lysimeter samples, and

- Soil moisture content at the time of sample collection.

Analytical Results and Discussion of Findings

The results of all chemical analyses should be presented. Analytical results for all compounds of interest should be presented along with information on analytical detection limits that were achieved. The study findings should be summarized, and the significance of the findings with respect to the demonstrated environmental fate of the test pesticide and degradates should be discussed. The use of graphics and/or computer models to illustrate this discussion is encouraged.

Quality Assurance

Compliance with good laboratory practices (GLPs) should be documented. For field activities, a description of the system for sample numbering and/or identification should be presented

For laboratory operations, the following should be reported:

- Identification of responsible party who acted as sample custodian,

- Copies of laboratory sample custody logs consisting of serially numbered standard lab-tracking report sheets, and

- Description of laboratory sample custody procedures for sample handling, storage, and dispersion for analysis.