

# **Fate, Transport and Transformation Test Guidelines**

## **OPPTS 835.7100: Guidance for Prospective Ground-Water Monitoring Studies**



## NOTICE

This guideline is one of a series of test guidelines established by the Office of Prevention, Pesticides and Toxic Substances (OPPTS), United States Environmental Protection Agency for use in testing pesticides and chemical substances to develop data for submission to the Agency under the Toxic Substances Control Act (TSCA) (15 U.S.C. 2601, *et seq.*), the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) (7 U.S.C. 136, *et seq.*), and section 408 of the Federal Food, Drug and Cosmetic (FFDCA) (21 U.S.C. 346a).

The OPPTS test guidelines serve as a compendium of accepted scientific methodologies and protocols that are intended to provide data to inform regulatory decisions under TSCA, FIFRA, and/or FFDCA. This document provides guidance for conducting the test, and is also used by EPA, the public, and the companies that are subject to data submission requirements under TSCA, FIFRA and/or the FFDCA. As a guidance document, these guidelines are not binding on either EPA or any outside parties, and the EPA may depart from the guidelines where circumstances warrant and without prior notice. The procedures contained in this guideline are strongly recommended for generating the data that are the subject of the guideline, but EPA recognizes that departures may be appropriate in specific situations. You may propose alternatives to the recommendations described in these guidelines, and the Agency will assess them for appropriateness on a case-by-case basis.

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## CHAPTER 1 - INTRODUCTION

This document provides guidance for conducting a Prospective Ground-Water (**PGW**) **monitoring study** for the registration of pesticides in the United States (listed as guideline number 166-1 in 40 CFR 158.29). The PGW study, which is required on a case-by-case basis, is conducted in a controlled setting and provides the Agency with data for evaluating the impact of legal pesticide use on ground water quality. After assessing the overall environmental fate of a pesticide, the Agency may require the pesticide manufacturer (registrant) to conduct a PGW study, with input from EPA on key aspects of the study design. The Agency's assessment is based on a review of laboratory data on mobility and persistence of the compound, estimates of potential exposure, available monitoring and modeling information, and a consideration of the potential for risk from drinking water exposure. Data generated from these field studies have proven valuable to EPA scientists and risk managers as they are specifically designed to relate pesticide use specified on the label to measurements of the pesticide and its degradates in ground water used as a source of drinking water. This document provides guidance on how to conduct a PGW monitoring study, describes milestones for consulting with EPA, and describes how results should be reported to EPA.

EPA uses the results of PGW monitoring studies to help answer questions such as: (1) Will the pesticide leach in portions of the pesticide use area that are similar to the study area? (2) How do pesticide residues change over time? (3) What measures might be effective in mitigating the pesticide leaching? Monitoring data generated in these studies provide a time-series of concentrations that can be used in exposure and risk assessments as a reasonable surrogate for pesticide concentrations in drinking water drawn from shallow private wells in agricultural areas. PGW studies have been used to test alternative mitigation strategies for pesticides that have adversely affected ground water quality to determine, for example, if a reduction in application rate or specific irrigation technology will reduce or eliminate the impact. Data from these studies also have been used to develop the EPA regression screening model SCI-GROW, (<http://www.epa.gov/oppefed1/models/water/models4.htm#scigrow> ; see also ILSI, 1998), which is used to estimate screening-level pesticide concentrations in ground water used as a source of drinking water. Currently, the results of these studies are being used to evaluate models of subsurface pesticide transport, and as a basis for model scenarios for estimating pesticide concentrations in shallow ground water.

In the past, the Agency has required both retrospective and PGW studies on a case-by-case basis. The prospective study was designed to eliminate factors that confound the interpretation of retrospective monitoring studies. For example, in the site selection process, sites with prior use of the pesticide or with point sources of contamination are not selected for study. Also, since the pesticide is applied according to a current or proposed label, concentrations observed during the study can be directly linked to a known and current labeled use. The PGW studies are conducted at a field scale rather than a larger scale to ensure that adequate field quality assurance/quality control (QA/QC), collection of ancillary data (climatic data, soil characteristics), and level of



instrumentation can be implemented at a reasonable cost, while maintaining a scale that captures the natural variability in soils, hydrology, and other environmental factors, and under which standard agronomic practices can be implemented.

The original draft guidance for PGW monitoring studies was developed primarily in the early 1990s and has been subjected to substantial public review and comment, including a public workshop sponsored by EPA in 1995 and a Scientific Advisory Panel (SAP) review in 1998. The comments received during the workshop and SAP meeting provided valuable suggestions from both a technical and practical perspective and were used to revise this guidance and to address other issues identified in the Agency's review of studies conducted for the registration of over 50 pesticides. The recommendations in this guidance document also represent the Agency's substantial experience, over the last decade, in developing and articulating effective procedures for collecting high quality data on pesticide movement into ground water.

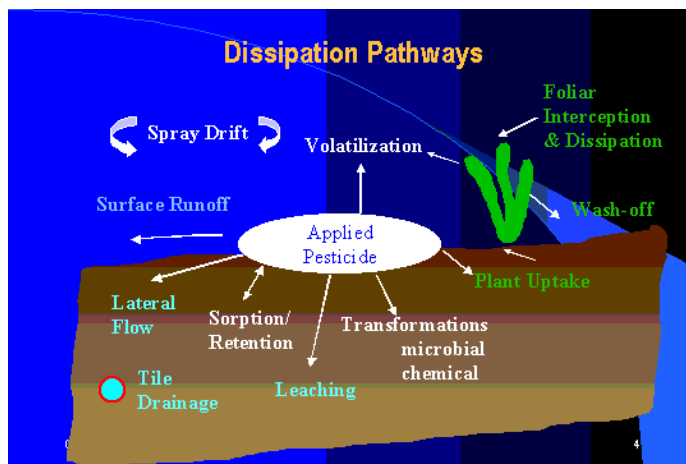
## **1.1 ENVIRONMENTAL EXPOSURE CHARACTERIZATION**

PGW studies may be required on a case-by-case basis, depending on an assessment of the pesticide's potential to impact ground water and the Agency's consideration of risk. Before a pesticide can be sold in the United States, EPA evaluates its safety to humans and to terrestrial and aquatic animals and plants, based on a wide range of laboratory and field studies. The environmental studies examine both the ecological effects (toxicity) of a pesticide and its chemical fate and transport. After EPA scientists review all the available information on toxicity, chemical fate and transport, and proposed use of a pesticide, they develop an environmental exposure characterization, which includes an exposure profile and conceptual model. The exposure characterization estimates the potential exposure of plants, animals, and water resources to pesticide residues in water, food, and air. The exposure profile describes:

- Degradation of the pesticide active ingredient (how fast and by what means it is degraded in the environment) and how persistent it is in the environment;
- Breakdown products or degradates that result from the degradation processes;
- Mobility of the pesticide active ingredient and its degradates and how these chemicals may be transported from the application site (*e.g.* volatilize into the atmosphere, move into ground or surface waters, or bind to the soil); and
- Accumulation of the pesticide and its degradates in the environment.

These environmental fate studies are designed to help identify which dissipation processes are likely to occur when a pesticide is released into the environment and to characterize the breakdown products that are likely to result from these degradation processes. The diagram below illustrates the potential dissipation pathways for a pesticide after it is applied.

**Figure 1. Pesticide Dissipation Pathways**



Based upon results of environmental fate and transport studies, EPA develops a preliminary, qualitative exposure assessment. This, in turn, may be used to design or trigger additional conditional field studies, such as the PGW study.

### **1.11 Fate and Transport Studies**

EPA reviews many laboratory and field studies to determine the fate of pesticides in the environment. The types of studies required depend on the use of the pesticide. Certain laboratory studies (*e.g.*, hydrolysis, photolysis, and soil metabolism) are routinely conducted for all outdoor-use pesticides. Other conditional studies (*e.g.*, PGW studies, photo-degradation in air, and field volatility) may be triggered by data from the initially required laboratory studies and/or use or application patterns and basic product chemistry data. The basic studies provide the following critical information for a pesticide active ingredient and its major degradates:

- Half-life of the parent (persistence)
- Identity of degradates
- Rates of formation and decline of degradates
- Bioconcentration potential
- Mobility of the parent and degradates

The Agency regulations found in 40 CFR 158.29 describe the types and amounts of data that the Agency needs for assessing the environmental fate of a pesticide active ingredient. These controlled laboratory and field studies, which are conducted under approved Guidelines and Good Laboratory Practices, are used to determine the persistence, mobility, and bioconcentration potential of a pesticide active ingredient and its major degradates. Generally, degradates formed at greater than or equal to 10% of the amount of applied pesticide are considered significant (*i.e.*,

major degradate) and should be identified in the study. In addition, degradates of known toxicological or ecotoxicological concern should be quantified and identified, even when present at less than 10% of the applied pesticide.

- **Physicochemical Degradation:** This includes hydrolysis and photo-degradation in water, soil, and air. Hydrolysis studies determine the potential of the parent pesticide to degrade in water, while photo-degradation studies determine the potential of the parent pesticide to degrade in water, soil or air when exposed to sunlight. During these studies, data are also collected concerning the identity, formation and persistence of degradates.
- **Biological Degradation:** These studies include aerobic and anaerobic soil metabolism, and aerobic and anaerobic aquatic metabolism. The soil metabolism studies determine the persistence of the parent pesticide when it interacts with soil microorganisms living under aerobic and anaerobic conditions. The aquatic metabolism studies produce similar data that are generated by pesticide interaction with microorganisms in a water/sediment system. These studies also identify degradates that result from biological metabolism.
- **Mobility:** These studies include leaching and adsorption/desorption, laboratory volatility, and field volatility. The leaching study assesses the mobility of the parent pesticide and its' degradates through columns packed with various soils. The adsorption/desorption study determines the potential of the parent pesticide and its' degradates to bind to soils of different types. The potential mobility of the parent pesticide and each degradate is determined by examining the data from both of these studies and may range from immobile to highly mobile.
- **Bioconcentration:** These studies use aquatic organisms to estimate the potential of a pesticide, under controlled laboratory conditions, to partition to the organisms from respiratory and dermal exposures. These studies also provide information on the degree a pesticide or degradate can be depurated should levels of the pesticide in the surrounding aquatic environment be reduced.
- **Field dissipation:** These studies track the dissipation of a pesticide from the surface soil layer, and the formation and dissipation of degradates. While laboratory environmental fate studies are designed to assess one dissipation process at a time, field dissipation studies assess pesticide loss as a combined result of chemical and biological processes (*e.g.*, hydrolysis, photolysis, microbial transformation) and offsite transport (*e.g.*, volatilization, leaching, runoff) as well as loss from plant uptake. These studies provide a field dissipation half-life, a lumped parameter that takes all routes of dissipation into account. Several field studies are usually conducted for each pesticide in typical use areas.

