

**NAFTA Guidance Document
for
Conducting Terrestrial Field Dissipation Studies**

Prepared by:

M. Corbin, W. Eckel, M. Ruhman, D. Spatz, and N. Thurman

**United States Environmental Protection Agency
Office of Pesticide Programs
Environmental Fate and Effects Division**

and

R. Gangaraju, T. Kuchnicki, R. Mathew, and I. Nicholson

**Health Canada
Pest Management Regulatory Agency
Environmental Assessment Division**

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I. Introduction

The harmonization of pesticide regulatory requirements being carried out under the auspices of the North American Free Trade Agreement (NAFTA) Technical Working Group (TWG) on Pesticides is important in achieving the goal of one North American market for pesticides. This goal is articulated in the document known as the *North American Initiative* (NAI). The NAI commits Health Canada's Pest Management Regulatory Agency (PMRA) and the United States Environmental Protection Agency (USEPA) to harmonize pesticide regulatory tools so that work sharing and joint review activities become routine.

This document represents the NAFTA harmonized guidance for terrestrial field dissipation (TFD) studies, which are conducted to demonstrate the transformation, transport and fate of pesticides under representative actual use conditions. These field studies are needed to substantiate the physicochemical, mobility and biotransformation data from laboratory studies. Environmental fate studies have shown that pesticide dissipation may proceed at different rates under field conditions and may result in degradates forming at levels different from those observed in laboratory studies.

The objective of this revised guidance document is to help ensure that TFD studies are conducted in a manner that will provide risk assessors and risk managers with more confidence in the data generated and with a better understanding of the assumptions and limitations of the data and estimated half-lives of the chemical. Properly designed field dissipation studies will also provide a feedback mechanism for testing the hypothesis generated during the problem formulation phase of the risk assessment. Often, the interpretation of the field results relative to the hypothesis of expected behaviour requires an understanding of the specific site conditions under which the study was conducted. Appendices I through VIII provide examples of the data elements EPA/PMRA believe are critical for evaluating the hypothesis.

In developing this guidance document, EPA and PMRA conducted an extensive outreach and review program, soliciting input from stakeholders and the technical community through several forums: three symposia (4) (5) (6), one Scientific Advisory Panel (SAP) meeting (7) and one workshop (8). Working closely with its stakeholders, PMRA and EPA developed a conceptual model for designing terrestrial studies that will evaluate the overall dissipation of a pesticide in the field. The conceptual model, which is specific for each pesticide, is based on the chemical's physicochemical properties, laboratory environmental fate studies, formulation type and intended use pattern. It is a prediction of the relative importance of each of the transformation and transport processes that may be involved in the dissipation of a pesticide under field conditions and represents the sum total of all potential dissipation processes (see Figure 1). As such, it can be used as a working hypothesis for TFD studies.

A conceptual model is developed for an individual pesticide using assumptions derived from laboratory data in combination with the formulation type and field conditions under which the study will be conducted; it includes only those fate processes that are "significant" to the pesticide in question. Although the responsibility for determining which processes are significant rests with the study sponsor, EPA and PMRA may be consulted after the

development of the pesticide-specific conceptual model if there is a question about whether a particular dissipation process (i.e., represented by individual study modules) should be included in the study protocol. Through the use of the conceptual model approach, study sponsors should be able to provide data that are useful in the assessment and characterization of exposure and risk, fully support claims of dissipation in the final analysis and reduce the number of rejected studies.

As ecological risk assessment evolves, so does the need for its risk assessments to be based on more precise characterization of the data. Critical in this characterization is an understanding of the assumptions and limitations inherent in the data. The TFD study is a keystone study that provides the primary means for testing the hypothesis of pesticide behaviour under actual use conditions. Although laboratory data is the foundation for the hypothesis and the basis for the conceptual model approach, the TFD study provides the primary mechanism for testing and refining the hypothesis for the environmental fate and transport of a pesticide under actual use conditions.

A. The Conceptual Model

Well-designed TFD studies answer the risk assessor's basic question: **“Where did the pesticide go when applied in the field?”** By using a conceptual model in the study design phase, the study sponsor can address this question by determining which routes of dissipation need to be evaluated in order to adequately characterize the behaviour of a pesticide in the field under actual use conditions. The study sponsor should consider the use pattern and ensure that the overall study design accounts for potential formulation effects. Different designs may be necessary for multiple formulation types, such as granular and emulsifiable concentrate.

Before conducting a study, the study sponsor needs to carefully consider all potential processes and routes of dissipation as well as determine which of these are critical to answering the risk assessor's basic question (Figure 1). A conceptual model, based on pesticide properties, laboratory environmental fate results, formulation type and anticipated use patterns, can focus the studies on the major routes of dissipation. A dissipation route should be included in the study design if it is expected to explain, in part, the observed rate of chemical dissipation from the surface soil.

One way to approach the study design is to consider each route of dissipation as a potential study module. Using the conceptual model, the study sponsor can determine which modules are needed to adequately characterize the active routes of dissipation in the field. An advantage of this approach is that it offers flexibility in addressing data needs by including modules either concurrent with or separate from the basic field study. With this approach, not all modules need to be performed in the same study. For example, runoff experiments may be conducted in small-plot studies, and volatility experiments may be conducted as separate experiments in either the field or the laboratory. Ultimately, the decision regarding when to include a module rests with the study sponsor.

Before initiating a TFD study, the study sponsor should develop a working hypothesis of the

pesticide-specific conceptual model. This working hypothesis can form the foundation for optional consultations with EPA/PMRA and can be included as a section in the final report. The working hypothesis is the foundation for the pesticide-specific conceptual model and forms the basis for determining how well the study design captures the fate of the pesticide in the field under actual use conditions. The working hypothesis should include the following parameters:

- Estimates for each module's contribution to the dissipation process (quantitative and/or qualitative) based on laboratory physicochemical and fate properties
- Basic study modules:
 - Soil abiotic/biotic transformation
 - Leaching
- Additional modules:
 - Volatilization
 - Runoff
 - Plant uptake
 - Deep leaching
 - Others

The conceptual model described above should then be modified based on the anticipated conditions in the individual TFD study sites. Modifications of the laboratory estimated contribution to dissipation for each module (both quantitative and/or qualitative) should be described for both the basic study modules and any additional modules that are necessary based upon a review of laboratory data. The modifications to the conceptual model should be based on field soil properties compared to soils used in laboratory studies, weather data, water balance, formulation type, mode of delivery, crop influence (if any), agronomic practices and other factors.

The study sponsor should consider the following when determining if a module should be included or excluded:

- Only those routes of dissipation that are included in the field study or measured by an acceptable guideline study can be claimed to “significantly” affect the fate of a pesticide and/or its degradates in the field.
- Additional modules should not be excluded from the study when data indicate that associated processes may contribute to “significant” pesticide dissipation or result in any pesticide dissipation of toxicological concern. (See I.B. for a discussion of indicators that are used to determine inclusion of additional modules.)
- Ideally, when all modules are chosen, total dissipation attributed to excluded modules should not exceed 10–20%.
- Because drift modules are not included in the study, special equipment should be used to

minimize any loss due to spray drift.

Ultimately, it is the responsibility of the study sponsor to establish a hypothesis of the routes of dissipation (i.e., the conceptual model) that will affect the outcome of the TFD study. The TFD study should test the established hypothesis, and the final report should include the hypothesis and the results analyzed in order to confirm or modify the hypothesis (Figure 2).

Figure 1 Conceptual Model of the Factors Affecting the Field Dissipation of a Chemical

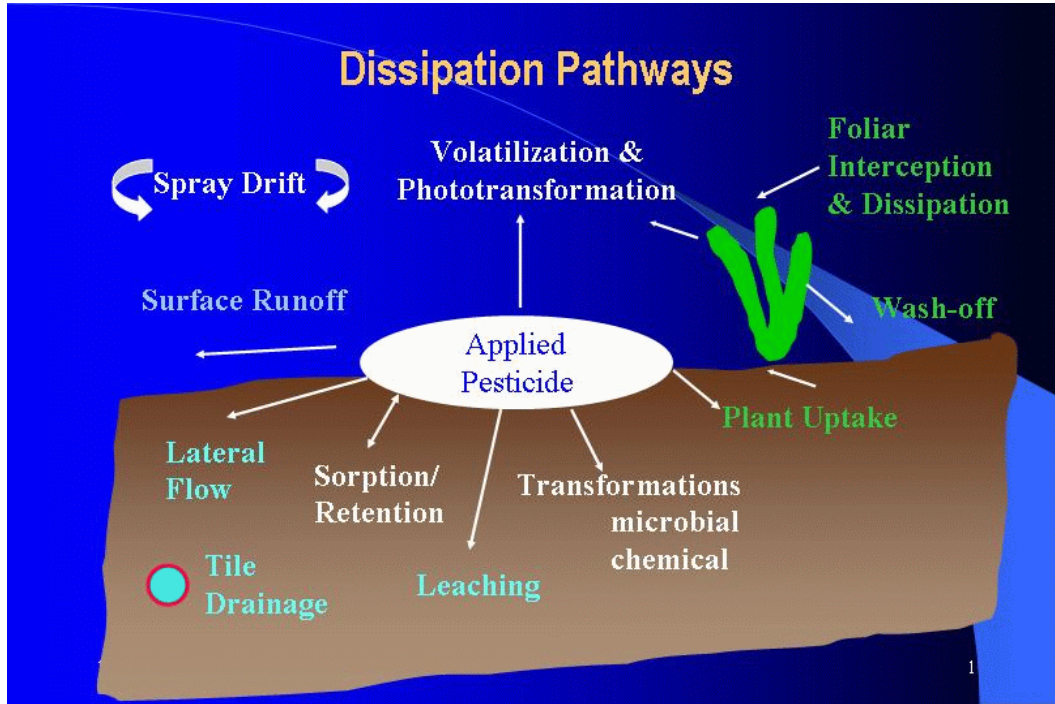
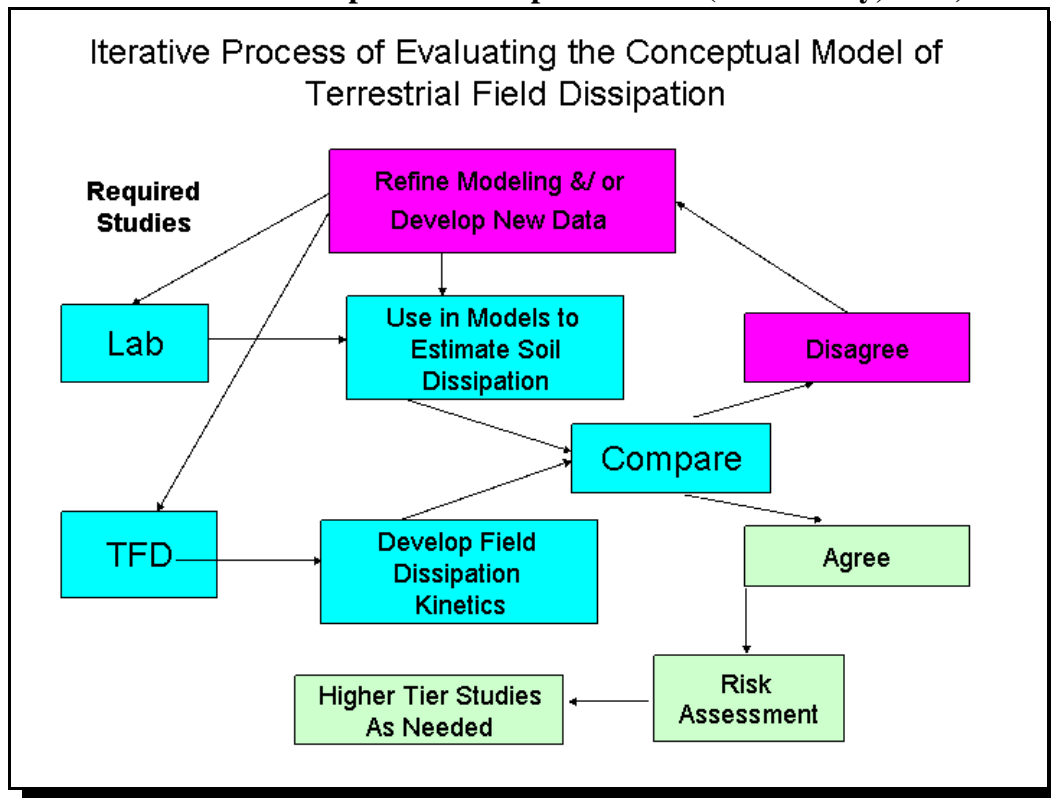


