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Terrestrial Field Dissipation

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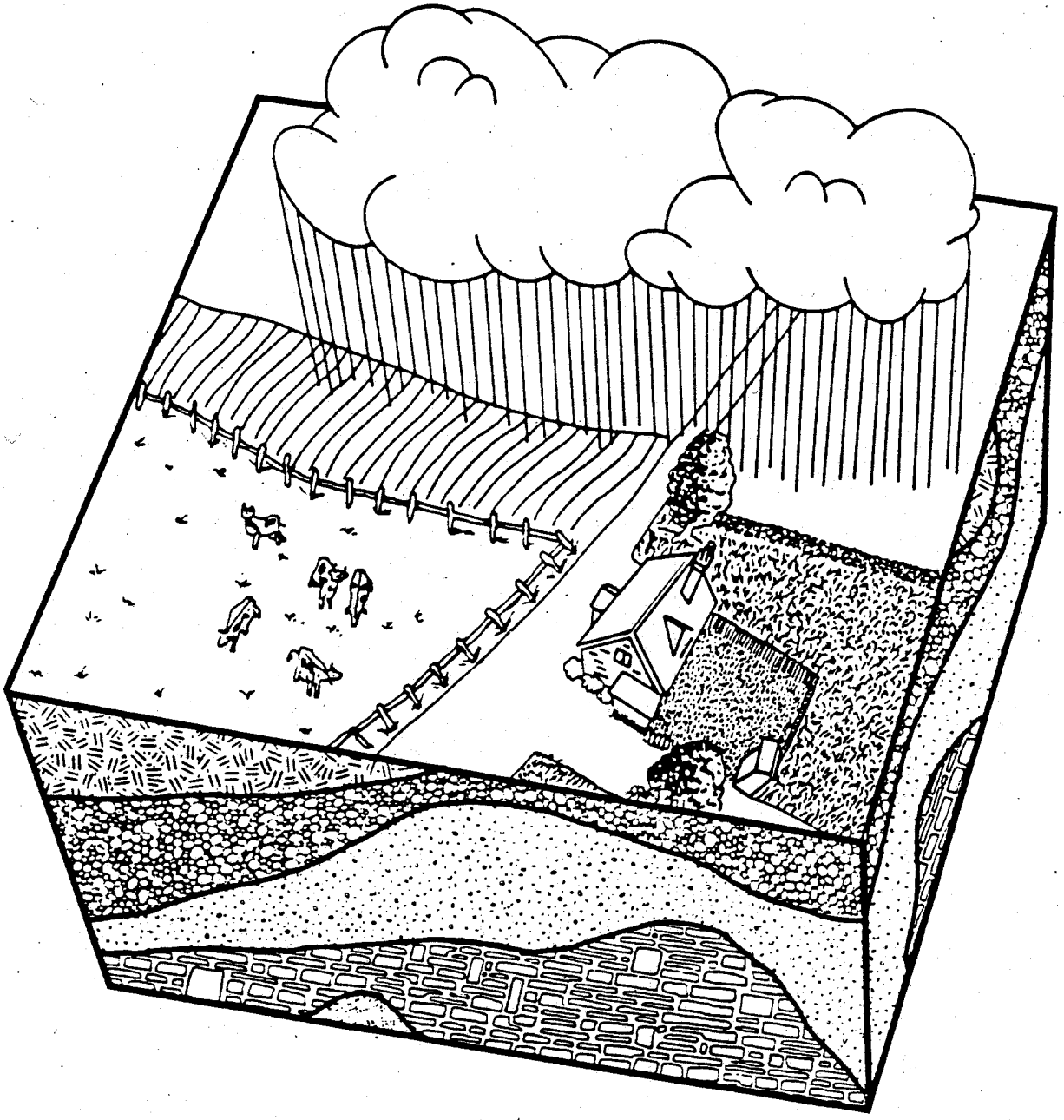

ENVIRONMENTAL FATE AND EFFECTS DIVISION

STANDARD EVALUATION PROCEDURE

TERRESTRIAL FIELD DISSIPATION STUDIES

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TERRESTRIAL FIELD DISSIPATION

I. INTRODUCTION

A. Objective of the Standard Evaluation Procedure

This Standard Evaluation Procedure (SEP) is to be used as an aid for the Environmental Fate and Ground Water Branch data reviewers in their evaluations of the terrestrial field dissipation studies submitted by registrants in support of pesticide registration.