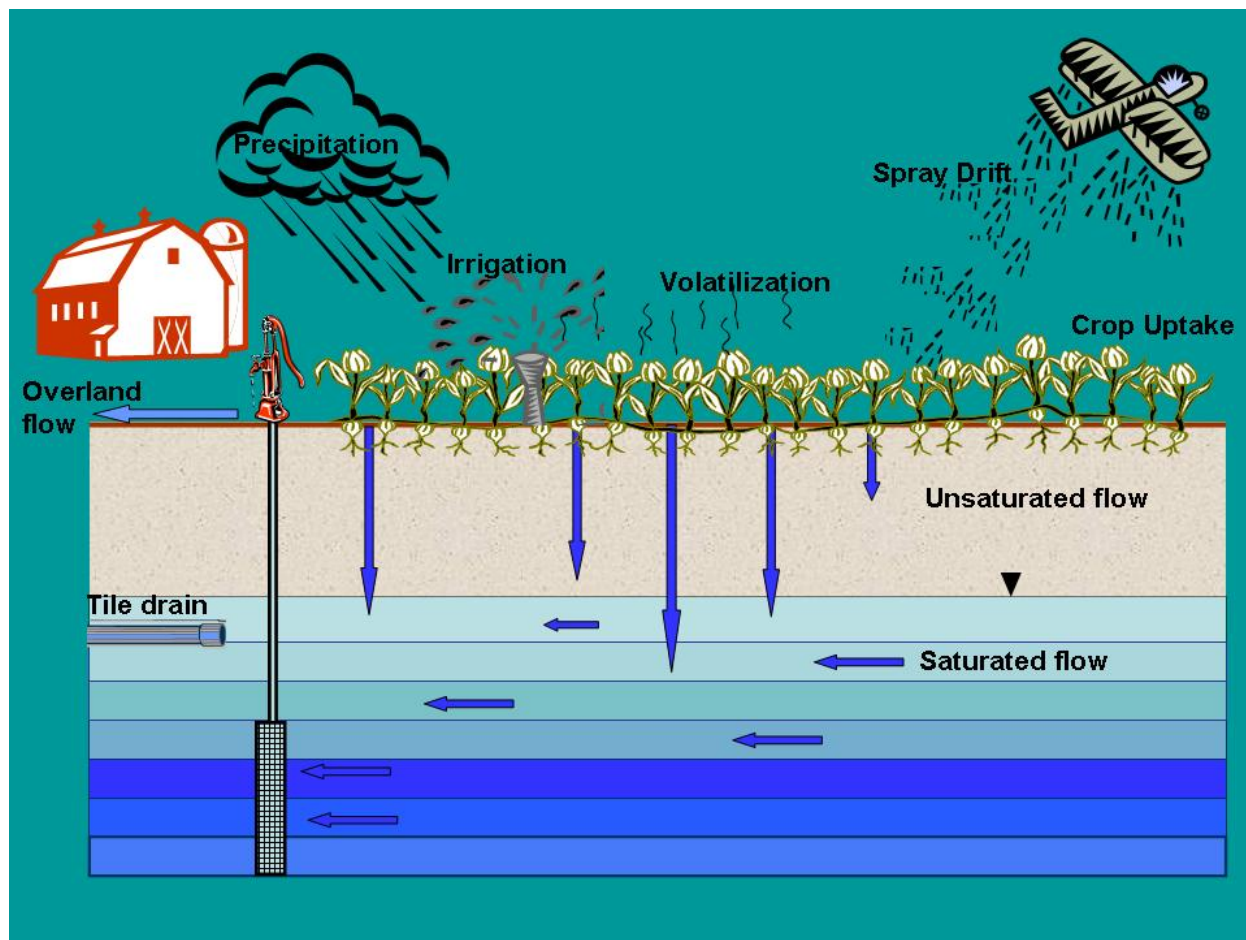
EPA's assessment may also identify whether pesticide mobility or persistence is affected by pH, temperature, or other factors. The exposure profile, combined with an evaluation of use and consideration of risk may trigger a PGW monitoring study.

### 1.12 Conceptual Model

The potential for pesticide movement to ground water depends on a variety of factors, including hydrologic properties of the overlying soil and vadose zone that affect downward movement of water and chemicals, travel time through the unsaturated zone to ground water, aquifer properties (conductivity, porosity, depth, type, location of recharge area), leaching potential of the pesticide (persistence and mobility), and type of well drawing water for drinking purposes (Focazio et al, 2002). These factors can vary significantly throughout the use area of a pesticide. While pesticide persistence and mobility parameters derived from laboratory studies are useful as a starting point for assessment, these parameters are not always sufficient to adequately characterize leaching of chemicals under actual field conditions. Data collected in PGW monitoring studies represent the integration of effects of multiple environmental and agronomic practices at a site where a specific crop is grown. The term *prospective* is based on a key aspect of the study design, namely, the pesticide has not been used previously at the site. If the pesticide is detected, then it is the result of the application during the study rather than a prior application (*e.g.*, at a different label rate) or mishandling of the pesticide during mixing, loading, or disposal activities.

A PGW monitoring study begins with the application of a pesticide and a mobile tracer compound to a site that has been instrumented (*i.e.* wells and other monitoring equipment has been installed) and where the crop is (or will be) planted. The crop is grown in a field during the study, following standard agronomic practices (*e.g.*, tillage, irrigation, crop cultivation). Figure 2 below depicts a generic conceptual model for pesticide transport to shallow, private rural wells in an agricultural area. Following pesticide application, residues can be washed off plant surfaces by precipitation or irrigation. They may adsorb to soils to varying degrees and may degrade as a result of chemical or biological processes. As water infiltrates through the vadose zone to the water table, pesticide residues can be transported to the subsurface and can adsorb and degrade further. Pesticides can be transported from a field in runoff after precipitation or irrigation, adsorbed to eroded soil, or volatilized in air. Pesticides also can be taken up to a varying extent by plants. A PGW study is designed to minimize the effect of some of these transport processes (*i.e.*, runoff or the impacts of artificial drainage) in the site selection process and to track the overall impact of other processes on water quality.

**Figure 2. Conceptual Model for Pesticide Transport to Shallow, Private Rural Wells.**



The vadose and saturated zones under the field are monitored over time (usually at least two years) for residues of the pesticide, significant degradates, and a conservative tracer. The tracer identifies the depth to which recharge has moved following the application of the pesticide. Weather data is also collected during the study. The pesticide and tracer are only applied one time, to enable the movement of the pesticide and the tracer to be tracked without interference. These studies track the movement of the pesticide, degradate, and applied water (using a tracer compound) through the soil into the water table and produce a time-series of concentrations over a period of several years. Adequate ancillary data are collected (*e.g.*, climate, timing and mass of pesticide applied, irrigation, soil characteristics) to enable the results to be interpreted. Study results should be evaluated, and concentrations adjusted accordingly to take into consideration the numbers and frequencies of application allowed on the label. The goal of the study is to determine whether a pesticide will move to ground water in some locations where it can be applied, and to determine the time-course concentrations in ground water of the pesticide, major degradates, and degradates of toxicological concern.

In order for the results to be applicable to regulatory decisions, the site selected for study should have certain characteristics. Depending on the objective of a particular study, a study site may be selected to represent an environment that is highly susceptible to leaching (*e.g.*, sites with coarse-textured soils that facilitate rapid transport) or a site that represents other conditions under which the pesticide is most typically used. Sites selected for study represent a specific use (or set of uses) of the pesticide, as well as soil, hydrology, and climatic conditions common to a use area; these conditions should be explicitly described in the site selection report. Site selection should also include consideration of other factors that dominate ground-water flow systems, *e.g.* regions dominated by karst topography or tile drains, especially if such factors dominate in an important use area. Ideally, multiple sites should be selected for monitoring that exhibit a range of characteristics of the broader use area. For example, selecting several sites that are highly vulnerable to leaching along with several sites presenting more typical vulnerability for a spatially diverse pesticide use area can provide a more complete understanding of the potential range of pesticide movement. Having results from a range of sites will enhance the Agency's ability to extrapolate results across the composite use area. When a single site is chosen for monitoring, the site should represent a highly vulnerability site. If the behavior of a pesticide (*i.e.*, its soil mobility and persistence) varies greatly from site to site, EPA may request site-specific measurements of degradation rates or sorption coefficients in the PGW study test soil. These data would aid in interpreting study results and in modeling.

## **1.2 GROUND WATER EXPOSURE AND ESTIMATING RISK**

Some pesticides and pesticide degradates pose a high risk at very low concentrations, while others pose less risk at these same low concentrations. Because of the substantial costs associated with conducting a PGW study, consideration is given to potential risk based on estimates of exposure from available monitoring data and from screening-level models.

### **1.21 Evaluation of Registered or Proposed Uses**

The way in which a pesticide is used can play a critical role in determining its impact on the environment. For example, pesticides that are exclusively used indoors pose negligible risk of direct ground-water contamination in comparison to those with outdoor uses. Some typical indoor uses include baits, greenhouse uses, and use in food handling establishments. While ground-water impacts associated with those uses can occur from improper handling or disposal, the PGW study focuses on water quality impacts resulting from use according to the registered label. Thus, a consideration of how the pesticide will be used is an important factor in assessing whether a study would provide data needed to reduce uncertainty in water exposure assessments.

### **1.22 Available Monitoring Data**

For the pesticide of concern, EPA may have available ground-water monitoring data collected by academic institutions, federal and state agencies, or pesticide registrants. Sources of these data include state monitoring databases, other federal agencies [e.g., United States Geologic Survey (USGS) monitoring programs like the National Water Quality Assessment Program (NAWQA) or the Toxic Substances Hydrology Program], Office of Pesticide Program's (OPP) Pesticides in Ground Water Database (USEPA, 1992), reports submitted to EPA under FIFRA § 6(a)(2), EPA's STORET database, the open literature, and monitoring conducted by public water supply facilities in compliance with the Safe Drinking Water Act. OPP compiles and evaluates available water monitoring data and examines the quality of the studies. In general, most monitoring studies are not designed to target and document impacts from the use of a specific pesticide at a specific rate, nor are they conducted with the level of quality assurance and quality control of a PGW study. Monitoring data typically provide a lower bound on potential exposure, especially where data are available to determine the amount of a pesticide applied (both the rate and numbers of applications) and the location of treated areas relative to sampling sites.