Figure 2 Iterative Process for Evaluation of TFD Results Relative to the Pesticide-specific Conceptual Model (after Purdy, 2002)



B. Additional Study Modules

The basic TFD study focuses on pesticide dissipation from the soil surface layer in a bareground study; it can be used to estimate field degradation only when other major routes of dissipation (e.g., sorption and binding, leaching, volatilization, runoff and plant uptake) are quantified and shown to be negligible. In addition to the guidance described in this document, EPA or PMRA may require other dissipation studies to answer specific risk assessment questions. In deciding if an additional study module is necessary in a field study, the study sponsor should ask the following questions:

1. What is the potential for dissipation of the parent compound and its major transformation products by a given route (e.g., volatilization, leaching, runoff, plant uptake, etc.)?
2. Is the potential great enough to warrant measurement under field conditions representative of actual use?

In most cases, using the suggested criteria found in Appendix IX or a lines-of-evidence approach based on physicochemical properties and laboratory fate data is the best way to answer these questions and to determine if an additional module(s) should be included in the TFD study. Using this approach, the following modules should be considered in all phases of the study design:

Leaching. Laboratory studies on adsorption/desorption, column leaching, solubility and persistence can predict the possibility of leaching beneath the root zone. The basic TFD study has traditionally incorporated a leaching component and requires analyses of soil cores extending below the surface (generally considered as 6 in. or 15 cm) to a given depth (1) (2) (3). If neither the parent nor degradates of concern are detected in all cores below a given depth, analysis of deeper cores is usually not necessary. However, if leaching mechanisms other than flow through a porous medium are suspected for the site in question (preferential flow or karst topography), then all soil core depths should be analyzed. A conservative tracer, such as bromide ion, should be applied to the test plot to verify the depth of water leaching over the course of the study.

Runoff. Runoff is possible for both weakly adsorbed, highly soluble chemicals and strongly adsorbed, slightly soluble chemicals. The former may run off in the dissolved phase, and the latter adsorbed on the particulate phase. However, the potential for runoff depends more on the type of formulation, cover crop, mode of application (e.g., surface application versus soil incorporation) and site factors (e.g., slope, type of soil, infiltration capacity and rainfall intensity) than on the chemical properties of the active ingredient(s) and transformation product(s). Depending on the conditions of the particular field dissipation study site, loss due to runoff may be a significant or insignificant component of pesticide dissipation from the surface. A simple runoff collector at the downslope edge of the field may be adequate to adjust for the amount of pesticide loss due to runoff from an unanticipated event (i.e., storm).

Volatility. Volatilization of an applied chemical is a function of partitioning of the chemical into solid, liquid and gaseous phases in the soil environment as well as other factors (e.g., wind speed, temperature and humidity). However, the application method of the chemical (e.g., soil-incorporation and watering-in) may serve to suppress volatilization. For example, soil-incorporation and watering-in are used to limit chemical losses to volatilization.

Plant Uptake and Translocation. For systemic pesticides and transformation products whose mode of action involves uptake through plant tissues (roots, leaves, etc.), this pathway may be a significant route of dissipation. The study sponsor can characterize this route by conducting a cropped-plot study in the field or by greenhouse studies on the same crop.

In summary, the process of selecting modules to include in the suite of TFD studies is the responsibility of the study sponsor. The study design should anticipate the needs of the risk assessor who will rely on a clear explanation of the assumptions used in the development of the study design. Although not required, the study sponsor may consult with the risk assessor and the risk manager on the design of the pesticide-specific conceptual model early in the process. Early consultation will give the study sponsor time to assess the needs of the risk assessor and

avoid unnecessary expenditure of time and resources. A well-developed pesticide-specific conceptual model should be prepared and used as the basis for such consultation.

As noted above, the TFD study is a keystone study, in that it provides the primary means for testing the hypothesis of environmental transformation/degradation, transport and fate developed during the problem formulation phase of a risk assessment. The current guidance has been developed to provide the risk assessor with a better understanding of the assumptions and limitations inherent in the data, an improved perspective on the estimate of error in the study results and, ultimately, better confidence in the data generated. The guidance has been written to provide maximum flexibility for the study design while increasing confidence in the data. Therefore, the study designer should look to the overall hypothesis of pesticide fate based on a combination of data, including laboratory studies and physicochemical properties as well as climate, soil, agronomic and site characteristics. Once a hypothesis is developed, the study design may include additional modules as needed. The modules may be run concurrently with the basic soil study or may be “plugged in” using other data, as long as the data are scientifically valid and appropriate. One of the most important points to remember when designing this study is that the results of the study describe the pesticide’s major routes of dissipation in the environment.

C. Use of Terrestrial Field Dissipation Study Results

The results of the TFD study are used to validate and/or refine the established hypothesis that the pesticide dissipates in accordance with the pesticide-specific conceptual model. Differences between field study findings and the established pesticide-specific conceptual model may suggest the need for revision of the pesticide-specific conceptual model and possibly the need for additional laboratory and/or field studies (Figure 2).

While this section provides examples of where the TFD study results may be used quantitatively, the value of this study in qualitative assessments should not be overlooked. A critical component of all risk assessments is the characterization of risk, in which the assumptions, limitations and uncertainties inherent in the risk assessment are captured and the potential effect of these factors on overall risk are explained. The TFD study results have been and will continue to be a critical element of the risk characterization component of the risk assessment; it is the only avenue by which the laboratory-based hypothesis of field behaviour can be tested.

Results of field dissipation studies are used to estimate the field persistence of parent compound, formation and decline of transformation products, residue carryover, and leaching potential under representative actual use conditions. When other modules are included in the study, results of these tests may provide important information on major dissipation routes such as transformation, transport, volatilization, plant uptake and runoff. Although not specifically relevant to this technical guidance document, a brief discussion of how the TFD study results can be used in risk assessments deserves consideration. In addition to its value in characterizing the dissipation of a pesticide in an actual field environment, field dissipation study results can be used to evaluate the algorithms and input data for environmental fate models, and the results

can be used to develop more refined ecological risk assessments. The following sections discuss some of the potential uses and limitations of using TFD results quantitatively.

1. Model Evaluation

The results of TFD studies can be compared with pesticide estimations generated by the Pesticide Root Zone Model (PRZM) to evaluate how well the model is performing. Although the current field study does not always track specific routes of dissipation and identify reasons for discrepancies, field dissipation studies can be designed to test hypotheses regarding routes of dissipation predicted by environmental fate models such as PRZM. Not only can modelling efforts be used to focus and interpret the results of field dissipation studies, but the study results can also be used to evaluate the model.

2. Input for Environmental Fate and Transport Models

Currently, EPA and PMRA do not routinely use dissipation rates determined in the field as degradation inputs for fate and transport modelling, such as the coupled PRZM and EXAMS (Exposure Analysis Modeling System). Such an application is misleading when reported dissipation half-lives (often DT_{50} [time for 50% dissipation of the parent chemical] values and not true half-lives) include the combined routes of dissipation (degradation/transformation and transport) from the surface. A rapid field dissipation rate may be due to degradation, movement out of the surface soil, or both. Thus, the reviewer would expect a persistent, highly mobile chemical to have a short half-life ($t_{1/2}$) in the surface (provided rainfall or irrigation occur) because it would move out of the surface.

Current models use inputs that represent the individual routes of dissipation (degradation half-life values, rate constants, sorption/partitioning coefficients) to simulate overall dissipation. Thus, substitution of a persistence half-life for a dissipation half-life would effectively treat movement out of the surface (and potentially into the compartment of interest, i.e., surface water or groundwater) as if it were degradation. It may be possible, in some instances, to replace the route-specific model inputs with a combined dissipation rate determined in a field study under the following conditions:

- The sole focus of the modeling effort is to simulate runoff into a water body and, thus, requires only an estimate of the amount of chemical that is available at the surface and subject to runoff over time.
- The weight of laboratory and field evidence indicates that dissipation in the field can be confidently attributed solely to degradation/transformation (i.e., negligible loss by the other dissipation routes, such as leaching, runoff, volatilization and plant uptake).

3. Terrestrial Exposure Assessment

Although terrestrial field study results can be used to determine the potential for pesticide residues to remain in the soil from year to year, most of these studies do not provide adequate

information on plant residue concentrations or residue concentrations in other food sources, such as seeds or insects, in a manner that can be used in refined terrestrial exposure assessments. However, when data are collected from foliage/food sources, they can provide estimates of residue concentrations over time under actual use conditions in refined risk assessments. In these cases, study results have been used to calculate estimated exposure concentrations (EECs) in soil for buffer zone determinations in terrestrial habitats. Finally, results from TFD studies can be used to evaluate the potential for carry-over of residues (both parent and degradates) from one crop season to the following. This is particularly important for persistent pesticides used in colder climates where the potential for persistence is greatest. Evidence of from TFD studies will have implications for long-term exposure to non-target organisms and may trigger additional studies (e.g., soil accumulation).

4. Refined Risk Assessments (RRAs)

Refined risk assessments produce a range or distribution of values instead of one fixed value produced in a deterministic approach. Current research is focused on refining risk assessment through the implementation of advanced probabilistic models that look at multiple pathways for exposure and allow for sensitivity analysis to determine the significance of exposures to overall risk. Well-designed TFD studies can provide results that are useful for interpreting and providing feedback on model assumptions and results, and may even be considered as possible inputs for Monte Carlo analysis.

D. Principle of the Study

Each TFD study should be designed in the context of a suite of TFD studies that identify the route(s) and rate(s) of dissipation of the active ingredient and major degradates/transformation products when a typical formulation/end-use product is applied under field conditions representative of the significant area(s) where pesticides are used. The studies should quantify the pathways of transformation and transport as well as the distribution of the parent compound and its major transformation products in each environmental compartment. In short, the studies should address the dissipation and fate of the active ingredient and major transformation products in the environment.

It may not be feasible or desirable to study each of the routes of dissipation, as identified by the pesticide-specific conceptual model, at one field site. For example, testing conditions for the evaluation of pesticide runoff would not be appropriate for an assessment of leaching. In this case, a modular approach is recommended in which concurrent dissipation pathways are studied at one site, while non-concurrent pathways are evaluated in separate studies (either field or laboratory, as appropriate). The suite of field dissipation studies may be conducted in an iterative fashion until the results:

- provide an integrated qualitative and quantitative environmental fate assessment that characterizes the relative importance of each route of dissipation for the parent compound and major transformation products (greater than 10% of applied) and/or toxicologically significant amounts of parent and transformation products. The study

design should acknowledge the relative importance of each route may be different depending on use pattern, formulation type and climatic conditions;

- determine whether potential routes of dissipation identified in the laboratory are consistent with field results;
- characterize the dissipation rates of the parent compound and formation product as well as decline of the major and/or toxicologically significant transformation products under field conditions;
- characterize the rates and relative importance of the different transport processes, including leaching, runoff and volatilization;
- establish the distribution of the parent compound and the major transformation products in the soil profile;
- characterize the persistence of the parent compound and major transformation products in soil, including retention and residue carryover in the soil to the following crop season;
- characterize foliar dissipation, if the compound is applied to plants; and
- characterize the effect(s) of different typical pesticide formulation categories, where applicable.