Terrestrial field dissipation studies are required by Section 158.290 of Title 40 of the Code of Federal Regulations (40 CFR 158.290) in support of registration of an end-use product intended for terrestrial use or domestic outdoor use (as defined by the Subdivision N Guidelines) and to support registration of a manufacturing-use product which may also be legally used to formulate such an end-use product. Section 164-1 in the Subdivision N Guidelines describes this study (short-term field dissipation) and provides a protocol for conducting it (1).

This SEP introduces the concept of using a tiered approach to requiring further field studies beyond the field dissipation study. Specifically, the field dissipation study is considered the first tier of field studies addressing movement and persistence of a chemical in the field. For a description of other field studies included in the tiered approach make reference to Cohen et al. and the Guidance for Ground-Water Monitoring Document(2,3).

The intention of the proposed tier approach is to provide a step-by-step procedure in assessing ground-water and surface-water impacts. This should ensure a gradual and consistent approach when requiring ground water or surface water monitoring studies. The "triggers" for further monitoring described in this SEP will not automatically cause any new data requirements. Results from the field dissipation study along with data from other Subdivision N Guidelines environmental fate studies data will be used to determine the leaching potential of a pesticide and need for further monitoring studies. However, the field dissipation study results are pivotal.

Currently, four field monitoring studies are a part of the tiered approach concept. They are: the field dissipation studies (164-1 and 164-5), the small-scale prospective ground-water monitoring study, the small-scale retrospective ground-water monitoring study, and surface-water monitoring studies. Depending on the results of a field dissipation study in conjunction with other laboratory data from environmental fate studies, a ground-water or surface-water monitoring study may be required. Depending on the period of registration and patterns of use for a given pesticide, a small-scale prospective or retrospective ground-water study or both may be required.

Specifically, the small-scale ground-water prospective study has been designed to address movement of pesticide residues through the unsaturated zone and into shallow ground water for new chemicals with a limited use history and some older chemicals suspected of leaching. The study is conducted under conditions providing a worst-case scenario for leaching in the field. The small-scale retrospective ground-water study has been designed to address the impact of a pesticide on shallow ground water after years of past usage. Surface-water monitoring will be used to assess the impact of pesticide residues in runoff on aquatic environments (ponds, lakes, and streams).

The surface and ground-water studies referred to here, as a part of the tiered approach concept, may be required to define potential surface and ground-water impacts from the use of pesticides. Although the toxicological significance of pesticide residues will be considered when determining the need for and type of field monitoring required, the toxicological significance of residues will not be the overriding factor in determining whether a surface or ground-water monitoring field study is warranted.

This SEP provides a detailed sampling and analysis procedure in Appendix 2. However, there may be specific cases where, because of the chemical/physical properties of a pesticide, some of the specific guidance provided in this Appendix may not be applicable. Modifications to the detailed procedures outlined in Appendix 2 will be considered on a case-by-case basis. For example, a field dissipation study for a pesticide known to be immobile, having no leaching potential, may not warrant deep sampling throughout the entire study. Any changes to the study design as detailed in this SEP must be formally approved by the Agency in a protocol prior to study initiation.

B. General Theory of Terrestrial Field Dissipation

Data from field dissipation studies are used to determine patterns of pesticide residue dissipation under actual field conditions. These studies are required because it is likely that patterns of pesticide degradation, such as the rate of formation and decline of degradation products, are influenced by environmental factors such as soil, climate, the presence of crops, and other factors not duplicated in laboratory degradation studies. As well, important information on pesticide mobility under typical use conditions is gained.

The reviewer should be acquainted with the processes which cause pesticides to degrade and move in the soil environment, and is directed to Appendix 1 for a brief discussion of pesticide dissipation processes.

II. THE SUBMITTED STUDY

A. Purpose

The purpose of field dissipation studies for pesticides with terrestrial uses is to determine the extent of pesticide residue dissipation under actual use conditions. These studies will generate data required for the evaluation of degradation, mobility, and other avenues of residue dissipation. In addition to parent compound, formation and decline of degradation products are monitored under actual field conditions.