While most available monitoring data are not likely to be of adequate spatial and temporal resolution to address uncertainties in exposure for a specific pesticide, data are useful in EPA's determination of the need for a PGW study and may also be helpful in determining preferred test sites. These data may highlight uses for which impacts appear to be lower, and, thereby help EPA focus evaluation efforts or further monitoring on specific uses or geographical areas where impacts may be higher.

### **1.23 Modeling Ground Water Exposure**

EPA routinely uses the screening-level model (SCI-GROW) to estimate potential ground water exposure for pesticide water assessments. SCI-GROW is an empirical regression model developed by EPA and is based on monitoring results of PGW studies. This model requires limited input parameters (e.g.,  $K_{oc}$ , aerobic soil metabolism half-life, and annual pesticide application rate). Using these values, the model estimates the concentration of the pesticide (90-day peak) in shallow, unconfined aquifers that are subject to relatively rapid recharge and under conditions similar to sites where the monitoring was conducted). The model can simulate multiple applications of the pesticide and the results are useful when reviewed in conjunction with the field study. A detailed description of this model can be found at EPA's Web site: [www.epa.gov/oppefed1/models/water/index.htm](http://www.epa.gov/oppefed1/models/water/index.htm).

When the screening model estimates that a particular pesticide may leach into ground water at levels of concern, risk managers may determine that a PGW study will provide quality data to reduce the uncertainty in the assessment.

EPA is currently evaluating mechanistic models such as LEACHM (Hutson and Wagenet, 1992), PRZM (Carsel et al., 1997), RZWQM (DeCoursey et al., 1989), and PEARL (Leistra, et. al., 2001) and comparing estimates to monitoring data from PGW studies and other studies. OPP's overall ground water modeling approach and conceptual model has been peer reviewed by the FIFRA Scientific Advisory Panel at meetings in February 2005 (USEPA, 2005a) and August, 2005 (USEPA, 2005b). This methodology was implemented in water modeling conducted for the Revised N-Methyl Carbamate Cumulative Risk Assessment (USEPA, 2007).

### **1.24 Consideration of Risk**

Before requiring a PGW study, risk managers at EPA take into consideration the potential for human exposure to pesticide residues in drinking water and related uncertainties. Consideration of risk may also take into account the potential for ground water containing pesticide residues to impact the quality of ecologically sensitive surface water, as well as the intrinsic value of ground water as an important natural resource. Ground water contamination can be difficult and costly to remediate, and it can take many years for contaminants to naturally degrade even when point sources are removed. Water from private rural wells is typically not treated prior to consumption, and over 27 million people in the United States rely on private rural wells as their primary water source.

## **1.3 CASE STUDY**

The following case study is an example of the exposure assessment process that occurs before a ground-water study is required for a (hypothetical) herbicide, Chemical H, proposed for use on corn and soybeans.

### **1.31 Exposure Characterization**

The registration standard for Chemical H required the full complement of environmental fate studies, and data submitted by the registrant were acceptable. Overall, Chemical H 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 Chemical H degradation may be more rapid (*i.e.*, within a few weeks) under certain conditions in some soils.

The aerobic soil metabolism half-life was determined to be 35 to 70 days in studies conducted in several soils, and the anaerobic soil metabolism half-life averaged about 170 days. Based on these studies, it appears that Chemical H could be persistent enough in the field for significant leaching to occur. However, at some field dissipation study sites, Chemical H dissipated more rapidly (half-lives were less than three weeks at four of the eight study sites) than other soil-applied pesticides that have been found to reach ground water. Overall, at eight study sites, field dissipation half-lives for the upper six inches of soil ranged from 8 to 46 days. The field dissipation data indicates that Chemical H 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 Chemical H or its major degradate, Chemical H-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 Chemical H is 0.10 lb ai/A).

Chemical H is fairly resistant to abiotic hydrolysis. It hydrolyzes slowly in sterile water at pH 5 (extrapolated half-life is 91 days) and does not appreciably hydrolyze at pH 7 and 9 over the 30-day study period. Chemical H, though, is very susceptible to photolysis, with an aqueous photolysis half-life of 1 day and a soil photolysis half-life of 7 days.

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

Chemical H partitions primarily into the soil water in most soils. In soil column leaching studies, it is mobile in a sandy soil containing 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 associated with a soil containing 12% organic matter. It should also be noted that Chemical H solubility is considerably reduced in alkaline soils.

Chemical H-acid is even more mobile than Chemical H, with  $K_{oc}$  values from batch equilibrium studies ranging from 4 to 17 in the same four soils in which Chemical H sorption was studied. The degradate 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 was fully retained in the upper six inches of soil.

### **1.32 Monitoring**

Chemical H parent was detected in ground water sampled in a small number (5) of studies reported in the Office of Pesticide Program's (OPP's) Pesticides in Ground Water Database (USEPA, 1992). Although three detections exceeded the pesticide's Maximum Contaminant Level (MCL) and Health Advisory Level (HAL) of 7 µg/L, the majority of the detections (75%) were below 1 µg/L. No monitoring data are available for Chemical H-acid in ground water. Sufficient monitoring data, though, are available for the parent to demonstrate that Chemical H does leach to ground water after registered applications in some areas. However, some of the higher concentrations reported may be due to chemical spills or other accidents. The monitoring

data have not been collected in a sufficiently systematic way to determine under what specific conditions Chemical H is most likely to reach ground water. Based on a gross examination of the monitoring data, it appears that ground-water contamination may be more likely in the northern part of the Chemical H use area.

### **1.33 Modeling**

Initially, evaluation of Chemical H was performed with the screening model SCI-GROW. Screening modeling demonstrates that Chemical H has the characteristics (at least in the majority of use sites) of other pesticides with long-established uses that have been found in ground water. This is especially true of Chemical H-acid, which is both more mobile and more persistent than Chemical H parent. The soil half-life of this degradate has not been directly measured, but it appears to be much longer than 6 months in at least some soils. Based on SCI-GROW concentration estimates, residues of Chemical H alone exceed the aggregate risks for drinking water alone in OPP's human dietary risk assessment; similar exposure estimates for the degradate, which is assumed to have similar toxicity, will add to the risk.

PRZM modeling was conducted at 10 representative use sites. A simulation of leached residues for Chemical H was compared with simulated Chemical P residues, the corn and soybean herbicide most commonly detected in ground water. Twenty separate application years were simulated at each site. At 1 of the 10 sites, measured Chemical P residues from a vadose zone and ground-water monitoring study were compared with simulations for both chemicals. PRZM only roughly predicted the overall amount of Chemical P and its chemical behavior as it leached through the soil profile. At this, and at most other sites, when aerobic metabolism half-lives and average  $K_{oc}$  values were used, modeling always predicted that Chemical H would leach to a depth of 3 or 6 feet more than Chemical P (as a percentage of the application rate). However, if the Chemical H degradation half-life was shorter (*e.g.*, less than two weeks), then predicted leaching as well as the magnitude of residues was generally less than that of Chemical P. Chemical H-acid, when formed in sufficient quantities, was also predicted to leach substantially at many use sites.

### **1.34 Data Evaluation**

The weight-of-evidence of the environmental fate properties of the pesticide are enough to raise concern about its potential to reach ground water. Since the photolysis half-life for Chemical H is 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 Chemical H residues leaching to ground water. Based on a comparison with monitoring data, both Chemical H and Chemical H-acid residues may impact the quality of ground water and exceed EPA's regulatory endpoint in at least a portion of the use area. Moreover, Chemical H-acid has been found in tissues of laboratory animals in studies used to calculate the MCL and has also been found in tissues of fish, which appear to be among the most sensitive non-target organisms. Ecotoxicity studies indicate that concentrations of 1 µg/L in water over a period of a few weeks exceed Levels of Concern (LOCs)

for freshwater fish (Risk Quotient (RQ) of 12-30). This exceedance may pose a risk in areas where ground water discharges to surface water bodies. A more definitive analysis of the scenarios under which Chemical H residues leach significantly to ground water cannot be made at this time because of the uncertainty regarding the subsurface behavior of Chemical H and Chemical H-acid. Such data could be obtained, however, from PGW studies.

Given the large potential use area (corn and soybeans) for this pesticide, at least two ground-water monitoring studies are recommended to characterize potential exposure: one in a high-exposure area and another in a more typical-use area. For these studies, the pesticide should be applied by soil incorporation at the maximum rate allowed on the label. EPA is also requesting that a more sensitive analytical method be developed for Chemical H and Chemical H-acid in water, which detects residues at 0.1 µg/L rather than the current 0.5 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 impact the quality of ground water as a result of normal agricultural use. The uncertainty in this analysis may be greater for chemicals that have never been used and for degradation products that have little environmental fate data. In these cases, scientists should rely exclusively on the environmental fate assessment to determine the likelihood of leaching, and on predictions of models to estimate the concentrations that may occur. PGW studies may provide EPA risk assessors and risk managers with particularly valuable information in these circumstances.

## **1.4 STUDY COMPONENTS**

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. This flexibility also allows the study director to install more sampling devices and collect more samples than stipulated to meet the goal of the study, when needed. For example, if EPA approves a site where the hydrology is more complex and the depth to ground water is greater, for the study to be successful, more site instrumentation may be needed, and the term of the study is likely to be longer in order to determine the concentrations of the pesticide and major degradates.

The major design components for PGW monitoring studies and guidance on how to carry out these studies are explained in detail in the following chapters of this document:

- Site Selection
- Site Characterization and Site-Specific Conceptual Model
- Monitoring Plan Design

- Site Characterization and Monitoring Plan Design Reports
- Monitoring Plan Implementation
- Reporting

## 1.5 STUDY RESULTS

As specific stages of a PGW 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 subsequent chapters of this guidance. The reports should include the following information:

- Site Selection Report: Maps, tables, and a brief interpretive text. EPA 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, more detailed interpretation, and a proposed monitoring plan, including maps. The Site Characterization and Monitoring Plan Design Reports should 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 are highlighted in these reports, and 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 that indicates study results and rationale for termination along with accompanying data summary.
- Final Report: The final report will consist of a final review of study results and appendices, containing 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 PGW monitoring study.

## 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) should 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 should 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 because it has the 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 an 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).

## **2.1 STUDY SCOPE**

### **2.11 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 and 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 contamination of ground water 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 contamination of ground water 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 contamination of ground water; 2) identify the vulnerability associated with a "typical use site"; 3) identify sites throughout the use area that are most vulnerable to contamination of ground water; and 4) characterize the vulnerability of the sites they propose to study. The registrant should provide a complete description of the tool used to assess vulnerability and how this tool was used to select the candidate sites.

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 or deep within the soil column, 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.

## **2.12 Compounds of Interest and Analytical Methods**

All pesticides, 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 only once using the method of application stated on the product label. The application should be made at the highest recommended label rate for the crop used in the study.