E. Applicability of the Test

TFD data are generally required by regulatory agencies (9) (10) to support the registration of an end-use product intended for outdoor uses and to support each application to register a technical grade active ingredient and manufacturing-use product used to make such an end-use product.

II. Description of the method

A. Information on the Test Substance

The test substance must be a typical end-use product for which TFD data are needed. (Appendix I contains a list of definitions and units discussed throughout this guidance document.) If the manufacturing-use product is usually formulated into end-use products from two or more major formulation categories, separate studies should be performed with a typical end-use product for each category (e.g., wettable powder, emulsifiable concentrate, granular).

Non-radiolabelled or radiolabelled substances can be used for the test, although non-radiolabelled substances are preferred. The application of radiolabelled substances to field environments is subject to pertinent national and local regulations.

The following information on the test substance should be included in the study report:

- Solubility in water (1) (3) (11) (12);
- Vapour pressure (1) (3) (11) (12);
- Henry's law constant;
- *n*-octanol–water partition coefficient (1) (3) (11) (12);
- Dissociation constant in water, reported as pK_a or pK_b (1) (11) (12);
- Hydrolysis as a function of pH (1) (3) (11) (13) (14);
- Photolysis on soil and in water (1) (3) (13) (15) (16);
- Soil aerobic biotransformation (1) (3) (13) (15) (17);
- Soil anaerobic biotransformation (1) (3) (13) (15);
- Adsorption/desorption coefficients (1) (3) (13) (15).

These data are important in developing the conceptual model, identifying the potential routes of dissipation (modules) to be studied and aiding in the experimental design with respect to the sampling strategies, site locations, sample size and quantity, frequency of sampling, etc. The data are also necessary to interpret the results of the study. (See Appendix II for a data sheet that can be used in providing this information.)

An appropriate analytical method of known accuracy, precision and sensitivity for the quantification of the active ingredient and major transformation products should also be included in the study. In most cases, “cold” (i.e., non-radiolabelled) analytical methods that are sufficiently sensitive to detect and monitor pesticide residues in the field are used. In order to be useful for terrestrial exposure assessments, the limit of quantitation (LOQ) of the chosen procedure should be between one and two orders of magnitude less than the expected concentrations and should ideally be less than the important endpoints for non-target organisms. The analytical methods are subject to independent laboratory validation (18). (Appendix III contains a description of environmental chemistry information that is needed for validating analytical methods used in conducting field dissipation studies).

B. Field Plot Systems

Plot size should be adequate to demonstrate the transformation, mobility and fate of the test material in soil under controlled field conditions representative of actual use. The decision concerning the plot size in field studies should be based on factors such as application methods, crop and management factors, site characteristics and anticipated total number of samples. For pesticides typically applied to cropped or conservation tillage plots (e.g., with at least 30% crop residues on the surface), bareground pesticide-treated plots are necessary to help distinguish dissipation pathways.

Large-scale studies (24) (25) (26) are conducted using normal agricultural practices (e.g., cultivation prior to planting, etc.) and equipment. These studies may be used in combination with other field studies, such as crop residue studies, provided the TFD studies are not disturbed. Small plots (19) (20) (21) (22) (23) are treated using research-plot application techniques (e.g., hand-held or backpack sprayers) that, in some cases, may reduce the variability seen in large-scale studies. These small-plot techniques can also limit the ability to interpret results and obtain satisfactory pesticide dissipation curves. Large-scale and small-plot studies

have the following characteristics:

1. Large-scale studies: Large-scale studies typically cover a treated area of 8 cropped rows by 25 m, but may range up to an entire field of several hectares, depending on the design of the experiment and the use for which the product is intended. Typical plot sizes range from 4×10 m to 10×40 m.
2. Small-plot studies: Small plots (e.g., up to $2 \text{ m} \times 2\text{--}6$ m or $4\text{--}12 \text{ m}^2$ in area) are preferable when pesticide dispersion is uneven and dissipation curves are difficult to generate or interpret.

Generally, cropped plots are not required in TFD studies. However, if a crop is expected to significantly influence the rate and/or route of pesticide dissipation (e.g., runoff from turf, accumulation in the turf layer, accumulation into the crop, or abiotic degradation and volatilization from leaf surfaces), then specific greenhouse or small-plot field studies (using the same crop) are needed to address these routes of dissipation. In some cases, though, the studies conducted to satisfy other environmental fate or human health data requirements may fulfill these data needs. In the case of foliarly applied pesticides that are systemic, the test substance should be applied to the intended crop, as specified on the label, to characterize the influence of plant uptake and subsequent foliar metabolism and to provide a complete picture of the dissipation of the pesticide from the terrestrial system. The influence of plant uptake and subsequent dissipation should also be characterized in the case of pre-plant and pre-emergent pesticides as well. When foliar processes interfere with the characterization of soil dissipation processes, a bare study plot (i.e., not sown to intended crops and maintained plant free) should be run in parallel to the cropped study. This analysis can be conducted either within the field design or using suitable laboratory or greenhouse data. However, the use of laboratory or greenhouse data will require an explanation of the conditions under which the data were collected and how any differences between conditions in the laboratory/greenhouse and the field study results and laboratory hypothesis may influence the evaluation of the field results. While the bare plot study may be an artificial system, it is useful in providing an interpretable pesticide dissipation curve in the soil.

Cropped plot field studies are needed when plants are an important factor in controlling field dissipation of the pesticide. Assessing the importance of plant processes in pesticide dissipation requires an examination of the mode of action of the pesticide, application timing relative to canopy development, target crop or environment, and an evaluation of data from confined rotational crop studies and foliar wash-off studies. Consideration of these factors requires integration of the data into the overall hypothesis testing on probable routes of dissipation. Cropped plots should be considered in the design of field studies when one or more of the following criteria have been met:

- Systemic pesticides, which are designed to move into and through the plant, are used. This type of pesticide is expected to become incorporated into the plant either through active or passive uptake.

- Foliar-applied pesticides applied at half to full canopy of the plant are expected to be predominantly deposited on leaf surfaces. Under these conditions, foliar dissipation is expected to be the dominant process in the field, although washoff can lead to increased loadings to soil.
- Pesticides applied to pasture, foliage crop, grass and turf are expected to strongly influence dissipation pathways of pesticides.
- Evidence of high foliar wash-off fractions or uptake of parent compounds (30-day emergency crop rotation interval) from rotational crop studies indicate plant processes may control pesticide dissipation. These studies should be conducted on the same crops as the TFD study crop(s).

Execution of a study using a cropped plot should be conducted concurrently with a bare ground study. Analyses of the data collected from the two plots should be similar except that plants should be sampled and analyzed for pesticide residues in the cropped plots. The separate collection, compositing and analyses of soil samples collected within and between the rows of the row crop(s) may also be necessary. Whole plant residues should be designed to capture either dissipation or accumulation in the plant. It is recommended that foliar wash-off half-lives, if available, and potential plant accumulation rates be considered for designing sampling frequency. Crop residues should be expressed as concentrations on both a dry weight and wet weight basis. Additionally, crop yields, expressed as the total crop mass (g) / unit area (m²), should be determined at each sampling time. Recording crop growth stage and area coverage can prove useful in the overall interpretation of the results.

C. Site Selection

Field study sites should be representative of the soil, climatic and management factors under which the pesticide will be used. The following factors should be considered in selecting field study sites:

- Number of uses/crops
- Geographic extent and acreage of the crops/use patterns
- Soil characteristics
- Climate (including temperature, amount and distribution of precipitation, solar exposure and intensity)
- Use and management practices
- Crop impacts on pesticide dissipation
- Pesticide formulation
- Timing, frequency and method of pesticide application
- Label restrictions regarding usage, sites or conditions

Differences between the field study sites and the use patterns of one or more of these factors could affect the fate properties and dissipation processes of the pesticide, thus reducing the applicability of field study results beyond the conditions of the study. Tools, such as the

PMRA/EPA geographic information system (GIS)-based decision support model or other GIS-based vulnerability assessment tools that account for the critical factors affecting pesticide dissipation, can be used to determine the most appropriate field sites (27) (28). The GIS decision support model utilizes ecological regions (e.g., the Ecological Regions of North America), geospatial soil and agricultural crops databases, climatic information, and pesticide properties, including laboratory fate data. Comparable field study area selection is based on environmental conditions and the conceptual pesticide dissipation model developed from laboratory fate studies.

The TFD study should include multiple field sites, generally four to six study sites. The actual number of sites needed depends on such factors as the number of formulations, the geographical extent of the use pattern, the number of uses and management practices as well as the range in soil and climatic conditions within the geographic extent of the uses. If pesticide use is limited geographically and/or to minor crops, a reduced number of field studies may be proposed.

D. Field Study Plot Design

An assessment of the fate of the pesticide in the terrestrial environment should include all processes that can affect the fate of the chemical, including transformation, leaching, volatilization, runoff, sorption to soil and plant uptake (1). Terrestrial field studies should be designed, conducted and evaluated to assess the most probable routes and rates of pesticide dissipation under conditions representative of actual use. The physicochemical properties of the pesticide, laboratory environmental fate data, application techniques and site characteristics should be considered in designing the study.

The basic field study design evaluates field dissipation in soil at a bareground site. If the pesticide-specific conceptual model suggests that volatilization, leaching, runoff or plant uptake are potentially important dissipation routes, then a modular approach is recommended whereby dissipation pathways that can be studied concurrently at one site are included, while those pathways that are incompatible are evaluated in separate studies.

The study design should encompass the range of practices and conditions that reflect the actual usage of the test substance. For all field dissipation studies, non-cropped (bareground) plots must be included. If the proposed use pattern includes application of a systemic pesticide on a standing crop and it is believed that uptake may be an important route of removal from the field, the trial should be conducted with a cropped soil in addition to the non-cropped (bareground) plots. Data generated from laboratory or greenhouse studies may be used to supplement the field data. However, the use of laboratory or greenhouse data will require an explanation of the conditions under which the data were collected and how any differences between conditions in the laboratory/greenhouse the field study results and laboratory hypothesis may influence the evaluation of the field results. The studies should also include an untreated control plot.

Because of field-scale variability, the experimental units in each TFD study should be replicated. Replication serves the following functions (29):

- Providing an estimate of experimental error
- Improving precision by reducing standard deviation of a mean
- Increasing the scope of inference of the experiment by selection and appropriate use of variable experimental units
- Effecting control of the error variance
- Allowing statistical comparisons of intra- and inter-site variability

E. Procedure

1. Site Characterization

Assessing pesticide dissipation requires detailed description of the site characteristics as well as characterization of “representative” soils at each test site. Ideally, the site selected for the TFD study should be represented by a single soil type in order to reduce variability in the field. Such information is critical to assess *in situ* chemical and physical properties of the test soil.

a. Site Description

The study site should be described according to geographic coordinates (e.g., latitude, longitude), location on a map (topographic map, aerial photograph or soil survey map), location within the watershed, landforms, landscape position, land surface configuration (e.g., slope length and gradient, aspect and direction, micro-relief, roughness, shape, elevation) and depth to groundwater. A suggested site description sheet can be found in Appendix IV.

b. Soil Characterization

At each site, a representative soil pedon should be identified, and a minimum of one soil profile should be described by soil horizons (preferably 2 m in depth) using standard soil morphological properties (depth to and thickness of horizons or layers, Munsell color, texture, structure, macroporosity, depth to a root restricting layer, etc.). Soil profiles will be described and classified to family or series level according to an internationally recognized system representative of the areas where the study is conducted. Examples of internationally recognized systems are the United States Department of Agriculture (USDA) Natural Resources Conservation Service (NRCS), Canadian or the Food and Agriculture Organization of the United Nations (FAO). In addition to the description of soil morphology, information on the soil parent material, vegetation, erosion class, natural drainage class, surface runoff, infiltration and saturated hydraulic conductivity should be reported. A suggested soil profile description can be found in Appendix V.