The study is an important component in assessing a chemical's leaching potential along with laboratory data. Results from the field dissipation study may act as a trigger to require other field studies, specifically, ground-water monitoring studies. The reviewer is directed to Appendix 2 for a brief discussion of the pertinent data resulting from a field dissipation study that may trigger the need for a ground-water monitoring study.

B. Study Design

The registrant's report should contain 1) a stated goal of the study, and 2) sufficient information on the test protocol (formulation of test material used; complete soil characterization of the test sites; dose level and method of application; sufficient description of sampling frequency, depth and methods; and field data) and the analytical protocol (description of methods used for quantitative and qualitative analyses and reports on the quality control procedures used to ensure the validity of the data).

Specific information that the registrant should include in the report is listed in Appendices 2 and 3.

III. THE EVALUATION PROCESS

A. Determine the Need for the Study

The reviewer should initially determine whether the study is required under 40 CFR 158.290. Normally, the study is required to support registration of pesticide products intended for terrestrial or domestic outdoor end uses and for manufacturing-use products intended for use in formulating such end-use products.

B. Read the Report

Reports of field dissipation studies are first reviewed to determine if the following information is present:

1. If an applicant's product is an end-use product, is the test substance a product whose formulation is typical of the formulation category?

2. If the applicant's product is a manufacturing-use product, is the test substance a product representative of the major formulation category which includes that end-use product?

3. Is the formulation of the test substance (the product) specified?

4. Is the complete soil characterization of the test sites included? This includes pH, moisture capacity, percent organic matter, bulk density, cation exchange capacity, textural composition (percent sand, silt and clay), textural class - all as a function of depth.

5. Are the field test data presented? This includes daily climatic data including precipitation, air temperature, and pan evaporation (if available), irrigation amounts and method, depth to the water table and how much this varies seasonally, slope of the test plots, soil temperature data, techniques and times of planting and harvesting, and other information as relevant to the specific study.

6. Was irrigation used to supplement rainfall in a dry year?

7. Are the application rates, dates, and methods described?

8. Is the sampling protocol, from soil core extraction to chemical analysis, described?

9. Were the samples taken to a sufficient depth and at close enough time intervals so that pesticide residues moving through the soil profile would not be missed? Were the samples collected after the immediate post-application sample taken <u>to a depth of 90 cm</u> throughout the study? If not, how deeply were the samples taken, and did the registrant receive prior approval of shallower sample collection depths?

10. Were sufficient samples taken per sampling interval? Were the samples composited? If so, how, and how many composite samples were used for final residue analysis? (See Appendix 2.)

11. Are the methods used for quantitative and qualitative analyses of the degraded compound and formation and decline of the degradation products described?

12. Were analytical method recoveries reported? How were they determined? Are adequate quality control measures described for sampling techniques, sample shipment and storage, soil extraction and cleanup, analytical instrument performance, etc.?

13. Are the raw data (i.e., soil core concentrations) from which a half-life can be calculated included, and is the half-life calculated?

The reviewer should determine if there are data gaps within the study. Failure to provide adequate information may be sufficient reason for the reviewer to reject the study. The Pesticide Assessment Guidelines Subdivision N, should be used as guidance in determining the data gaps. A study that is considered deficient in some way in comparison with the Subdivision N Guidelines may still be scientifically sound, and provide supplemental information pertinent to the environmental fate of the pesticide. This information should be reported in the review. In cases where considerable information is missing, the reviewer should not conduct an in-depth review of the study. Instead, a detailed list of the deficiencies and omissions in the review should be reported.

C. Prepare the Data Evaluation Record

After the reviewer has determined that there are no data gaps which would cause the report to be rejected, the reviewer prepares a Data Evaluation Record (DER) according to the Standard Format for Preparation of Environmental Fate Reviews.

1. Write the Technical Evaluation

The reviewer should use Appendices 2 and 3 as aids in this process. The technical evaluation should be prepared with the following points in mind:

a. The test procedure should provide adequate information as to how and under what conditions the study was conducted. Consult Appendix 2.

b. The analytical procedure should provide information on sensitivity and specificity of the analytical method(s) used and indicate how the results were determined. Consult Appendix 3.

c. Upon comparison with the laboratory soil metabolism studies, the recovery of the analytical method should be in a reasonable range, 70 to 120 percent (considering the loss due to volatilization of parent compound and/or degradation products).

d. The rate of disappearance of the active ingredient of the test material provides a half-life estimate of the active ingredient. It should answer the following questions:

- At what rate does the active ingredient of the test material degrade and/or dissipate?