A comprehensive description of the methods (USEPA, 1992) selected for the analysis of all compounds of interest should 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) should 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 should be developed, validated, and approved by EPA before beginning the prospective study, to ensure that the study is acceptable.

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 should 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 should provide or develop a state-of-the-art analytical method for pore-water or ground water for the parent pesticide and its degradates that has an MDL at or below 0.01% of the label application rate (calculated as the average concentration if the applied pesticide amount were distributed over the top 12 inches – which normally weighs about 4 million pounds / acre), or 0.05  $\mu\text{g/L}$ , whichever is lower. Unless the agency determines from submitted data by the registrant that a somewhat less sensitive method is acceptable and likely to still provide a basis for a practical accounting of the subsurface fate of the pesticide residues at the study site(s). PQL refers to the lowest concentration at which the laboratory can confidently quantify the concentration of the compound of interest. The study authors should 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 should 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 should also be reported.

## **2.2 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, and general hydrology including aquifer type and depth, and climate. Aquifers are herein defined as a saturated geologic unit that can transmit significant quantities of water under ordinary hydraulic gradients. However, many individuals rely on shallow ground water sources (*i.e.* shallow saturated soils) that do not necessarily meet this definition. The term "aquifer" used throughout this guidance is intended to cover both types of drinking water sources. 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 should 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.

### **2.21 Unconfined Aquifer**

Prospective ground-water monitoring studies are designed to monitor the downward movement of pesticides toward the water table. The quality of ground water in shallow, unconfined aquifers 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 measured 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 study maybe required to continue for a longer period of time. 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).

### **2.22 Shallow Depth**

Depth to the uppermost aquifer material is an important variable in determining the vulnerability of shallow unconfined aquifers to contamination 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. Therefore, professional judgment should be exercised to avoid picking a site with too shallow a ground water table. Sites with drain tiles, drainage ditches, etc. may also need to be considered for some pesticide uses particularly in those geographic use areas where they dominate. As noted above, sites with preferential flow and tile drains will require specialized protocols which will need to be reviewed on a case-by-case basis.

### **2.23 No Flow Restrictive Layers**

Sites with soil layers that may restrict the downward movement of water should 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 that 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.

## **2.24 Preferential Flow**

Consideration should be given to selecting sites with a documented history of preferential flow where the pesticide may be used in that area. Pesticides which will be used in areas dominated by preferential flow (*i.e.* soils with macropores or fingered flow in sandy soils) may leach faster in these soils than conventional flow transport processes and may be more representative of a “high exposure” scenario for that chemical. The consideration of sites dominated by preferential flow should be considered on a case by case basis.

Completion of test pits are a quick and inexpensive method for evaluating soil variability and determining if preferential flow is likely to be an important process at a site. Data collected during a study may also indicate if preferential flow processes are important. Site specific data can answer questions which provide insight into the presence of preferential flow processes. Examples of the types of questions are “did the tracer reach ground water quicker than expected, or not at all?”, “did pesticide leach to ground water faster than expected from modeling?”, and “is there variability in occurrence time and concentration of tracer and pesticide in lysimeters?”. The answers to these questions can provide information which suggests that preferential flow process may, or may not, be important at a specific site.

## **2.25 Tile Drains**

In some instances, a pesticide may be proposed for use in an area dominated by tile drains. Site selection should consider the occurrence of tile drains. However, care should be used when considering a site with tile drains. Installation of tile drains can fundamentally alter the structure of subsurface soils and result in “artificial” pathways for leaching. In no cases, should a site selected with tiles drains eliminate ground-water monitoring as part of the design due to the presence of tile drains. Sampling of tile drains may be considered as a supplement to the study, but not as a substitute to other required elements. The consideration of sites dominated by tile drains should be considered on a case by case basis.

## **2.26 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 % if the soil properties are more limiting and 25 % 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 NRCS. Refinement of NRCS 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 should be consistent with the conditions the study is intended to evaluate. For instance, soils appropriate for high-exposure ground-water monitoring studies should 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.

## **2.27 Low Topographic Slope**

The site should 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.

### **2.28 Stable Hydraulic Gradient**

It is recommended 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.

## **2.3 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 should be contacted about past agricultural practices and the long-term availability of the site for extended monitoring. If the farmer has not owned the property for at least the past five years, the previous owner should be contacted if possible to establish additional site history.

### **2.31 No Prior History of Test Pesticide Use**

The history of the site should 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 should 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 (an additional two to five years of site history, when possible).

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. In addition, sites that have received fill material from off-site sources should be identified due to potential contamination issues. 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.

### **2.32 Long-Term Availability of Study Site**

Ground-water monitoring studies are typically conducted over a 2 to 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-water and well-water samples. The site owner should be made aware that time estimates are imperfect, and that study conditions or chemical properties (i.e. very persistent chemicals) may require the site to be available for more than 3 years. Additionally, in cases where leaching of the pesticide is being investigated at multiple sites or in cases where application to sandy soils has already been excluded from the registration label, then studies may need to be conducted at sites where travel times to ground water are longer. If a site is not available for a minimum 2 to 3 years, the site should be eliminated from further consideration at this stage.

## **2.4 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 with 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 NRCS 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.

#### **2.41 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.

## **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. 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. Descriptions of agronomic practices (including irrigation and tillage) and climate (rainfall frequency, amount, and seasonal distribution) are also fundamental. 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 should be summarized and described in the Site Characterization Report (Chapter 5).

### **3.1 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.

### **3.11 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, an initial set of possible study site locations can be determined in part with a published United States Department of Agriculture (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. National Oceanic and Atmospheric Administration (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 to measure rainfall amount and intensity, soil and air temperature and pan evaporation is strongly recommended. Historical rainfall at or near the study site should be determined to ensure that water input during the study is consistent with historical data. A water balance should be developed to provide an estimate of the net historical recharge at the site.

### **3.12 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 a study site should have a low slope overall, small-scale natural variations in slope within a field can direct the flow of water to runoff or cause it to 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, weather stations, 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.

### **3.13 Information Sources**

Sources of information on soils, geology, hydrology, topography and climate include: local experts, USDA agricultural extension service, the USGS and state geologic surveys, USDA NRCS soil surveys, and the 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.

## **3.2 SOIL AND VADOSE ZONE INVESTIGATION**

Soil structure and variations in soil texture, surficial geology, topography, hydrology, and the impact of years of agricultural practices (e. g. tillage, irrigation, drainage structures) influence the extent to which precipitation or irrigation will infiltrate or runoff from a field. If site

characterization is inadequate, these real-world complexities will limit the interpretation of the monitoring data. 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 as to 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.

### **3.21 Exploratory Coring Program and Field Testing**

All site characterization programs should 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 can be identified. Before initiation of the exploratory coring program, an effort should be made to identify and locate utilities, irrigation systems, tile drains, etc. to avoid damage and costly repairs.

At least one continuous soil core (from the surface to the water table) from at least eight locations throughout the study site, as well as one continuous core from a control area assumed to be up-gradient of the study site, will be collected. A detailed drilling log should 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. Methods for collecting soil samples (such as split spoon or thin-walled Shelby tube) can be found in the open literature. A soil core 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, depth to the water table should be recorded.

Soil sub-samples should 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 should be divided into either six-inch intervals or by soil diagnostic horizon, whichever 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 should 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 should be taken from the 4-foot interval, to characterize the differences between soil types. Each

sample should be described in the field by an experienced geologist and/or soil scientist. In addition, all soil sub-samples should 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), 1 bar, 5 bar, and wilting point (15 bar) (all measured on undisturbed soil samples),
- 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 should not 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). Consideration should be given to conducting these tests on undisturbed samples where possible.

The compounds of interest (ie. pesticide, degradates and tracer), should also be analyzed for 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.

### **3.22 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 should 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.

### **3.23 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 be 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. Consideration should also be given to developing breakthrough curves to determine dispersivity and the likelihood for preferential flow and to estimate an effective porosity for soil samples.

### **3.24 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 should be followed in every case. The field personnel should follow all relevant Department of Transportation (DOT) and International Air Transport Association (IATA) hazardous materials and dangerous goods 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.

### **3.25 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 should be prepared and archived for all subsurface samples, and subsurface samples that are not destroyed by analytical procedures should be retained as reference samples for the duration of each study.

### **3.26 Test Pit Excavation**

The Agency views the completion of test pit excavations during the initial phases of the site characterization process as a quick and inexpensive way to assess the heterogeneity of a site and the potential for preferential flow. The 1998 Scientific Advisory Panel (SAP) identified the presence of preferential flow as a critical element to be assessed in the site selection/site characterization process. If a pesticide is to be used in an area dominated by preferential flow (e.g. in a karstic region or with extensive tile drainage) then site characterization should evaluate this process and consider sites with documented preferential flow. The completion of test pits at the subject site is a quick and inexpensive way to assess whether preferential flow is likely (at least in the near surface) at a site. Unusual conditions which may prove problematic for a Prospective Ground-Water Study (*i.e.* restrictive layers) can quickly be identified and result in significant cost savings. Test pits may also be considered during the course of the study when unusual conditions are noted. Test pits should not be located within the active monitoring area but should be located in close proximity to the area of pesticide application (*i.e.* immediately adjacent to the site or within a control plot).

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 common and should be investigated through use of test pits when considering a 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. 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 Division 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. All test pit activities should be conducted under the supervision of an Occupational Safety and Health

Administration (OSHA) required “competent person”. OSHA 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 should be undertaken and documented in the First Quarterly Report.

### **3.27 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 should 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. If additional fill material is required to complete the abandonment process, “pesticide-free” soil should be used.

## **3.3 SATURATED ZONE INVESTIGATION**

A limited investigation of the saturated flow regime should 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.

### **3.31 Hydraulic Head**

Piezometers should be installed at the site to measure the hydraulic head. If done simultaneously, piezometers may 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 should 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 should 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.

### **3.32 Direction of Ground-Water Flow and Hydraulic Gradient**

A map of the potentiometric surface of the surficial aquifer should 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).

### **3.33 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 a conservative tracer (or 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 should 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.

### **3.34 Background Water Quality**

Basic data should be collected to establish the background quality of ground water, irrigation water and precipitation at the study site. Analyses should include major ions (dissolved oxygen, alkalinity, etc.), major nutrients (nitrate, nitrite, ammonia, organic nitrogen, and phosphate), 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 should 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.

Ensure that the irrigation well is run long enough to ensure communication with the underlying aquifer.

### **3.4 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 should 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.

#### **3.41 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 should 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.

### **3.42 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) and tracer 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 should 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 should also be discussed.