Soil samples from each horizon should be collected and characterized by determining the physicochemical properties in the laboratory. The physical properties should include particle size distribution (i.e., % sand, % silt and % clay, with size fractions specified), textural class (USDA), undisturbed bulk density, and soil moisture characteristic curve (0–15 bar) to help determine the soil water balance throughout the study. The soil chemical properties should include pH, percentage of organic carbon and cation exchange capacity. Standardized methods

should be used and referenced for the determination of these properties. (See (30) and (31) for examples.) Depending on the chemical properties or use site, additional analyses, such as clay mineralogy, specific surface area, and anion exchange capacity (especially in soils dominated by low activity clays or derived from volcanic materials) of the surface soil layer or epipedon and the subjacent horizon (layer), may be helpful for determining sorption potential at the field site. A suggested format for reporting the soil properties is given in Appendix VI.

c. Environmental Conditions

Measurement of meteorological variables is necessary to understand pesticide dissipation in the field. Daily records of maximum, minimum and mean temperature (air and soil), total precipitation, mean wind speed and potential evapotranspiration are recommended from five days prior to the first application of the pesticide through to the conclusion of the study. When irrigation is used to supplement rainfall, timing and amounts of irrigation water should also be reported. Historical climatological data should be obtained to help evaluate site data with respect to long-term regional variation, and the source and location of the historical data should be specified. Historical climatic information should include monthly average rainfall, average monthly minimum and maximum temperatures, and the dates and the number of days in the average annual frost-free period. A suggested format for reporting the historical meteorological conditions is given in Appendix VII.

d. Management History

Information on the use of the study site, for example, crops grown, pesticides and fertilizers used, should be provided for the previous three years. The site selected should not have a history of the use of the study pesticide or other pesticides of similar nature (chemical class, common nonvolatile transformation products, etc.) for at least three years prior to the study. This requirement is necessary to reduce analytical interferences and potential microbial adaptations for the test. Management factors, such as tillage and cultivation methods, irrigation practices, etc., should be described in detail. A suggested format for reporting the land use and management history can be found in Appendix VIII.

2. Application of the Test Substance

The TFD study should address the effect of pesticide formulation on dissipation. Different formulations are expected to change the fate or transport properties of the pesticide. For example, granular or microencapsulated formulations may release the active ingredient more slowly than emulsifiable concentrate formulations. For this reason, separate studies should be performed on at least one representative formulation from each of the applicable formulation groups listed below. If the various commercial formulations of a given pesticide are not expected to change the fate of the active ingredient, the applicant should provide the necessary data in support of this assumption within the body of the study report. In general, it may be possible to compare a field study conducted using water soluble liquids/water soluble powders/emulsifiable concentrates with water dispersible liquids/wettable powders/water dispersible granules. However, separate field studies will be needed for microencapsulated and

granular formulations.

The recommended groupings of pesticide formulations are as follows:

Water soluble liquids, water soluble powders and emulsifiable concentrates

The release of an active ingredient into the environment is controlled by the formulation type and the site-specific environmental conditions. Water soluble liquids and powders form true solutions when mixed with water, and emulsifiable concentrates consist of oil soluble pesticides and emulsifiers. These formulations are expected to have little effect on the transport of the pesticide in soil (32).

Water dispersible liquids, wettable powders and water dispersible granules

Water dispersible liquids, wettable powders, and dispersible granules consist of finely ground solids of various dimensions. Various studies indicate that these formulations may affect the transport of pesticides in soil (33) (34) (35). For example, Ghodrati and Jury (33) showed wettable powder formulations may be more resistant to preferential flow than emulsifiable concentrates and technical grade material dissolved in water.

Granules

After precipitation or irrigation, granular formulations release the active ingredient gradually as a function of diffusion or leaching (36). Therefore, this formulation may have a significant effect on transport of the active ingredient if a rain event or irrigation occurs after application.

Microencapsulated pesticides

Microencapsulated/controlled-release formulations can reduce the potential of leaching through soil (32) but may result in higher surface losses of a chemical when compared to other formulations (37). Available literature on the effects of microencapsulated and controlled-release formulations is inconsistent, and testing of this formulation type needs to be evaluated on a case-by-case basis.

In the TFD study, the pesticide product should be applied at the maximum proposed use rate utilizing the same application method(s) as stated on the label. In limited instances (e.g., for ultra-low application rates), it may be necessary to apply the pesticide at a rate greater than the maximum proposed use rate due to analytical detection limits.

Recommended equipment for pesticide delivery in the TFD study should be of high precision, suited for the particular pesticide formulation (some pesticides may need to be homogenized by a continuous mixing device in the tank) and outfitted with a device to keep drift loss to a minimum.

The pesticide application, including timing and the number of applications, should be consistent with labelling. The pesticide application should:

- occur at the typical time(s) of the year and stage(s) in crop development when it is normally used;

- be performed according to label instructions for the specific formulation (e.g., a granular pesticide typically applied as a band should be applied as a band in the field dissipation study);
- be incorporated if the pesticide is typically incorporated; and
- be measured by spray cards or similar verification techniques and related to the target application rate and measured concentration in the spray tank.

Where multiple applications are allowed, an experimental design that enables assessments of dissipation should be used. The study design should include collection and analysis of samples prior to and after each application with a full set of samples collected after the final application in order to estimate a dissipation rate. Replicated treatment plots will evaluate both single and multiple applications. This guidance acknowledges that the use of multiple applications can complicate the analysis of data generated during the course of the study. However, a critical aspect of the TFD study is that the conditions under which it is conducted reflect actual use conditions for the pesticide as closely as possible. Also, the use of a seasonal maximum amount of pesticide in a single application can alter the conditions of soil microbial populations which may alter the results of the study. Given these factors, it is recommended that the TFD study be conducted using multiple applications at the maximum allowable rate specified on the labels for that compound.

3. Study Duration

The duration of the TFD study, which has historically taken up to two years to complete, should be sufficient to determine the DT_{75} of the parent compound as well as the pattern of formation and decline of major transformation products in the soil. In determining the decline of the major transformation products, the study duration should be sufficient to determine the time required for major transformation products to dissipate to 25% of their maximum detected values in the soil. A major transformation product is one accounting for $\geq 10\%$ of the applied amount at any time during the laboratory studies, or one that has been identified as being of potential toxicological or ecological concern.

4. Management

The management (e.g., fertilization, seed bed preparation, weed control, sowing and tillage) of the field dissipation study site should be carried out in accordance with good agricultural practices. Tillage practices (conventional tillage, conservation tillage or no-till) should be typical of those used for the particular crop and label recommendations.

5. Irrigation

It is essential that the study design include sufficient water to meet the crop need in quantity and timing. If the use pattern includes irrigation to supplement the water requirements of the plant,

then the study should be conducted under irrigated conditions. In this case, the study design should ensure appropriate timing and sufficient water to meet 110% to 120% of the crop need. Also, in the case of bare plots, the site should receive sufficient water at the appropriate time to meet the crop water need for the intended crop in that use pattern. In other words, a bare plot site conducted for a corn use should receive 110% to 120% of the water need for corn in that use area. Alternatively, if the use pattern does not involve irrigation, then the field studies do not necessarily have to be conducted with supplemental irrigation. However, it may be necessary to prepare the site for irrigation in case of drier than normal conditions. For non-irrigated sites, the study design should ensure that 110% to 120% of normal monthly rainfall is delivered to the site.

6. Environmental Conditions and Monitoring

The following environmental conditions should be recorded daily at the study site:

- Precipitation
- Mean air temperature
- Potential evapotranspiration or pan evaporation (can be determined from a nearby site, or evapotranspiration may be calculated from other environmental data)
- Hours of sunshine and intensity of solar radiation
- Mean soil temperature
- Soil moisture content

a. Soil Water Balance

Soil water content can affect the mode of degradation, degree of microbial activity, potential for volatilization, plant growth and potential for movement (i.e., up or down in the soil profile). To interpret routes and patterns of dissipation of the test substance, the soil water content needs to be measured on a regular basis to adequately determine the flux of soil water. Continuous or daily measurements are preferred, but, at a minimum, readings should be collected at each sampling time. Various methods of measuring soil water include tensiometers, time domain reflectometry (TDR), neutron probes, gypsum blocks and direct measurement of the moisture content of the soil samples (30).

b. Using Tracers to Track the Potential Depth of Leaching

A conservative tracer can be applied along with the test chemical to help determine the direction, depth and rate of soil water movement through the vadose zone. Tracer selection should consider the chemistry of the tracer, including potential sources of interference, background/baseline levels, analytical detection limits and potential losses such as plant uptake. If a tracer is used, background concentrations need to be analyzed prior to the study.

c. Soil Temperature

The soil temperature can also affect the rate of degradation, degree of microbial activity,

potential for volatilization, plant growth, and potential for and direction of water movement (i.e., up or down in the soil profile). Modern on-site weather stations typically include readily available measurements of soil temperature, which should be used in interpreting the results of field dissipation studies.

7. Soil Sampling

Soil samples for residue analysis should be representative of each replicate plot at each sampling time. Replicate plots can be defined as repetitive, homogeneous sections of a field treated with the test pesticide in a similar manner to allow comparison between treatments. Sampling procedures can have a major effect on variability of pesticide concentrations in soil; accurate and consistent sampling is vital for meaningful results. Variables such as plot size, soil variability, crop management practices, pesticide application method and existing knowledge of the behaviour of the pesticide in the environment should be considered in designing an appropriate soil-sampling protocol.

a. Sampling Patterns

Soil core holes should be marked after sampling. Plugging holes with soil from untreated areas of the site will prevent the cross-contamination at greater depths and subsequent anomalous results.

A random or systematic soil sampling pattern (38) may be followed, depending on the type of pesticide application and other variables listed above. For example, the soil may be sampled in-row only (e.g., seed furrow or band treatment) or by a random pattern that covers the entire treatment area (i.e., broadcast application). Because it may be difficult to obtain interpretable results using an in-row sampling pattern, extreme care should be taken in the application and sampling procedures.

In order to avoid variability resulting from possible under-coverage, drift or edge effects, outside rows of treated areas should be excluded from sampling.

In small plots, systematic sampling is preferred to ensure that all treated sectors of the plot are represented and to make it easier to avoid sampling in a previous core hole or in zones where spray patterns in successive passes of the application equipment may have overlapped or failed to cover the surface adequately.

Larger diameter cores are expected to reduce variability in the field. Typically, a core of one to two inches in diameter has been used in TFD studies, but use of larger diameter cores should be considered in the field design.

b. Depth of Soil Sampling

In order to fully demonstrate the fate and transport of the pesticide under study, soil should be collected from a depth sufficient to encompass the vertical distribution of the pesticide and its

major transformation products at each sampling time. Data from laboratory studies (physicochemical properties, mobility and transformation) can be used in conjunction with water recharge estimates (e.g., average rainfall data and expected irrigation coupled with evapotranspiration estimates) and soil permeability properties to establish appropriate core depths. Soil sampling should proceed to at least a depth of one metre, particularly for pesticides with laboratory fate characteristics that indicate leaching is an important route of dissipation.