## **CHAPTER 4 - MONITORING PLAN DESIGN**

Once the site has been characterized, the variability of soil properties and the ground-water 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 be conducted under FIFRA GLP, as described in 40CFR160. Written standard operating procedures (SOP) should 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
- Soil Water Monitoring Plan
- Ground-Water Monitoring Plan

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

### **4.1 SETTING UP**

#### **4.11 Agricultural Management Practices**

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 should be stored away from the study site so as to eliminate the possibility of contamination.

#### 4.12 Irrigation

The following guidelines assume that leaching of the pesticide is being investigated at a site selected because conditions exist at that site that are more likely to promote ground-water vulnerability and will provide data on the leaching of the pesticide under those conditions. Some alterations may be approved in the irrigation scheme at selected sites when leaching at multiple sites representing different levels of ground-water vulnerability is being investigated. Irrigation should 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 should be scheduled to occur within three days after the pesticide application, unless sufficient precipitation occurs during this time. Following the first irrigation event, dates should 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 should 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 should indicate the irrigation method, rate, schedule, and duration. Actual dates of irrigation events should be documented and reported in the Final Report.

Estimate target water requirement by month (for example: 120% of crop water demand or 120% of historical rainfall data, whichever is greater). However, it should be noted that the estimated target water requirement for a specific study site may be much greater than 120% of crop water demand or 120% of historical rainfall data. State agricultural agents should be consulted to determine an appropriate target irrigation rate in order to ensure recharge of irrigation water to ground water. For example, historical irrigation efficiencies in the San Joaquin Valley of California are estimated at 60% for surface (flood) irrigation and 70% for sprinkler irrigation (DWR, 1983; Snyder et al., 1986; California Agricultural Technology Institute, 1988). These efficiencies translate to water application rates of 167% and 143% of plant demand, respectively. In addition, extensive agricultural areas in California have been identified as vulnerable to ground water contamination due to the presence of coarse soils and shallow ground water. CA DRP has calibrated the LEACHM transport and fate model to these conditions and has estimated concentrations of pesticides in ground water from simulated water application of 167% of plant demand. These values agree well with measured well water concentrations (Spurlock, et al., 2006). California indicated they have limited water applications to 125% of plant demand to mitigate ground water contamination for some contaminants. Attached as a reference are two example spreadsheets that were developed by the California Department of Pesticide Regulation, Environmental Monitoring Branch to estimate drainage from a prospective ground water study. These goals should be maintained at the study site through each and every agronomic season starting from the initial pesticide application date throughout the entire monitoring period for the study unless alternate goals are agreed to by the Agency during the latter years of the study. Calculations for target water requirements should be based on 20-year data distributions (crop, study site/region, rainfall, irrigation, etc). Document calculations, assumptions, and reference 20-year data used in determining target water demand. Procedures used to determine the timing and amounts of water as a function of rainfall and other

climate conditions should be provided. The type of irrigation system, the frequency of irrigation, and the minimum amount of irrigation applied should conform with local agronomic practices for the specific crop and study soil. Consultation with state agricultural agents may be helpful in identifying the most suitable sites and applicable agronomic practices for the study. All irrigation events should be conducted so as to minimize surface pooling and runoff while maximizing the potential for infiltration.

#### **4.13 Initial Post-Pesticide Application Irrigation Event**

In general, the timing and rate of irrigation is more important during the initial days and weeks after application than it is as the study progresses into the second year and beyond. The relationship between rainfall timing and intensity and pesticide 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.

After initial pesticide application, a minimum of 1.0 inch of natural rainfall or irrigation should occur within 3 days and the application rate should be between 0.5 and 1.0 inches per hour. The first month's targeted rainfall plus irrigation amounts should be divided into four periods of 7-8 days each, and at least one fourth of the target monthly water requirement should occur in each of the four periods (apply additional irrigation water amounts in increments of 0.3 inches or greater as needed to meet the total month's targeted amount).

#### **4.14 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 ground water is recharged during the study. 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.

Beginning with the second month after application, at least the target water requirement for the specific month (as specified in Agency-approved Monitoring Plan Design report) should occur either in the form of natural rainfall or applied as irrigation. Irrigation does not have to be applied when the crop is not present. For example, irrigation should not be applied during winter months when freezing would destroy irrigation equipment. On occasion, at sites where precipitation has fallen well below historical norms for months or longer, some irrigation water might be applied during fallow months in order to meet the previously established water balance targets. Irrigation is not required at times when damage to the crop would occur (during times when drying is essential).

Sprinkler irrigation is preferred except in instances where other crop-specific methods (flood irrigation as an example) are required to assess movement under typical agronomic practices. Documentation should be provided, including references and names, for such crop-specific irrigation practices.

#### **4.15 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 down slope 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.

#### **4.16 Control Plot**

To establish background ground water quality, at least one well should 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 should be sampled on the same schedule as monitoring wells in the treated field. The control area and control well location(s) should be identified on the base map.

#### **4.17 Decontamination Area**

Prior to sampling soils or ground water, equipment should be cleaned to minimize the likelihood of cross-contamination. This should 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 should be identified on the base map. Additionally, rinsate should not be disposed of in “ecologically sensitive” areas, such as wetlands or down other wells.

#### **4.18 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 should 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. The weather station should be located close to the test plot in an open, exposed area without trees.

## **4.2 APPLICATION OF PESTICIDE AND TRACER**

### **4.21 Pesticide**

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

### **4.22 Tracer**

A conservative tracer should 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 soil and water samples (higher background levels of bromide, for example, at a study site can interfere with the ability to track the subsurface movement of the ion unless a relatively high initial application rate is used). Analytical methods, calibration procedures and amount of tracer applied should be documented and reported in the Monitoring Plan Design and Final Reports. The tracer should only be applied once at the same time as the initial pesticide application.

## **4.3 SOIL MONITORING PLAN**

The primary purpose of soil sampling in these studies is to verify pesticide application rate and to provide information on the dissipation of the compounds of interest in the zone of application, and not to track the movement of the test compound through the subsurface. Experience with prospective studies over the past 10 plus 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 should be measured for each sample collected.

#### **4.31 Soil Sampling Methods and Instrumentation**

Soil samples to verify the application rate should be collected using methods that ensure 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 should 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.

#### **4.32 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.

#### **4.33 Soil Sampling Timing and Frequency**

In general, soil samples should be collected until a pattern of persistence or decline of the compounds of interest has been established. 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) should 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 should be continued until at least three consecutive (normally monthly) samples show no residues above the minimum detection (not quantitation) limit or until termination of soil sampling is approved by EPA.

### **4.4 SOIL-WATER MONITORING PLAN**

Tracer and pesticide residues in soil water are monitored to provide an indication of the movement of water and the test pesticide through the vadose zone. Soil-water 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 by more than an order of magnitude. Also, water is likely the medium via which the solutes will be transported. Thus, soil-water 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.

#### **4.41 Soil Water Content Measurements**

The amount of water in soil, or the soil water content, is an important component of assessing 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 least monthly (preferably more frequently). Soil moisture measurements are a necessary piece of information needed for modeling flow and for onsite water management; for example, to determine when irrigation is needed. Soil water content should be determined for soil samples collected for pesticide and tracer residue analysis because these parameters should be reported on a dry-weight basis.

#### **4.42 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 soil 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.

#### **4.43 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.

#### **4.44 Soil water 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, should 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 should be used to collect samples of soil water for analysis of the applied chemical, degradation products, tracers and other species of interest.



#### **4.45 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 soil-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.

#### **4.46 Depth and Number of Lysimeters**

A minimum of eight clusters of four lysimeters each should 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. If the study is conducted at a site with a ground water table less than 15 feet below grade, fewer lysimeters will be required per cluster.

#### **4.47 Time of Emplacement**

Lysimeters should 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 should therefore be tested for operational effectiveness prior to the field application of the compounds of interest.

#### **4.48 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 should 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 should 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; however the practice of sample compositing should be avoided if at all possible. Criteria for termination of sampling are presented in Chapter 6. Approval for termination of monitoring should be received from EPA in writing.

## 4.5 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 should be collected and analyzed for all compounds of interest (Chapter 2).

### 4.51 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 ground water, and that well materials do not affect sample quality. Local and state monitoring well construction, installation and location requirements should be taken into account in planning well design. Studies have recommended against using existing drinking water wells for monitoring pesticide concentrations, finding a significant difference in detections between existing wells and stainless steel monitoring wells (Smith et al., 1998). Well abandonment at the completion of the study should be done in accordance with local and state regulations. To minimize site disturbance, borings completed for site characterization should be used to install monitoring wells.

#### **4.52 Number, Emplacement, and Screen Lengths of Wells Within a Cluster**

Ground-water monitoring wells should be installed as clusters. At each ground-water sampling location at least two depths should 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 should be placed to intercept the shallowest occurrence of ground water. This generally means that it will be screened across the water table. The top of the screen for the second well should be placed at the depth of 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 should be no longer than 1.5 meters; generally a smaller screen is preferable. 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 fluctuates due to seasonal or other influences a greater thickness of the aquifer should be screened.

#### **4.53 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 possibly down gradient of the treated field. A minimum of eight monitoring well locations should be spatially distributed within the treated field. The placement of a monitoring well down gradient of the treated field is not critical for a PGW study, but may be useful for the purposes of assessing impacts to nearby off-site water quality. State agricultural agents should be consulted during the planning stage in order to determine if a down gradient well is beneficial to the study being conducted (in addition to on-site wells) or even required by the state. The depth of the well should be determined based on local hydrology to ensure that water recharged on the treated field is intercepted by the well. State and local requirements for ground-water 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 not be placed in areas susceptible to runoff.

#### **4.54 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 ground water for site characterization prior to pesticide application.

#### 4.55 Sampling Frequency

Ground-water samples should be collected more frequently in the early part of the study and coordinated with the collection of soil and soil water samples and irrigation events. One pre-application sample should also be collected from all wells. Ground-water samples should be collected 14 days after the initial application, and at least once a month after that time from all monitoring wells. Additional samples should be collected before 14 days if there is reason to believe the compounds of interest may move rapidly (for example, following a large rainfall or irrigation event). 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 soil water sampling, additional ground-water sampling events may be scheduled. Criteria for termination of sampling are presented in Chapter 6. Approval for termination of monitoring should 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

#### **4.56 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 should be constructed of materials that will not contaminate or alter sample integrity. Typically teflon or stainless steel sampling equipment is 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 should be used.

#### **4.57 Sampling Methods**

Before any well is sampled, the static water levels should be obtained. Water levels should 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 should be purged before sampling. Samples should 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.