The major transformation processes usually occur within the “biologically active” zone of the soil. For sampling purposes, this zone can be defined as the maximum depth of tillage, rooting depth of agronomic plants or the depth of an impermeable soil layer, whichever is deepest. If the laboratory studies indicate a low potential of a pesticide to leach, the emphasis of soil sampling designs should be placed on this zone of soil rather than subsoils. The “biologically active” soil zone concept will allow flexibility in experimental design because of different agronomic practices, types of soil and site characteristics.

For most studies, soil cores should be collected to 1 m in depth and divided into six or more depth increments for analysis (e.g., 15 cm, 15 cm, 15 cm, 15 cm, 20 cm and 20 cm). For low application rate pesticides or where the results of the laboratory studies indicate very low mobility of the parent chemical and its major transformation products in soil, core depths could be sectioned into shorter increments to circumvent dilution of the chemical residues with excess soil. In all cases, analysis of the sectioned cores should clearly define the extent of leaching of the parent chemical and its major transformation products in the soil profile.

Soils should be sampled to a sufficient depth such that the lowest section of the sampled cores does not contain detectable amounts of the active ingredient or major transformation products. In the absence of rainfall or irrigation, the initial or zero time samples can be taken to at least one sample increment below the depth of incorporation. For example, a pesticide incorporated to 3 inches below the surface should be sampled from 0 to 6 inches and from 6 to 12 inches, assuming a 6-inch interval.

c. Times of Soil Sampling

Soil sampling should be carried out prior to treatment, immediately after treatment (zero time) and at increasing intervals (daily, weekly, monthly) between sampling times. If more than one application is made, then soil sampling should be done before and immediately after each application and then at increasing intervals after last application. Time intervals should be based on the results of laboratory studies and other field studies, if available. Sampling frequency should consider laboratory half-life estimates with increased frequency of sampling for shorter half-life compounds. Other factors that may affect sampling frequency include compound mobility and site-specific environmental conditions (e.g., rainfall and micro-climate). The frequency of sampling should be concentrated after each application time to characterize the dissipation of the test substance. However, the number and distribution of sample times should also be sufficient to adequately characterize the formation and decline of the transformation products.

The dissipation of a product used in multiple applications over a season should be studied through a full cycle of applications (22).

Residue data should be obtained until at least 75% of the pesticide and/or its major transformation products have dissipated from the soil profile or the pattern of dissipation has been clearly delineated (41) (42). The study sponsor should determine the DT_{50} and DT_{75} from the initial concentration because the dissipation rate constant often decreases with time (i.e., the half-life is not constant as in first-order kinetics). If 75% dissipation is not reached by the time it freezes in the fall, the study should be continued in the following year(s).

The plot should be sampled at the end of the growing season to determine residue carryover to the next season; sampling in subsequent years may be necessary. Long-term studies may be recommended if dissipation is slow to occur. This is particularly important for persistent, low mobility pesticides or for those chemicals that show pesticidal activities at low concentrations.

If a control plot is included in the study design, then soil sampling need only be conducted during the early stages of the study with a limited number of samples. The intention of the control sample is to ensure that the pesticide is not present prior to application and to provide information concerning potential loss of the pesticide from drift.

d. Time Zero Sampling

The time zero concentration lays the foundation for all subsequent sampling and is used to build confidence that the pesticide was applied uniformly and accurately. The following points should be considered in developing a time zero sampling protocol for a single application on bare ground:

- Availability of an appropriate analytical method with limits of quantitation low enough to detect the parent and key degradates at relevant concentrations
- Handling of all fortification samples in the same manner as soil samples
- Testing of verification devices before use to provide confidence in compatibility with the test substance
- Application of reasonable correction factors provided they are within 10% to 20%, although correction is not necessary
- Verification of the actual rate applied
- Calculation of an expected concentration in the field
- Comparison of time zero concentrations with the expected concentration

For multiple applications, each application should be treated as time zero, and concentrations prior to and immediately after application should be determined.

For cropped plots, the time zero sampling strategy should be modified to measure the portion of pesticide reaching foliage as well as the portion reaching the ground surface.

The initial concentration in the soil immediately after treatment (“time zero”) is a crucial

benchmark value. Time zero sampling is recommended to verify residue concentrations reaching the target and confirm uniformity of its distribution. The pesticide residues in all subsequent soil samples are evaluated in relation to this value. An initial residue value that is significantly lower than the value found for a subsequent sample may jeopardize the utility of the study by rendering estimation of dissipation times (DT_{50} and DT_{75}) meaningless. It cannot be emphasized enough how critical the accurate delivery and accounting of a pesticide at time zero are for the evaluation of the study results. Ideally, a study should utilize techniques that maximize the delivery of the pesticide to the field at the target rate and keep corrected time zero (time zero concentration after applying corrections related to delivery efficiency and field monitoring results) results within 10% of that rate. However, it is recognized that this is a “goal” and that may not always be obtainable.

Determination of time zero concentration involves the following steps:

- Analysis of the spray tank mixture before and after application
- Use of collection devices such as filter paper, spray cards, etc.
- Soil sampling immediately after application

Preferably, time zero sampling is conducted in duplicate, and the two sets of soil samples are processed separately to provide two estimates of the mean time zero concentration. Time zero sampling data should be used to confirm that the pesticide was uniformly applied to each plot at the intended rate. Techniques used and any deficiencies associated with the delivery of the pesticide to the field should be described and accounted for when analyzing the study results.

Although not routinely required, there may be instances where a cropped plot should be sampled concurrently with a bare soil plot. In this case, the following factors should be considered in the sampling strategy of a well-designed protocol:

- Time zero samples
- Types of sample (i.e., soil versus plant) and sampling frequency
- Sample locations (e.g., between rows, under rows)
- Accounting for plant uptake versus foliar dissipation
- Residues in roots
- Chemical factors such as formulation and application method
- Crop characteristics

e. Number and Pooling of Samples

The purpose of soil sampling in the TFD study is to measure the mean concentration of the pesticide (and its degradates or transformation products) so that dissipation may be followed quantitatively over time. In order to generate a reliable estimate of the mean concentration that represents the entire treated plot, a sufficient number of core samples should be taken to achieve acceptable variability in the concentration across the plot. The number of cores needed to estimate the mean concentration (statistically, the sample size) will then depend on the desired precision (i.e., standard deviation around the mean) and the variability of the pesticide

concentration in the field (the field or population variability).

The statistics of this estimation were developed several years ago (Gilbert, 1987) and have been made into a calculator (DQO-PRO) by EPA's Superfund program to support the development of Data Quality Objectives (DQOs). The DQO process is an experimental design exercise intended to quantitatively define the sampling effort, given the data precision needed to support decision-making.

In the case of the TFD study, the major DQO is measurement of the mean concentration at each sampling time with a small enough error (standard deviation) that the means at different sampling times over the course of the study can be used to calculate a statistically significant rate of dissipation from the soil. Data presented by Jones et al. in 2004 (47) at the 227th American Chemical Society National Meeting suggest that the standard deviation among 16 samples individually analyzed from a variety of TFD studies is about 110%. (This analysis provides an estimate of field or population variability.) Further analysis by industry (I. van Weesenbeck, 2004 (48)) suggests that the variability in calculated half-lives is less than the variability of the mean concentrations from which they are calculated (assuming constant variability of the soil means over the course of the study), and that standard deviations of up to 100% in the mean concentration result in tolerable error for half-lives up to one year in length.

The following table, based on calculations with DQO-PRO, provides the number of individually analyzed cores needed to estimate, at a 95% confidence level, the mean concentration at any time, within a known error (standard deviation), given various assumptions about the population variability. Using the assumption of 110% for a population, a sample size of 15 or 16 cores is expected to estimate the mean concentration to within 60% standard deviation. (The actual number of cores calculated by DQO-PRO was 16, but 15 facilitates the use of 3 replicate subplots.)

The TFD study sponsor may use 15 cores per sampling episode as a minimum, although this minimum number implies that the mean concentration calculated from the 15 cores is no more precise than the 60% coefficient of variation (CV). If the cores are composited before analysis, the standard deviation of the results should be corrected for compositing. (Note: If the standard deviation calculated from the core analysis is greater than the expected 60%, the assumption of 110% CV in the field population may not be valid, and a larger number of cores should be collected.)

If greater precision is desired to support more quantitative uses of TFD study results, or if greater than 110% variability in the field is expected, then the study sponsor should use the table provided in II.F.7.e. (Table 1) or the DQO-PRO calculator to find the number of cores necessary to achieve the desired level of precision.

In Table 1, the shaded area indicates the tolerable error that can be achieved in estimating the mean concentration (top row) when 30 to 45 cores are taken from fields having variability in concentration indicated by CV figures in the left-most column (population). These calculations assume that samples are analyzed individually or that a correction for compositing is made. For

example, if a 200% population (field) CV is assumed, 34 cores will estimate the mean concentration to within 70% error, and 46 cores will estimate it to within 60% error, after correction for compositing. If a 100% population (field) CV is assumed, then 46 cores will estimate the mean concentration to within 30% error, after correction for compositing.

Table 1 Tolerable Error in Estimation of Mean Concentration

Population (field) % CV	Tolerable Error in Estimation of Mean Concentration (%) Number of Non-composited Cores Needed to Estimate Mean to Within Tolerable Error at 95% Confidence									
	100%	90%	80%	70%	60%	50%	40%	30%	20%	10%
200	18	22	27	34	46	64	99	174	387	1540
190	17	20	25	31	41	58	90	157	350	1390
180	15	18	22	28	38	53	81	141	314	1248
170	14	17	20	26	34	47	72	126	280	1113
160	13	15	18	23	30	42	64	112	249	986
150	12	14	16	21	27	38	57	99	219	867
140	11	13	15	18	24	33	50	87	191	756
130	10	11	13	16	21	29	44	75	165	652
120	9	10	12	14	18	25	38	64	141	556
110	8	9	11	12	16	22	32	55	119	468
100	8	9	9	11	14	18	27	46	99	387
90	—	8	9	10	12	15	22	38	81	314
80	—	—	8	8	10	13	18	30	64	249
70	—	—	—	8	9	11	15	24	50	191
60	—	—	—	—	8	9	12	18	38	141
50	—	—	—	—	—	8	9	14	27	99
40	—	—	—	—	—	—	8	10	18	64
30	—	—	—	—	—	—	—	8	12	38
20	—	—	—	—	—	—	—	—	8	18

Finally, certain principles apply to the study design, regardless of the intended use of the study results. The number and diameter (typically 3 to 12 cm) of soil cores should be based on the size of the plot, the type of soil and the amount of soil necessary for analysis. Corresponding depths of soil cores from a single replicate plot can be pooled and mixed thoroughly to produce one representative composite sample that can be analyzed. An adequate number of cores per

plot should be collected at each sampling time to ensure the sample is representative of the plot. For example, a composite sample from a 2-m × 1-m small plot may consist of 15 soil cores (3-cm diameter) per sampling time over a period of one year (19) (20) (39) (40). In large plots, cores of greater diameter are usual (24) (38). The variability within a large plot is typically greater than in a small plot because of less uniform pesticide application and soil spatial variability. For field studies of longer duration with small plots, the plot area should be increased to accommodate collection of a greater number of cores, resulting from an increased number of sampling times. If a large-scale plot contains areas of different types of soil, soil organic matter content, etc., or knolls/depressions, then representative cores from areas of different soil types should be pooled and analyzed separately from other samples.

f. Handling of Samples

Soil samples should be handled in the following manner.