#### **4.58 Integrated Sampling Schedule**

Once design decisions have been made about how and when to sample soil, soil water, 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:

<b>ROUND</b>	<b>TIMING</b>	<b>MEDIA SAMPLED</b>
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 feet), ALL Monitoring Wells
Sample 7	1 month after application (irrigate)	Soil (0 - 2 feet), Soil Water (3, 6, 9 feet), 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 Wells

Sampling of soil water and ground water should continue until the patterns of transport and decline have been established for the test pesticide and associated 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.

## **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 should 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 should 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.

### **5.1 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, ground water 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.

### **5.11 Site Base Map**

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

### **5.12 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.

### **5.13 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.

### **5.14 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 that 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.



### **5.15 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.

### **5.16 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.

### **5.17 Saturated Zone Investigations**

The procedures used to gather information on the hydraulic characteristics of the shallow saturated zone should 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 should be reported, and the methods used to determine these estimates should 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.

### **5.18 Background Water Quality**

Basic data should be collected to establish the background quality of ground water, irrigation water and precipitation at the study site. Analyses should include major ions, major nutrients, 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).

### **5.19 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
- 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 depicts 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.

## **5.2 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 should 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 should 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 should be provided:

- Application rates,
- Compounds to be analyzed, including degradates and tracer,
- 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 should 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, should 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 soil water 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, soil water, soil water content, matric potential and ground-water sampling schedules.

The Monitoring Plan Design Report should 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 at least 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 soil water and ground water should continue until the patterns of transport and decline have been established for the test pesticide and associated 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
- Soil Water Monitoring
- Ground-Water Monitoring
- Sample Handling and Tracking

## **6.1 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 should 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 should 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 should be consistent with FIFRA Good Laboratory Practices (GLP).

## **6.2 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 should 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.

### **6.3 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 should 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 should carefully document procedures in the field notebook, noting any problems or deviations from the Monitoring Plan Design.

#### **6.31 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 should be cleaned prior to sample collection at each sampling interval. Field-blank water samples should be taken with each sampling round to test the effectiveness of the soil-equipment decontamination methods. All rinsate used in the decontamination process should be disposed of away from the study site. Additionally, rinsate should not be disposed of in “ecologically sensitive” areas, such as wetlands or down other wells.

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.

#### **6.32 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 should 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.

## **6.4 PORE-WATER MONITORING**

The primary purpose of soil water monitoring is to track the movement of dissolved pesticide and tracer toward the water table. Detection of tracer in the soil column indicates that downward movement is occurring; detection of tracer in the ground water indicates that recharge has occurred. Monitoring pesticide residues gives an indication of the relative rate of transport of the pesticide.

### **6.41 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 should 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 US EPA (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 should record problems encountered during installation or deviations from procedures and describe them in the First Quarterly Report and in the Final Report.



#### **6.42 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 should 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. Additionally, rinsate should not be disposed of in “ecologically sensitive” areas, such as wetlands or down other wells.

#### **6.43 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 should 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 should 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 water 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. A trip blank sample should be included to ensure cross-contamination of samples does not occur during shipment to the laboratory.

Any problems or variations in procedures in the Monitoring Plan Design Report should be described in the Quarterly Reports and in the Final Report. Reasonable effort should 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.

## **6.5 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 should be documented and discussed as they arise in each Quarterly Report and in the Final Report.

### **6.51 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 are returned to the state within a specific time following the emplacement of monitoring wells. States may also have specific monitoring-well construction requirements that should be followed. Wells should be installed by licensed drillers familiar with all relevant state and local requirements and supervised by an experienced geologist, professional engineer or environmental scientist. In addition, before initiation of the monitoring well installation program, an effort should be made to identify and locate utilities, irrigation systems, tile drains, etc. to avoid damage and costly repairs.

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 should 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 and,
- Weather conditions during the drilling activities.

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

### **6.52 Well Development**

Well development procedures should 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 should include: date of development and development method, volume of water removed, and a log of parameters monitored.

### **6.53 Decontamination**

Unless dedicated pumps are used for sampling, all ground-water sampling equipment should 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 et al., 1985). Other options are given in Driscoll (1986). All solvents used in decontamination activities should 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 non-dedicated equipment should 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 non-dedicated pumps are used for sample collection, deionized 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. Additionally, purge water should not be disposed of in “ecologically sensitive” areas, such as wetlands or down other wells. 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.

### **6.54 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 should 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. 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. Peristaltic pumps, low-flow submersible pumps and bladder pump are suitable for sampling for volatile pesticides.

Ground-water samples should be collected in containers that will not interact with the sample. Consult with the laboratory that the samples will be analyzed at to determine if preservation methods beyond the use of ice will be necessary to prevent additional degradation of the target compounds. Ensure that use of chemical preservatives will not interfere with analysis of target compounds. Ground-water samples should 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. A trip blank sample should be included to ensure cross-contamination of samples does not occur during shipment to the laboratory.

If the volume of available pore water 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 should be used and documented. Duplicate samples and field spike samples should be collected.

## **6.6 SAMPLE HANDLING AND TRACKING**

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

- Samples should 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 should 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 should follow all hazardous material labeling requirements.

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

All samples should be stored after collection according to GLP-compliant procedures and the stability should 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 should 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 should 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 should be shipped in such a way as to avoid breakage of sample containers and maintain sample integrity.

## CHAPTER 7 - REPORTING

Quarterly status reports for each prospective ground-water monitoring study should be submitted following the application of the compounds of interest. Required elements of these status reports are described in Section 7.1. 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 (i.e. no formal write-up of review will be submitted to registrant from the US EPA) 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 7.2 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 should also be submitted to EPA. Required elements of this report are described in Section 7.3. 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 which can be found at the US EPAs' Water Quality Data Submissions: OPP Standard Operating Procedure home page ([http://www.epa.gov/oppsrrd1/registration\\_review/water\\_quality\\_sop.htm#appendix\\_a](http://www.epa.gov/oppsrrd1/registration_review/water_quality_sop.htm#appendix_a)). All reports and supporting data should be submitted in an editable electronic format and as one hard copy.

### 7.1 QUARTERLY REPORTS

Quarterly status reports should 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,
- Concentrations or mass accounting 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. Individual results should be reported. Results should not be averaged over samples or time.
- Provide graphical representation of chemical analysis

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.

### **7.11 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 should 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 should 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.

### **7.12 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 monitoring well should be approximated.

### **7.13 Protocol Deviations**

Any deviations from the protocol established and approved as part of the Monitoring Plan Design should 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.

### **7.14 Analytical Results**

The results of all chemical analyses (*i.e.*, analyses for the test pesticide, degradates, and tracer) conducted on samples should 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.



## **7.2 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 should continue until EPA reviews the Study Termination Report and concurs that sampling can end. EPA will review the Study Termination Report within sixty days of receipt of the report. No study will be terminated before the questions for which the study was designed have been reasonably answered.

## **7.3 FINAL REPORT**

A Final Report should be submitted to EPA at the conclusion of each study. This report should 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. Individual results should be reported. Results should not be averaged over samples or time; 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.

### **7.31 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.

### **7.32 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.

### **7.33 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.

### **7.34 Quality Assurance**

Field studies should be conducted in compliance with good laboratory practices (GLPs) and should be properly 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.

## 7.4 ELECTRONIC DATA REPORTING GUIDELINES

Data generated from PGW 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. As part of an effort to update the Agency guidance for the PGW studies OPP has developed specific guidance for data submissions to improve the reliability, completeness, transparency, and consistency in the PGW reports and facilitate further use of these data for complete assessments of exposure to pesticides through ground water (*e.g.*, using leaching models to explore the potential for the pesticide of interest to leach under a variety of conditions). Specific requirements on the submission of electronic data are a matter that will be addressed for each study by EPA when Prospective Ground-Water study candidate site information is submitted to the Agency for approval. In general though, submission of this data electronically is likely to be requested and will help the Agency not only in the specific interpretation of the implications of the study results for the overall potential to impact ground water of the test pesticide but also to develop higher tier models and continue the advancement of pesticide risk assessments.

The following guidelines have been developed to assist in reporting of PGW monitoring information in electronic format. Listed below are eight major information fields which focus on the key areas for prospective ground-water monitoring data collection and reporting. These major information fields are;

- study area and conceptual site model;
- application of pesticide and tracer;
- crop information;
- soil properties;
- ground water data;
- weather data;
- irrigation application and
- chemical monitoring results.

Each major information field lists specific data types and requested data formats which serve as guidelines for submission of prospective ground-water monitoring study data.

#### **7.41 Study Area and Conceptual Site Model**

The following study area information is requested to provide background information as well as to develop a study-site conceptual model. The conceptual model should include graphs, charts, maps and data collected during site characterization. Integration of site hydrogeology, surface hydrology, and historical climatic data is acceptable.

##### **Study Area Information**

- Base map in GIS readable format (E.g., Arc shape files, \*.dxf files, a format specifically approved by EPA);
- NRCS soil surveys;
- Other historical information and
- Site Characterization Data of Study Area.
- Sample locations identified and reported in consistent coordinate system format (GPS; x,y coordinates; northing, easting; lat.,long.).
- Soil cores (coordinates) see soil properties below for listing of data to be reported, unsaturated and saturated hydraulic conductivity measurements at a minimum of 6 locations (coordinates) and soil horizons with depth (bgs, ft) and soil water content measurements at same 6 locations.
- Piezometers - if not placed in soil core holes need coordinates, measuring point surveyed with U.S. Geodetic Vertical Datum, hydraulic head measurements, hydraulic conductivity (slug tests and/or pumping test results), potentiometric surface diagrams, background water quality data from upgradient well and influence of existing irrigation wells in the area on subsurface hydraulics.

#### **7.42 Application of pesticide and tracer**

The following pesticide and tracer information is requested.

##### **Pesticide information**

- Chemical properties of test substance;
- molecular weight;
- CAS number;
- formulation and
- verification of formulation (method and results).
- Date(s) of pesticide application;
- Incorporation depth;
- method of application;
- total amount applied;
- rate;
- area covered (coordinates of locations where pesticide applied and/or boundary where pesticide applied) and
- soil monitoring results after application (field dissipation data).
- Topographic map detailing results of all surface soil samples collected to confirm application rate of pesticide. Determine if any hot spots of pesticides were detected post-

application. This may be used to determine if any detection of pesticides in monitoring wells, lysimeters, etc. can be correlated to a “hot spot” detected in surficial soil samples.

- If determined, any site-specific measurements of degradation or soil sorption should be reported

#### Tracer information

- Chemical;
- Formulation;
- locations where tracer applied (coordinates);
- method of application;
- rate of application and
- total amount applied.

### 7.43 Crop information

The following crop information is requested (include this for the entire course of the study, not just the year in which the pesticide is applied).