- Soil samples should be frozen if they cannot be extracted immediately.
- Air-drying of soil samples before extraction is not recommended because of possible loss of chemical residues from the samples via volatilization.
- To check the stability of pesticide residues during storage, untreated soil samples should be fortified in the field with analytical standards (parent chemical and major transformation products), stored, and then extracted and analyzed within the same time period and in the same manner as samples from treated field plots (21). Recovery results from field-fortified samples are preferred to recovery data from more conventional storage stability studies such as laboratory-fortified samples.

8. Sampling of Other Media

Measuring pesticide residues in soil over time provides direct information on a limited number of dissipation routes, e.g., transformation, sorption and leaching. Other dissipation routes that often play major roles in the environmental fate of a compound include accumulation and metabolism in plants; volatilization from soil, water and/or plant surfaces; soil binding; runoff; and spray drift. To meet the objectives of the TFD study and to determine where the pesticide goes in the environment, the study sponsor may need to design the sampling scheme to account for routes of dissipation that cannot be accounted for through soil core sampling alone.

a. Sampling Plants and Foliage

When the pesticide is applied to cropped plots, plant material should be sampled. The sampling scheme should be designed to track the decline in pesticide residues from foliage with time, and foliage sampling should include a time zero residue level. Pesticide residues may also be affected by abiotic degradation (hydrolysis and/or photolysis), be translocated into plant foliage and volatilize from foliage more readily than from soil. If any of these processes from foliage are a likely route of dissipation, the study design should ensure that appropriate measurements

are made. In contrast to soil sampling times, foliage samples need to be collected more frequently at the beginning of the study in order to adequately characterize foliar dissipation.

It may be appropriate to use existing laboratory and/or greenhouse plant studies as a substitute for a full scale field sampling of plant material. However, when relying on laboratory/greenhouse data to support a route of dissipation in the field study, the registrant needs to characterize any differences between the conditions under which the laboratory/greenhouse studies were conducted relative to the field dissipation study. These laboratory/greenhouse studies should be conducted using similar conditions as those present in the field study, e.g., plants, application, treatment, etc., if possible. The registrants should consider collecting a set of benchmark samples from the field study to determine how much of the pesticide was removed by the crop and for comparison with the laboratory/greenhouse studies.

b. Air Sampling

Monitoring studies have found pesticide residues in the atmosphere, demonstrating that some pesticides have the potential to volatilize from the field (43). Many pesticides are soil-incorporated, though, to retard volatilization and enhance efficacy. In cases where the vapour pressure and Henry's law constant of the pesticide or site-specific environmental conditions (e.g., warm temperatures, windy conditions) suggest potential volatilization, the TFD study should provide meaningful data on volatilization losses from the field. In this case, air sampling, with methods that measure pesticide residues in the vapour phase, may be needed to determine whether volatilization is a route of dissipation. Air samples need to be collected more frequently at the beginning of the study to adequately characterize the volatilization of the test substance.

c. Sampling for Pesticide Residues in Runoff

Laboratory studies may indicate the potential for pesticide residues to move offsite dissolved in runoff water or through erosion. Typically, the TFD study is conducted on a site that is essentially flat. However, if the use pattern suggests that the pesticide will be used in areas of significant slope (e.g., orchard uses) or that there are significant risks associated with aquatic exposures from runoff, then a runoff component may be necessary (44).

9. Sampling Strategies to Increase Sensitivity

Strategies that could be used to increase the detection sensitivity of pesticides in TFD study samples include the following:

- Decreasing the thickness of sample soil depth (thinner increments)
- Increasing the area of soil or foliage samples
- Increasing the volume of runoff water or air samples
- Increasing the application rates

- Increasing the number of replications
- Refining/improving analytical methods for parent and major transformation products
- Improving recovery efficiencies

III. Data Analysis, Interpretation and Reporting

A. Statistical Analysis

Data gathered from the study should be analyzed by statistical methods that describe the pesticide's rate of dissipation. Methods should be specified and consistent with the study design; goodness of fit of the data to the statistical analysis should be provided. Analysis should emphasize the dissipation of the pesticide from the upper soil layer to which the pesticide is applied, as well as comparisons of within-site and among-site variability.

B. Data Interpretation and Quantitative Assessment

An evaluation of the data collected in the field dissipation study and interpretation of the results should include the following considerations:

- Half-life and times for 50% and 75% dissipation of the parent chemical (DT_{50} and DT_{75} , respectively) under field conditions, determined from the residue data
- Dissipation parameters of the major transformation products (e.g., quantities and rates of formation and decline, including DT_{50})
- Mobility of the parent compound and the major transformation products under field conditions
- A comparison of the dissipation and mobility parameters from the field studies with corresponding results from laboratory studies and predictions based on the pesticide's physical/chemical properties (e.g., solubility in water, vapour pressure, Henry's law constant, dissociation constant and *n*-octanol–water partition coefficient)
- Plant uptake of pesticide residues in the field compared with that under laboratory or greenhouse conditions, within the context of the experimental parameters at the field site, e.g., application, climatic (precipitation and temperature), edaphic (soil properties and moisture conditions) and cropping parameters
- Identification and discussion of discrepancies between the results of field studies and laboratory studies

C. Mass Accounting Considerations

The residue data for the parent chemical, each of the major transformation products and the total major chemical residues should be expressed in terms of equivalent amounts of parent

chemical on a dry-weight basis, and then as percentages of the 0-day concentration. These percentages can then be summed for the sampled environmental compartments (e.g., soil depths, air, water, plants) and plotted versus time to estimate an overall mass account. If the overall mass accounting is unexpectedly low, major route(s) of dissipation were possibly not adequately addressed in the field study design.

D. Reporting

The study report should be clear and succinct with definitive conclusions regarding the environmental fate and transport of the pesticide after field application. Soil samples results should always be reported on a dry-weight basis along with percent moisture. The study conclusion should be discussed both in terms of the data developed in the field study and in terms of the expected route(s) of dissipation suggested by the laboratory studies. Discussion of how the study compares with other field studies of this active ingredient should be included. The report should clearly identify those aspects of the study having a direct bearing on the author's conclusions and the validity of the study results.

In addition to a full description of the analytical methods used, the following data should be reported:

- Information on the test substance and relevant transformation products:
 - Formulation of the test substance
 - Limits of analytical detection/quantification
 - Physicochemical and environmental fate properties
 - Specific activity and labelling positions (if appropriate)
- Information on the field study site:
 - Location
 - Climatic conditions and history
 - Soil taxonomic classification and properties with depth
 - Hydrologic setting
 - Size and configuration of the treatment and control plots
 - Crop, management and pesticide-use history
 - Depth to the water table
- Application of the test substance:
 - Time(s) of application
 - Rate(s) of application
 - Method of application
 - Confirmation of application rate
 - Field condition at the time of application
 - Meteorological conditions at the time of application
- Tracer(s) used, if any:
 - Type of tracer(s)
 - Rate and method of application

- Maintenance activities:
 - Type of vegetation
 - Agricultural practices (date of seeding, time of harvest, yields, etc.)
 - Weed control

- Conditions during test:
 - Daily air temperature (minimum, maximum)
 - Daily precipitation and irrigation (reporting of single rainfall events), intensity and duration
 - Irrigation technique
 - Weekly and monthly sums of precipitation and irrigation
 - Weekly mean soil temperature
 - Soil water content
 - Daily evapotranspiration or pan evaporation
 - Movement of tracers (if used)

- Residues in soil (as mg/kg dry weight and % of applied amount) at each sample interval:
 - Concentration of test substance in each soil depth
 - Concentration of transformation products in each soil depth
 - Concentration of extractable radioactivity in each soil depth, if applicable
 - Concentration of non-extractable radioactivity in each soil depth, if applicable
 - Total amounts of test substance, transformation products, other unidentified extractable residues and non-extractable radioactivity, if appropriate

- Residues on and in plants (in mg/kg fresh weight and % of applied amount) at each sample interval, if appropriate. In addition, plant residues should be reported based on how much of the pesticide was removed from a unit-area of the field in order to be useful in mass accounting.

- Residues detected via other avenues of dissipation (e.g., volatility, runoff, leaching), if appropriate
- Mass accounting (recovered percentage of applied test substance) at each sample interval

- Appropriate statistical analyses of the collected data

- Protocol deviations and amendments

Data should be presented in both tabular and graphical forms.

E. Study Conclusions

After an extensive outreach and review program involving stakeholders and the technical community, EPA and PMRA developed harmonized guidance for conducting a TFD study. Central to this guidance is the development of a conceptual model, using assumptions derived

from laboratory data along with the intended use pattern and physicochemical properties of the pesticide. As such, the conceptual model is a prediction or working hypothesis for the TFD study.

Although laboratory data is the foundation for the hypothesis and the basis for the conceptual model approach, the TFD study provides the primary mechanism for testing and refining the hypothesis for the transformation, fate and transport of a pesticide under actual use conditions. As the keystone environmental fate study, the TFD study allows the risk assessor to directly compare the laboratory hypothesis of the transformation, fate and transport of the pesticide with those processes measured in the field. Without the terrestrial field study, the assessor will not have a feedback mechanism to evaluate the laboratory hypothesis of environmental behaviour.

Well-designed TFD studies characterize the transport, transformation and biological assimilation processes of a pesticide in the field as well as the dissipation rates of the parent compound and major breakdown products. In contrast to laboratory studies, TFD studies highlight the potential simultaneous processes that may occur in the field. For example, biodegradation can occur during leaching or runoff. Hydrolysis and photolysis can be enhanced by certain soil components in the field that may be absent during laboratory studies. Also, initial products of hydrolysis and photolysis can serve as substrates for microbial degradation.

As pesticide risk assessment moves from a deterministic approach to a more sophisticated probabilistic approach, the need for better characterization of the data used in a risk assessment increases. In characterizing the data, the risk assessor needs to understand the assumptions, limitations and error in the study results. This guidance has been developed to address this need and to provide the study sponsor with flexibility in designing a study without increasing the cost of conducting the study.

List of Abbreviations

CV	coefficient of variation
DQO	data quality objectives
DT ₅₀	see Appendix I
DT ₇₅	see Appendix I
EEC	estimated exposure concentration
EPA	United States Environmental Protection Agency
EXAMS	Exposure Analysis Modeling System
FAO	Food and Agriculture Organization of the United Nations
GIS	geographical information system
NAFTA	North American Free Trade Agreement
NRCS	Natural Resources Conservation Service, USDA
PMRA	Pest Management Regulatory Agency
PRZM	Pesticide Root Zone Model
RRA	refined risk assessment
t _{1/2}	see Appendix I
TDR	time domain reflectometry
TFD	terrestrial field dissipation
USDA	United States Department of Agriculture

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Appendix I Definitions and Units

50% dissipation time (DT₅₀): The amount of time required for 50% of the initial pesticide concentration to dissipate. Unlike the half-life, the dissipation time does not assume a specific degradation model (e.g., a first-order degradation).

75% dissipation time (DT₇₅): The amount of time required for 75% of the initial pesticide concentration to dissipate. Unlike the half-life, the dissipation time does not assume a specific degradation model (e.g., a first-order degradation).

Dissipation: Overall process leading to the eventual disappearance of substances from the site of its application or an environmental compartment. Dissipation comprises two main types of processes: transport processes, such as volatilisation, leaching, plant uptake, runoff or erosion that transfer substances to different environmental compartments; and transformation processes such as microbial degradation, hydrolysis and/or phototransformation that produce transformation products.

First-order kinetics: A model that assumes that the rate of degradation/dissipation is proportional to the concentration of the reactant and remains constant during the reaction time period.