- Type of crop;
- planting dates;
- emergence dates;
- harvest date;
- date when chemicals applied (pesticide, herbicide, fertilizer, etc.) and
- other relevant crop maintenance activities and crop growth / land cover information.

### 7.44 Soil properties

All data need to be separately reported for each depth increment of each soil core analyzed. Some soil characteristic data may have been collected as part of the site characterization testing of the study area. If so, there is no need to repeat that information here. Pesticide property data essential for modeling of leaching of the test pesticide ( $K_{OC}$  and other measures of soil sorption and measures of soil degradation rate) for the specific test soil should be provided (along with background data relevant to the determination of these properties) if specifically collected in association with the prospective ground-water monitoring data in electronic format. In cases where pesticide property data are not specifically collected for the test soil, the extrapolated property data should be submitted along with the methodology for their calculation and citations for the studies these property data are derived from.

- Soil core location (coordinates);
- Minimum depth of the soil sample;
- Maximum depth of the soil sample;
- textural properties;
- sand/silt/clay fractions (%);
- CEC, or AEC;
- Mineralogy;

- bulk density (undisturbed);
- $K_{OC}$  of the pesticide in the test soil or extrapolated from data for other soils;
- $K_d$  of the pesticide in the test soil or extrapolated from data for other soils;
- $K_f$  (Freundlich) adsorption constant of the pesticide in the test soil or extrapolated from data for other soils;
- degradation rate of the pesticide in the test soil or extrapolated from data for other soils,
- organic matter content;
- field capacity (1/3 bar);
- 1 bar soil water content;
- 5 bar soil water content;
- wilting point (15 bar);
- saturated hydraulic conductivity;
- soil water content;
- matric potential;
- Munsell color and
- pH.

#### **7.45 Ground-water data**

Some of these data may have been collected as part of the site characterization of the study area. If so, there is no need to repeat that information here.

- Well location (coordinates);
- total depth of well;
- depth to water table;
- screened interval;
- background water chemistry;
- hydraulic head;
- flow;
- subsurface geology,;
- cross sections (descriptions, fence diagrams) and
- location (in 3-dimensions) of known aquitards.

#### **7.46 Weather data**

The following site-specific weather data collected during the PGW study is requested from a weather station located close to the test plot in an open, exposed area without trees;

- location of monitoring station (coordinates);
- rainfall, daily time step or shorter;
- pan evaporation;
- air temperature and
- soil temperature (including depth measured at).

In addition, site-specific historical weather data for the previous 20-years (or as recent a 20+ year period that is available) should be provided or referenced for analyses purposes.

#### **7.47 Irrigation input**

The following site-specific irrigation information is requested;

- irrigation method;
- irrigation application date (days after treatment (DAT));
- rate and
- total amount applied.

#### **7.48 Chemical monitoring results**

The following chemical monitoring data for soil and ground water is requested. All headings should be clearly labeled and explanations provided in an accompanying text file for clarity. See attached template for example. All analyses above the minimum detection limit should be reported as the nominal concentration. If the nominal concentration of a sample is below a Minimum Reporting Limit or Minimum Quantification Limit is applicable (whether calculated as a uniform limit or on a sample-by-sample basis) this information should be captured in a separate data field. Specific data fields are;

- study identifier;
- study type;
- media sampled;
- analytes (CAS numbers for parent compound and metabolites);
- sample location (coordinates);
- date of sample;
- depth of sample;
- analytical result (not averaged over samples or time) and
- analytical QA/QC data (method description, method quantification limit, method reporting limit, sample quantification limit, data qualifiers).
- At a minimum, provide analytical results for each monitoring well in x-y graph format so a trend in increase and/or decrease will be easily visualized. Graph results for each monitoring well separately for entire sampling period (i.e. 24 months).

All tabular data should be in either ASCII or MS Access format (or a format specifically approved by EPA).

## CHAPTER 8.0 - REFERENCES

Aller, L.T., T.W. Bennett, G. Hackett, R.J. Petty, J.H. Lehr, H. Sedoris, D.M. Nielsen and J.E. Deene. 1990. *Handbook of suggested practices for the design and installation of ground-water monitoring wells*. National Water Well Association. Dublin, OH. p. 398.

American Water Works Association. 1984. *Appendix I: Abandonment of test holes, partially completed wells and completed wells*. Standard for Water Wells. American Water Works Association. Denver, CO. p 45-47.

ASTM Committee D-18 on Soil and Rock. 1994. *ASTM standards on ground water and vadose zone investigations*. 2<sup>nd</sup> ed. ASTM. Philadelphia, PA . p. 432.

Barcelona, et al. 1985. *Sampling tubing effects on ground water samples*. Analytical Chemistry, 57: 460-464.

Barcelona, M.J. 1989. *Overview of the sampling process*. In: Keith, L.H. (ed.). Principles of environmental sampling. American Chemical Society. Washington, DC.

Barth, D.S., B.J. Mason, T.H. Starks and K. W. Brown. 1989. *Soil Sampling Quality Assurance Guide*. 2<sup>nd</sup> ed. EPA 600/8-89/046. USEPA. EMSL-LV. Las Vegas, NV.

Boulding, J. R. 1996. *Subsurface characterization and monitoring techniques: A desk reference guide*. DIANE Publishing. Upland.

Burkart, M.R., S.L. Oberle, M.J. Hewitt, and J. Pickus. 1994. *A framework for regional agroecosystems characterizations using the National Resource Inventory*. J. Environ. Qual. 23:866-874.

California Agricultural Technology Institute. (1988) Irrigation systems and water application efficiencies. CATI Center for Irrigation Technology, publication 880104. California: California State University, Fresno, pp. 6.

Cambardella, C.A., T.B. Moorman, T.B. Parkin, and D.L. Karlen. 1994. *Field-scale variability of soil properties in Central Iowa soils*. Soil Sci. Soc. Am. J. 58:1501-1511.

Carsetl, et al. 1997. R. Carsel, J. Imhoff, P. Hummel, J. Cheplick and A. Donigan, *PRZM 3.1 Users Manual, National Exposure Research Lab*, Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia (1997).

Cassel, D.K. and A. Klute. 1986. Intake Rate: Cylinder Infiltrometer. p. 825-844. In: A. Klute (ed.) *Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods*. Agronomy Monograph No. 9 (2<sup>nd</sup> ed.). ASA, Madison, WI.



Decoursey, D.G., Rojas, K.W., Ahuja, L.R., 1989. *Potentials for non-point source groundwater contamination analyzed using RZWQM*. Paper No. SW892562, presented at the International American Society of Agricultural Engineers' Winter Meeting, New Orleans, Louisiana.

Diaz-Diaz, R., J.E. Garcia-Hernandez and K. Loague. 1998. *Leaching potentials of four pesticides used for bananas in the Canary Islands*. J. Environ. Qual. 27:562-572.

Dorrance, D.W., L.G. Wilson, L.G. Everett and S.J. Cullen. 1991. *Compendium of in situ pore-liquid samplers for vadose zone*. In: Nash, R.G. and Leslie, A.R. (ed.) Groundwater-residue-sampling-design. ACS Symposium Series 465. American Chemical Society. Washington, DC.

Driscoll, F.G. 1986. *Groundwater and wells*. 2<sup>nd</sup> ed. Johnson Division. St. Paul, MN.

DWR. (1983). The California Water Plan: projected use and available water supplies to 2010. California Department of Water Resources Bulletin, 160-83, pp. 268.

Everett, L.G., E.W. Hoylman and L.G. Wilson. 1983. *Vadose zone monitoring at hazardous waste sites*. EPA 600/X-83/064. USEPA. ORD. Washington, DC.

Everett, L.G. and L.G. McMillion. 1985. *Operational ranges for suction lysimeters*. Ground Water Monitoring Review. 5:51.

Everett, L.G., L.G. Wilson and E.W. Hoylman. 1984. *Vadose Zone Monitoring for hazardous waste sites*. Noyes Data Corporation. Parkridge, NJ.

Fetter, C.W. 1988. *Applied Hydrogeology*. 2<sup>nd</sup> ed. Merrill Publishers. Columbus, OH.

Focazio, M.J., Reilly, T.E., Rupert, M.G., and Helsel, D.R., 2002. *Assessing Ground-Water Vulnerability to Contamination: Providing Scientifically Defensible Information for Decision Makers*. U.S. Geological Survey Circular 1224, 33 p.

Freeze, R.A. and J. A. Cherry. 1979. *Groundwater*. Prentice-Hall. Englewood Cliffs, NJ.

Gardner, W. H. 1986. *Water content*. p. 493-544. In: A. Klute (ed.) Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods. Agronomy Monograph No. 9 (2<sup>nd</sup> ed.). ASA, Madison, WI.

Gardner, W. H. 1986. *Water Potential: Tensiometry*. p. 563-596. In: A. Klute (ed.) Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods. Agronomy Monograph No. 9 (2<sup>nd</sup> ed.). ASA, Madison, WI.

Gibbons, R. D. 1994. *Statistical methods for ground-water monitoring*. John Wiley & Sons. New York. p. 286

Hershfield, D.N. 1961. *Rainfall Frequency Atlas of the United States*. U.S. Weather Bureau Tech. Paper 40. Department of Commerce. U.S.Govt. Printing Office. Washington, DC

Hutson, J.L., and R.J. Wagenet. 1992. *LEACHM: Leaching Estimation and Chemistry Model: A process-based model of water and solute movement, transformation, plant uptake and chemical reactions in the unsaturated zone*. Water Resource Institute, Cornell University, Ithaca, NY.

ILSI. 1998. *Assessment of Methods to Estimate Pesticide Concentrations in Drinking Water Sources*. Report of a workgroup on Aggregate Exposure Assessment, International Life Science Institute, Washington, DC.

Isensee et al., 1990. A.R. Isensee, R.G. Nash and C.S. Helling, *Effect of conventional vs. no-tillage on pesticide leaching to shallow groundwater*. Journal of Environmental Quality. **19** (1990), pp. 434–440.

Israelson, O.W. and V.E. Hansen. 1962. *Irrigation Principles and Practices*. J. Wiley and Sons, Inc. New York, NY.

Jensen, M.E. et al. 1973. *Consumptive Use of Water and Irrigation Water Requirements. Technical Committee on Irrigation Water Requirements of the Irrigation and Drainage Division*. American Society of Civil Engineering.

Jury, W.A., W.R. Gardner and W.H. Gardner. 1991. *Soil Physics*, 5<sup>th</sup> ed. John Wiley and Sons. New York. p. 328.

Kellog, R.L., M.S. Maizel, and D.W. Goss. 1992. *Agricultural Chemical Use and Ground Water Quality: Where are the Potential Problem Areas?* SCS/ERS/CSRS USDA. Washington, DC

Klute et al. 1986. *Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods*. Agronomy Monograph No. 9. 2<sup>nd</sup> ed. ASA, Madison, WI.

Kolpin, D.W., M.R. Burkhardt, and E. M. Thurman. 1993. *Hydrologic, water quality, and land-use data for the reconnaissance of herbicides and nitrate in near-surface aquifer of the midcontinental United States*. U.S. Geol. Surv. Open File Rep., 93-114.

Leistra, M., A.M.A. van der Linden, J.J.T.I Boesten, A. Tiktak and F. van den Berg. 2001. *PEARL model for pesticide behaviour and emissions in soil-plant systems. Description of processes*. Alterra report 13, RIVM report 711401009, Alterra, Wageningen, 107 pp.

- Litaor, M.I. 1988. *Review of solution samplers*. Water Resour. Res. 24:727-733.
- Mason, B.J. 1983. *Preparation of soil sampling protocol: techniques and strategies*. EPA 600/4-83-020. USEPA. EMSL-LV. Las Vegas, NV.
- McLay, C.D., K.C. Cameron, and R.G. McLaren. 1991. *Effect of time of application and continuity of rainfall on leaching of surface applied nutrients*. Aust. J. Soil Res. 29:1-9.
- Mehnert, E., S.C. Schock, M.L. Marnhardt, M.E. Caughey, S.F.J. Chou, W.S. Dey, and G.B. Dreher. 1995. *The occurrence of agricultural chemicals in Illinois' rural private wells: Results from the pilot study*. Ground Water Monit. Rem. 15:142-149.
- Mickam, J.T., R. Bellandi and E.C. Tiffet, Jr. 1989. *Equipment decontamination procedures for ground water and vadose zone monitoring programs: status and prospects*. Ground Water Monitoring Review. 9:2. p 100-121.
- Morrison, R.D. 1983. *Ground-water monitoring technology*. Timco Manufacturing Co. Prairie du Sac, WI.
- Nash, R. G. and A. R. Leslie. 1991. *Groundwater residue sampling design*. Washington: American Chemical Society.
- National Ground Water Association. 1989. *Handbook of suggested practices for the design and installation of ground water monitoring wells*. National Ground Water Assoc. Westerville, OH.
- Nielsen, D.M. 1991. *Practical handbook of ground water monitoring*. Lewis Publishers. Boca Raton, Fl. p. 728
- Nielsen, D.M. and A.I. Johnson. 1990. *Ground water and vadose zone monitoring*. ASTM special technical publication 1053. ASTM. Philadelphia, PA. p. 313
- Parizek, R.R. and B.E. Lane. 1970. *Soil-water sampling using pan and deep pressure vacuum lysimeters*. J. Hydrology. 11:1.
- Rawlins, S. L., and G. S. Campbell. 1986. *Water potential: Thermocouple psychrometry, in Methods of Soil Analysis, part 1*, Physical and Mineralogical Methods, Agronomy, no. 9, 2nd ed., edited by A. Klute, pp. 597–617, Soil Science Society of America, Madison, Wisconsin.
- RCRA ground water monitoring: Draft technical guidance*. Government Institutes Incorporated.
- Schwab, G.O., R.K. Frevert, T.W. Edminster, and K.K. Barnes. 1981. Chapter 2. *Precipitation* (pgs. 17-48). Soil and Water Conservation Engineering. J. Wiley and Sons, New York, NY.

Shipitalo, M.J., W.H. Edwards, W.A. Dick, and L.B. Owens. 1990. *Initial storms effects on macropore transport of surface-applied chemicals in no-till soil*. Soil Sci. Soc. Am. J. 54:1530-1536.

Shirmohammadi, A. 1991. *Use of ground penetrating radar to improve water quality monitoring in the vadose zone*. In: Kung, K.J.S., J. Boll, J.S. Selker, W.F. Ritter, T.S. Steenhuis and T.J. Gish(ed.). *Preferential flow: proceedings of the National Symposium*. Chicago, Illinois. American Society of Agricultural Engineers. St. Joseph, MI.

Sigua, G.C., A.R. Isensee, and A. M. Sadeghi. 1995. *Influence of rainfall intensity and crop residue on leaching of atrazine through intact no-till soil cores*. Soil Sci. 156:225-232.

Sigua, G.C., A.R. Isensee, and A. M. Sadeghi. 1995. *Influence of tillage, antecedent moisture, and rainfall timing on atrazine transport*. Weed. Sci. 43:134-139.

Smith, C.N., W.R. Payne, Jr., J.D. Pope, Jr., J.H. Winkie and R.S. Parrish. 1998. *A Field Study to Compare Performance of Stainless Steel Research Monitoring Wells with Existing On-Farm Drinking Water Wells in Measuring Pesticide and Nitrate Concentrations*. U.S. Environmental Protection Agency, Athens, GA. Publication No. EPA/600/R-98/025.

Snyder, R.L., Hanson, B.R. and Coppock, R. (1986). *How farmers irrigate in California*. University of California Division of Agriculture & Natural Resources, Leaflet 21414. Oakland, California, pp. 6.

Soil Survey Division Staff. 1993. *Soil Survey Manual*. USDA. Agricultural Handbook 18. U.S. Government Print Office. Washington, DC.

Soil Survey Staff. 1975. *Soil Taxonomy*. USDA. Agricultural Handbook 436. U.S. Govt. Print Office. Washington, DC.

Soil Survey Staff. 1992. *Keys to Soil Taxonomy*, 5<sup>th</sup> ed. SMSS Technical Monograph No. 19. Pocahontas Press, Blacksburg, VA.

Soil Survey Staff, 1993. *Soil Survey Manual*. U.S. Dept. Of Agric. Handbook No. 18. U.S. Govt. Printing Office. Washington, DC.

Soil Survey Staff. 1996. *National Soil Survey Handbook*. USDA Natural Resources Conservation Service, National Soil Survey Center. Lincoln, NE

Spurlock, F., Clayton, M. and Troiano, J. (2006). *Modeling herbicide movement to ground water in irrigated sandy soils of the San Joaquin Valley, California*. Water, Air, and Soil Pollution 176:93-111.

Stannard, D.I. 1990. *Tensiometers—theory, construction and use*. In: *Ground Water and Vadose Zone Monitoring*. ASTM STP 1053. p. 34-56.

Stephens, D.B. 1995. *Vadose zone hydrology*. CRC Lewis Publishers, Boca Raton, FL.

Topp, G.C. 1993. *Soil Water Content*. p 541-557. In: M.R. Carter. (ed.). *Soil Sampling and Methods of Analysis*. Canadian Soc. of Soil Sci. Lewis Publishers. Boca Raton, FL.

United States Department of Agriculture. 1993. *Soil survey manual*. [Rev. ed.]. Agriculture handbook no. 18. U.S. Department of Agriculture. Washington, D.C. p. 437.

USEPA. 1986a. *Permit guidance manual on unsaturated zone monitoring for hazardous waste land treatment units*. EPA 530-SW-86-040. EMSL-LV. Las Vegas, NV. p. 111.

USEPA. 1986b. *Permit guidance manual on unsaturated zone monitoring for hazardous waste land treatment units*. EPA 530-SW-86-040. Office of Solid Waste and Emergency Response. Washington, DC.

USEPA. 1986c. *RCRA ground-water monitoring technical enforcement guidance document. OSWER 99501.1*. Office of Waste Programs Enforcement. Office of Solid Waste and Emergency Response. Washington, DC. p. 317.

USEPA. 1990. *Ground Water. Volume 1: Ground Water and Contamination*. EPA 6256-90/016a. USEPA. ORD. Cincinnati, OH.

USEPA. 1992a. *Glossary of Quality Assurance Terms*. USEPA Quality Assurance Management Staff. Washington, DC.

USEPA. 1992b. *Pesticides in Groundwater Database*. Washington, DC.

USEPA. 2005a. *N-Methyl Carbamate Pesticide Cumulative Risk Assessment: Pilot Cumulative Analysis, Session 3: Drinking Water Exposure Assessment, February 15 – 18, 2007*, <http://www.epa.gov/oscpmont/sap/meetings/2005/index.htm#feb22>, accessed 11/28/2007.

USEPA. 2005b. *Preliminary N-Methyl Carbamate Cumulative Risk Assessment, August 23 - 26, 2007* <http://www.epa.gov/scipoly/sap/meetings/2005/index.htm#august>, accessed 11/28/2007.

USEPA. 2007. *Revised N-Methyl Carbamate Cumulative Risk Assessment, September 24, 2007*, Docket Number: EPA-HQ-OPP-2007-0935, Document ID: EPA-HQ-OPP-2007-0935-0003. [http://www.epa.gov/pesticides/cumulative/common\\_mech\\_groups.htm#carbamate](http://www.epa.gov/pesticides/cumulative/common_mech_groups.htm#carbamate), accessed 11/28/2007.

- United States Soil Conservation Service. 1994. *Keys to soil taxonomy*. 6<sup>th</sup> ed. Washington, D.C.: U.S. Dept. of Agriculture. Soil Conservation Service. p. 524
- United States Soil Management Support Services. 1990. *Keys to soil taxonomy*. 4<sup>th</sup> ed. SMSS technical monograph ; no. 19. Virginia Polytechnic Institute and State University, Blacksburg, VA. p. 422.
- Walton, W.C. 1987. *Ground Water Pumping Test Design and Analysis*. National Water Well Association. Dublin, OH. p. 160.
- Webster, R. 1985. *Quantitative spatial of analysis of soil in the field*. Adv. Soil Sci. 3:1-70.
- Weintraub et al. 1989. *Summary of state ground water quality monitoring well regulations*. Westerville: National Ground Water Assoc.
- Weiss, L.L. 1962. *A General Relationship between frequency and duration of precipitation*. Monthly Weather Rev. 87-88.
- Wilson, L.G. 1990. *Monitoring in the vadose zone: a review of technical elements and methods*. EPA 600/7-80-134. USEPA. EMSL-LV. Las Vegas, NV. p. 168.
- Wilson, Lorne G., L.G. Everett, and S.J. Cullen. 1994. *Handbook of Vadose Zone Characterization and Monitoring*. Lewis Publishers. Boca Raton, FL. p. 730.
- Wilson, L.G., D.W. Dorrance, W.R. Bond, L.G. Everett, and S.J. Cullen. 1995. *In situ pore-liquid sampling in the vadose zone*. p. 477-521. In L.G. Wilson, L.G. Everett, and S.J. Cullen (ed.) *Handbook of Vadose Zone Characterization and Monitoring*. Lewis Publishers, Ann Arbor, MI.