The single first-order model is derived from the differential equation:

$$\frac{dM}{dt} = -kM \quad M(0) = M_0$$

with

M = mass of the compound
 M_0 = initial mass of the compound
 k = rate constant for the compound

The integrated form of the above equation is a simple exponential equation with two parameters (M and k):

$$M = M_0 e^{-kt}$$

with

M = mass of the compound at time t

Half-life (t_{1/2}): The time required for a concentration of a pesticide to be reduced (i.e., degrade, metabolize or otherwise dissipate) to one-half. With each half-life period, half of the remaining concentration of pesticide will disappear from the system.

Half-life versus 50% dissipation time: When the reaction follows first-order degradation kinetics, the half-life will be equivalent to the 50% dissipation time. In this case, the reaction rate is proportional to the reactant concentration and constant over time. However, when the degradation rate is not first-order, the half-life and the 50% dissipation time will differ. In this situation, the half-life is usually greater than the 50% dissipation time. Discrepancies between the $t_{1/2}$ and the DT_{50} may suggest that pesticide degradation follows something other than a first-order reaction model.

Ideal application and planting techniques: The use of specially adapted application machinery to accurately apply a pesticide in small plot field trials in a manner approximating field methods.

Major transformation products: Degradation products/metabolites of the parent compound that are observed at any time in the laboratory or field studies at a level equal to or greater than 10% of the initial concentration of the parent compound. In addition, major transformation products may include other compounds of toxicological significance.

Plot: A single experimental unit, e.g., a control plot, a treated plot.

Replicate plot: One of two or more plots treated in an identical manner at one site.

Site: Exact geographical location of a study.

Appendix II Data Sheet to Characterize Test Substance Properties

This table contains the physicochemical properties of the test substance and the environmental fate laboratory studies necessary to design a TFD study.

Property/lab study	Values	Classification	Reference
Solubility (mg/L)			
Vapour pressure (Pa) Henry's law constant (atm·m ³ /mol)			
Dissociation constant (pKa or pKb)			
<i>n</i> -octanol–water partition coefficient (K_{ow})			
Hydrolysis (half-life) Major transformation products			
Soil photolysis (half-life) Major transformation products			
Soil aerobic biotransformation (half-life and persistence) Major transformation products			
Soil anaerobic biotransformation (half-life and persistence) Major transformation products			
Adsorption/desorption (K_d and K_{oc}) Mobility class			
Others			

Appendix III Analytical Method Reporting, QA/QC and Validation

Environmental chemistry information that is needed for the independent validation of analytical methods used in conducting field dissipation studies is listed below.

Documentation. A full description of the analytical methods used in all steps of the analytical protocol should be submitted, including the following information:

1. Name and signature, title, organization, address and telephone number of the person(s) responsible for the planning and supervision/monitoring and laboratory procedures/analyses
2. Analytical method(s) title/designation/date
3. Source of analytical method(s) [e.g., *Pesticide Analytical Manual (PAM)*, Vol. II, scientific literature, company reports]
4. Principles of the analytical procedure (description)
5. Copy of the analytical method(s) detailing the following procedures:
 - a) extraction
 - b) clean-up
 - c) derivatization
 - d) determination and calculation of the magnitude of the residue
6. Reagents or procedural steps requiring special precautions to avoid safety or health hazards
7. Identification of the chemical species determined
8. Modifications, if any, to the analytical method(s)
9. Extraction efficiency
10. Instrumentation (e.g., GC)
 - a) make/model
 - b) type/specificity of detectors
 - c) column(s) packing materials and size
 - d) gas carrier and flow rates
 - e) temperatures
 - f) limits of detection and sensitivity
 - g) calibration procedures
11. Interferences, if any

12. Confirmatory techniques
 - a) other column packings
 - b) detectors
 - c) mass spectrometry
 - d) nuclear magnetic resonance
13. Date(s) of sampling, extraction and residue analyses
14. Sample identification (coding and labelling information)
15. Residue results (examples of raw data, laboratory worksheets, stepwise calculation of residue levels, dilution factors, peak heights/areas, method correction factors applied [e.g., storage stability and method validation recovery values], standard curve(s) used, ppm of total residues and of individual components if they are of special concern, range of residue values, representative chromatograms, spectra of control and treated samples)
16. Statistical treatments of raw data
17. Other additional information that the study sponsor/researcher considers appropriate and relevant to provide a complete as well as thorough description of residue analytical methodology and the means of calculating the residue results

Quality Assurance/Quality Control. A complete description of the measures taken to ensure the integrity of the analytical results should include information on the following:

1. Logbooks and/or record keeping procedures, representative instrument printouts, such as chromatograms, spectral analyses, etc.
2. Sample coding
3. Use of replicate samples and control blanks
4. Use of written and validated analytical methodology for residue analyses involved in all test and analytical procedures, including modifications made
5. Skills of laboratory personnel
6. Laboratory facilities
7. Use of high quality glassware, solvents and test compounds to ensure minimal contamination
8. Calibration and maintenance of instruments
9. Good laboratory practices in handling the test substance(s)
10. Quality assurance project plan

11. Internal and external auditing schedule established by the study director using an independent quality assurance unit

Independent Laboratory Method Validation. A full description of the method validation procedures performed by an independent laboratory should be submitted and include the following information:

1. Recovery level(s) of the test compounds from the soil (substrate) at various fortification level(s) using the residue analytical methodology
2. A validated method sensitivity level
3. Results of the study and statistical test applied, including a stepwise presentation of the procedure for calculating percent recovery from the raw data
4. All the data/information necessary to independently verify the results
5. Summary of the results
6. Discussion and conclusions of the results

Appendix IV Site Characterization Data Sheet

This table can be used to describe the pertinent site characteristics that can influence the dissipation of the test substance in terrestrial environments.

Parameter	Site Description	Information Source
Geographic coordinates Latitude Longitude Data Source FIPS Code for State, County		
Location within watershed		
Landforms		
Landscape position		
Land surface Slope gradient Slope length Direction Micro-relief Roughness Elevation Data source(s)		
Depth to groundwater		
Average rainfall (yearly/monthly)		
Average air temperature (daily/weekly/monthly) Minimum Maximum		
Average soil temperature (daily/weekly/monthly) Minimum Maximum		
Average annual frost-free period Dates Number of days		
Others		

Appendix V Sample Description of the Soil Profile (USDA)

TAXONOMIC CLASS: Fine-loamy, mixed, thermic Aridic Paleustalfs; Amarillo Series

PEDON DESCRIPTION: Amarillo fine sandy loam—grassland. (Colours are for dry soil unless otherwise stated.)

- A 0 to 11 inches; brown (7.5YR 4/4) fine sandy loam, dark brown (7.5YR 3/4) moist; weak fine granular structure; hard, very friable; many fine roots; many fine and medium pores; many wormcasts; mildly alkaline; clear smooth boundary. (5 to 19 inches thick)
- Bt 11 to 27 inches; reddish brown (5YR 4/4) sandy clay loam, dark reddish brown (5YR 3/4) moist; moderate coarse prismatic structure parting to weak medium subangular blocky structure; very hard, friable; many fine and medium pores; thin patchy clay films on faces of prisms; clay bridged sand grains throughout; common wormcasts; mildly alkaline; gradual wavy boundary. (8 to 25 inches thick)
- Btk1 27 to 38 inches; yellowish red (5YR 4/6) sandy clay loam, moist; weak medium subangular blocky structure; hard, friable; clay bridged sand grains; common films and threads of calcium carbonate on faces of peds; interiors of peds noncalcareous; moderately alkaline; gradual wavy boundary. (8 to 30 inches thick)
- Btk2 38 to 56 inches; pink (5YR 7/3) sandy clay loam, light reddish brown (5YR 6/3) moist; weak medium subangular blocky structure; hard, friable; estimated 60 percent calcium carbonate equivalent; 30 percent by volume is concretions of calcium carbonate less than 1 inch in diameter; calcareous, moderately alkaline; gradual wavy boundary. (6 to 36 inches thick)
- Btk3 56 to 85 inches; yellowish red (5YR 5/6) sandy clay loam, yellowish red (5YR 4/6) moist; weak very coarse prismatic structure parting to weak medium subangular blocky structure; slightly hard, friable; thin patchy clay films and clay bridging of sand grains; few, mostly vertical stringers of soft bodies of calcium carbonate are concentrated along faces of prisms; few calcium carbonate concretions less than 1 inch in diameter; calcareous, moderately alkaline; gradual wavy boundary. (8 to 50 inches thick)
- Btk4 85 to 99 inches; light reddish brown (5YR 5/4) sandy clay loam, yellowish red (5YR 4/5) moist; weak very coarse prismatic structure parting to weak medium subangular blocky structure; hard, friable; thin patchy clay films and bridged sand grains; few soft bodies of calcium carbonate are concentrated in vertical columns along faces of prisms; calcareous, moderately alkaline.

Appendix VI Physicochemical Properties of Soil

Property	Horizon					Method
	H ₁	H ₂	H ₃	H ₄	H ₅	
Depth						
Texture						
% sand						
% silt						
% clay						
Textural class (USDA)						
Bulk density						
Soil moisture characteristic						
0 bar						
0.1 bar						
α bar						
1 bar						
5 bars						
10 bars						
15 bars						
pH						
Organic carbon (%)						
Cation exchange capacity (meq/100 g)						
Base saturation (%)						
Clay mineralogy						
Specific surface						
Anion exchange capacity						
Others						

Appendix VII Meteorological History Data Sheet

This table can be used to describe the pertinent meteorological factors that can influence the dissipation of the test substance in terrestrial environments.

Parameter	Site Description	Information Source
Average monthly rainfall January February March April May June July August September October November December		
Average minimum/maximum air temperature January February March April May June July August September October November December		
Average annual frost-free period Dates Number of days		
Others		

Appendix VIII Site Use and Management History for the Previous Three Years

Use	Previous Year	Previous 2nd Year	Previous 3rd Year
Crops grown			
Pesticide and fertilizer use			
Cultivation methods Tillage Irrigation practices			
Others			

Appendix IX Suggested Criteria for Module Selection

Field Study Indicators

In deciding what modules to incorporate into a field study, the study sponsor should ask the following questions:

1. What is the potential for dissipation of the parent compound and major transformation by a given route (e.g., volatilization, leaching, runoff, etc.)?
2. Is the potential great enough to warrant measurement under field conditions representative of actual use?

In many cases, several criteria or a weight-of-evidence approach based on physicochemical properties of the test substance and laboratory studies is the best way to answer these questions. No single laboratory study by itself can absolutely predict transformation, transport or dissipation in the field. Laboratory data can, however, provide quantitative or semi-quantitative indices of the inherent persistence and mobility under field conditions.

Volatilization Potential

Important physicochemical properties influencing volatilization are vapour pressure and solubility in water. The partitioning of a chemical between air and water is described by Henry's law and can increase or decrease the volatilization potential. Adsorption to soil is an important process that reduces volatilization. When needed, volatilization from soil and water may be specially studied under laboratory conditions to gain additional knowledge. Quantification of trapped volatile organics in standard laboratory studies of biotransformation/metabolism in soil and aquatic systems also addresses volatilization of the parent compound and transformation products.

Other factors that may be considered include method of application (e.g., foliar versus soil surface versus soil incorporated, injected and watered-in), temperature, soil moisture content, soil organic carbon content, soil texture, soil porosity, residue persistence and leaching.

Vapour Pressure

The measured vapour pressure of a chemical compound is a guide to its volatility and to the probability of its movement into the atmosphere. A volatility classification based solely on vapour pressure is best suited to dry, non-adsorbing surfaces. In general, pesticides with vapour pressures $\leq 1 \times 10^{-6}$ mm Hg (1.33×10^{-4} Pa = 1.33×10^{-1} mPa) are considered relatively non-volatile under field conditions, whereas pesticides with vapour pressures $\geq 3.9 \times 10^{-5}$ mm Hg (5.20×10^{-3} Pa = 5.2 mPa) are considered to be of intermediate to high volatility under field conditions (Kennedy and Talbert, 1977). Thus, a vapour pressure $\geq 3.9 \times 10^{-5}$ mm Hg or 5.2 mPa at 25°C raises concern regarding potential volatilization and vapour drift of the active ingredient.

Henry's Law

Henry's law addresses the partitioning of a compound between water and air, a process that can increase or decrease the overall volatilization of the compound from a water or moist surface. A unitless water/air distribution ratio can be calculated by the following equation (Burkhard and Guth, 1981; EPA, 1975):

$$\frac{C_{\text{water}}}{C_{\text{air}}} = \left(\frac{S \times T \times 82.08 \times 760}{P \times \text{GMW} \times 10^6} \right)$$

where:

- C_{water} = concentration of the compound in water [$\mu\text{g/mL}$]
- C_{air} = concentration of the compound in air [$\mu\text{g/mL}$]
- S = the solubility of the compound [$\mu\text{g/mL}$]
- T = absolute temperature [$^{\circ}\text{K} = ^{\circ}\text{C} + 273.15$]
- 82.08 = gas constant, R , [($\text{mL} \times \text{atm}$) / ($^{\circ}\text{K} \times \text{mol}$)]
- 760 = mm/atm
- P = vapour pressure [Torr] of the compound
- GMW = gram molecular weight of the compound [g/mol]

A volatility classification from a water surface based on $C_{\text{water}}/C_{\text{air}}$ is found in the following table (EPA, 1975)

$C_{\text{water}}/C_{\text{air}}$	Volatility Class
$< 10^2$	Rapidly lost from a water surface
10^2-10^3	Volatile from a water surface
10^3-10^5	Slightly volatile from a water surface
$> 10^5$	Non-volatile

Soil Adsorption Effects

Because adsorption to soil can significantly reduce volatilization, volatilization from a moist soil is assumed to be volatilization from water modified by adsorption. The distribution ratio between wet soil and air can be calculated by the following equation (Burkhard and Guth, 1981; EPA, 1975):

where

e:

C_{water}
+ soil
=

$$\frac{C_{\text{water+soil}}}{C_{\text{air}}} = \frac{C_{\text{water}}}{C_{\text{air}}} \left(\frac{1}{r} + K_d \right)$$

conce

ntration of the compound in wet soil (w/w on a dry weight basis)

- C_{water} = concentration of the compound in water (w/v),
- C_{air} = concentration of the compound in air (w/v),
- r = (weight of soil)/(weight of water), and
- K_d = linear adsorption coefficient

Although no generic classification of volatility from moist soil was presented by EPA (1975) and Burkhard and Guth (1981), several non-fumigant compounds were categorized as volatile, slightly volatile and non-volatile from moist soil, based on their wet soil/air distribution ratios and assuming a

standard soil containing 2% organic carbon and a value of 6 for r, the soil/water weight ratio.

Estimated Tendency of Compounds to Volatilize from Water and Moist Soil
(Burkhard and Guth, 1981, and EPA, 1975)

Compound	Vapour Pressure		Solubility in Water ($\mu\text{g/mL}$)	$C_{\text{water}}/C_{\text{air}}$	K_d^a	$C_{\text{water + soil}}/C_{\text{air}}^b$
	(mm/hg)	(mPa)				
<i>Fumigants</i>						
<i>cis</i> -1,3-D	2.5×10		2700	1.77×10	0.51	1.2×10
<i>trans</i> -1,3-D	1.85×10		2800	2.49×10	0.56	1.81×10
EDB	7.7×10^{-1}		3370	4.33×10	0.65	3.54×10
DBCP	5.8×10^{-1}		1230	1.67×10^2	2.58	4.59×10^2
<i>Volatile from moist soil</i>						
chloroneb	3.0×10^{-3}		8	2.35×10^2	23.2	5.49×10^3
EPTC	1.97×10^{-2}	2.62×10^3	370	1.84×10^3	5.66	1.07×10^4
dichlobenil	5.5×10^{-4}	7.32×10	18	3.48×10^3	3.28	1.2×10^4
<i>Slightly volatile from moist soil</i>						
disulfoton	1.8×10^{-4}		15	5.55×10^3	42.6	2.37×10^5
diazinon	—	9.71	40	3.29×10^4	10	3.34×10^5
gamma-HCH	3.2×10^{-5}	4.26	10	1.96×10^4	26.8	5.29×10^5
isazophos	—	4.26	150	2.73×10^5	2.06	6.08×10^5
DDT	1.9×10^{-7}	2.53×10^{-2}	0.0012	3.26×10^2	4860	1.58×10^6
<i>Non-volatile from moist soil</i>						
parathion	3.8×10^{-5}	5.05	20	3.3×10^4	209	6.9×10^6
metolachlor	—	1.73	530	2.63×10^6	2.73	7.62×10^6
chlorpropham	1.0×10^{-5}		88	8.0×10^5	11.8	1.0×10^7
atrazine	8.9×10^{-7}		33	3.2×10^6	3.44	1.2×10^7
methidathion	—	1.33×10^{-1}	240	1.45×10^7	3.71	5.62×10^7
monuron	5.0×10^{-7}	6.65×10^{-2}	230	4.2×10^7	1.66	7.67×10^7
metalaxyl	—	2.93×10^{-1}	7100	2.11×10^8	0.75	1.93×10^8

^a soil adsorption coefficient corrected for a standard soil containing 2% organic carbon

^b soil to soil water (w/w) = 6; soil water to soil air (v/v) = 1

Considering the values calculated for $C_{\text{water + soil}}/C_{\text{air}}$ in the previous table, the following categorization seems reasonable for volatilization from moist soil with 2% organic carbon and a soil to water ratio

(w/w) of 6.

Volatility classification from moist soil based on $C_{\text{water + soil}}/C_{\text{air}}$

$C_{\text{water+soil}}/C_{\text{air}}$	Volatility from Moist Soil ^a
$< 1 \times 10^3$	Rapidly lost from moist soil
$1 \times 10^3 - 1.5 \times 10^4$	Volatile from moist soil
$1.5 \times 10^4 - 1 \times 10^5$	Intermediately volatile from moist soil
$1 \times 10^5 - 2 \times 10^6$	Slightly volatile to non-volatile from moist soil
$> 2 \times 10^6$	Non-volatile from moist soil

^a 2% soil organic carbon, soil to soil water (w/w) = 6 and soil water to soil air (v/v) = 1

Based on the above data and categorization, volatilization of chemicals from soil under laboratory conditions should be investigated for chemicals with a volatility ($C_{\text{soil + water}}/C_{\text{air}}$)-value $\leq 10^6$. Furthermore, values $\leq 10^5$ indicate the need for volatility studies under field conditions.

Leaching Potential

The movement of a chemical through soil is dependent on several factors including rainfall and irrigation and the properties of the chemical and the soil. In general, leaching is faster and more extensive in coarse-textured soils and soils that have low organic matter and clay content. An assessment of leaching potential at sites in specific use areas should also consider the likelihood of potential preferential flow through relatively large soil voids, e.g., cracks, root channels and Karst topography.

A mobility classification based on soil column leaching was developed by Guth and Hörmann (1987). Monuron has been proposed as the reference compound.

Relative mobility factors¹ (RMF) from soil column leaching studies and corresponding mobility classes for a variety of pesticides are presented in the table below (adapted from Guth and Hörmann, 1987):

RMF—Range	Compound (RMF)	Mobility Class
< 0.15	fluorodifen (< 0.15), parathion (< 0.15)	I immobile
0.15–0.8	profenophos (0.18), propiconazole (0.23), diazinon (0.28), diuron (0.38), terbuthylazin (0.52), methidathion (0.56), prometryn (0.59), alachlor (0.66), metolachlor (0.68)	II slightly mobile
0.8–1.3	monuron (1.00), atrazine (1.03), simazin (1.04), fluometuron (1.18)	III moderately mobile

1.3–2.5	prometon (1.67), cyanazin (1.85), bromacil (1.91), karbutilate (1.998)	IV fairly mobile
2.5–5.0	dioxacarb (4.33)	V mobile
> 5.0	monocrotophos (> 5.0), dicrotophos (> 5.0)	VI very mobile

The relative mobility factor is calculated as follows:

$$\text{RMF} = \left(\frac{\text{leaching distance of test compound (cm)}}{\text{leaching distance of reference compound (cm)}} \right)$$

Adsorption of a chemical to soil, expressed as the adsorption coefficients, K_d and K_{OC} , is a major determinant of leaching potential. The following mobility classification of McCall et al. (1981) is based on the soil organic carbon adsorption coefficient, K_{OC} , and is best suited to non-ionic chemicals.

The following table describes the classification of soil mobility potential of chemicals based on HPLC retention times (McCall et al., 1981).

K_{oc}	Mobility Class
0–50	Very high
50–150	High
150–500	Medium
500–2000	Low
2000–5000	Slight
> 5000	Immobile

Leaching potential is indicated by a mobility classification of medium to very high.

Dissociation of ionic compounds in response to the ambient soil pH affects adsorption and, therefore, mobility in soil. Anionic species that have a negative charge at ambient soil pH are likely to have a very high leaching potential. The effects of soil pH on the adsorption of acids and bases by soil is summarized by Tinsley (1979).

Effect of pH on Adsorption of Acids and Bases by Soils (Tinsley, 1979)

Compound	Molecular/Ionic Species		pH Effect
	Low pH	High pH	
Strong acid	Anion	Anion	Small
Weak acid	Neutral molecule	Anion	Large effect: less adsorption at $\text{pH} > \text{pK}_a$

Strong base	Cation	Cation	Decrease at very low pH
Weak base	Cation	Neutral	Increasing adsorption to $\text{pH} = \text{pK}_a$, decreasing with $\text{pH} < \text{pK}_a$
Polar molecule	Neutral molecule	Neutral molecule	Small effect
Non-polar molecule	Neutral molecule	Neutral molecule	Little effect

Other factors, such as the compound's persistence, affect its leaching potential. Cohen et al. (1984) summarized the various physicochemical, transformation and mobility characteristics of a chemical that has the potential to leach under standard soil conditions:

- Solubility in water > 30 ppm
- $K_d < 5$ and usually < 1 or 2
- $K_{oc} < 300$ to 500
- Henry's law constant $< 10^{-2}$ atm·m³/mol
- Negatively charged (either fully or partially) at ambient pH
- Hydrolysis half-life > 25 wk
- Photolysis half-life > 1 wk
- Half-life in soil > 2 to 3 wk

Note that all of these criteria should be considered together, not individually, in the assessment of leaching potential.

Gustafson (1989) developed the following leaching potential index, based on persistence in soil and adsorption:

$$GUS = \log_{10}(t_{1/2 \text{ soil}}) \times (4 - \log_{10}(K_{oc}))$$

where: $t_{1/2 \text{ soil}}$ = 50% decline time in soil under field conditions
 K_{oc} = soil organic carbon adsorption coefficient

This index is best suited for non-ionic compounds. More importantly, it is better to use laboratory soil metabolism / biotransformation values for $t_{1/2 \text{ soil}}$, as field values include decline via leaching (which is what is being assessed). In any case, based on the calculated GUS score, the leaching potential of compounds can be categorized as follows:

Classification system based on calculated GUS scores (Gustafson, 1989)

GUS Leaching Potential

> 2.8	Leacher
> 1.8 and < 2.8	Borderline leacher
< 1.8	Non-leacher

The leaching potential of compounds with GUS scores > 1.8 should be investigated further.

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