- Is it persistent in the soil environment under field conditions?

e. The soil degradation products identified under aerobic and anaerobic soil laboratory conditions at 0.01 part per million (ppm) or 10 percent of the application rate (whichever is lower) must be analyzed for in the field dissipation studies. As stated in the Subdivision N Guidelines (160-5), "Analysis and identification of pesticide residues in field studies are required only for those degradation products that were found to form in the lab studies (1)." Any residues present at 0.01 ppm or greater in the lab studies should be identified and analyzed for in the field studies. The 0.01 ppm level is suggested as a goal to be met or surpassed. "However, registration applicants will not be penalized for not being able to meet the 0.01 ppm goal due to limitations of the analytical method (1)." This is not dependent upon the toxicological significance of the pesticide residues. The rate of formation and decline of those compounds provides the answers for the following questions:

- Are the degradation products persistent in the soil environment under field conditions?
- At what rate do they decline?

f. Detection of active ingredient and/or its degradation products in successive soil increments is an indication of the leaching tendency of the compound. Although the laboratory leaching studies provide information on the leaching potential of the compound, the residue analysis in soil increments can provide additional important information on leaching. Relevant questions on the field data include:

- How far has the active ingredient or its degradation product(s) leached through the soil under field conditions? Have they leached to greater than or equal to 90 cm?
- Were the soil increments sampled and analyzed consistently so the pesticide residues could be tracked with each sampling interval? Or could the pesticide residues have leached below the depth of sampling? This would be indicated by significant concentrations at the lowest depth of sampling or long time periods ($\geq$ 1 month) between sampling. For a pesticide known to be persistent and mobile, extended time periods between sampling dates may allow the pesticide residues sufficient time to move beyond the depths sampled.

- Were rainfall patterns and events correlated to residue movement? Or did rainfall patterns have little effect on the movement of residues in the soil profile?

- If the study was conducted during a dry year, was irrigation used to supplement natural rainfall to provide the average amount of rainfall expected during any given month of the study as based on monthly averages from sets of 10, 20 or 40 year rainfall data?

- Based upon the field dissipation tests' results along with mobility and persistence information, under what conditions does the pesticide have a potential to contaminate ground water? Is a more thorough leaching assessment of the pesticide necessary?

g. Quality control information provides assurance of the integrity of the study. This information answers the following question:

- Was the study run using Good Laboratory Practices (GLP)?

2. Determine Study Acceptability

The stated goals of the study should be appropriate and clearly defined. The study should be conducted in a scientifically sound manner to accomplish those goals. If so, the reviewer then determines the acceptability of the study and considers whether the study, as it stands alone or in light of other studies (combined testing, surrogate studies, or waivers), supports the requested registration action. The Pesticide Assessment Guidelines Subdivision N should be used as guidance in determining the study's acceptability.

If the study is considered deficient in any way, a detailed description of the deficiencies and recommendations on how to rectify the deficiencies is prepared and included in the DER. A study that is considered deficient in some way in comparison with the Subdivision N Guidelines may still be scientifically sound, however, and provide supplemental information.

3. Determine Need for Deferral/Referral to Other HED Branches

If the reviewer concludes either that 1) the test chemical or its degradates have a potential for reaching ground or surface water due to their persistence; 2) residues may occur in rotational crops because of their persistence and mobility; and/or 3) there may be exposure to other nontarget organisms

because of persistence, then the Toxicology, Dietary Exposure, and/or Ecological Effects Branches may have to be notified. Final decision on the need for deferral/referral is to be made after the evaluation of the other environmental fate studies.

4. Make Regulatory Determination

Based on the technical evaluation, the reviewer determines whether the study satisfies the data requirement for a field dissipation study as listed in 40 CFR 158.290. As well, the reviewer should make qualitative statements concerning persistence and mobility which could influence a regulatory decision on the pesticide, such as the need for further field monitoring studies, if warranted.

APPENDIX 1

General Theory

Pesticide products reaching soil either degrade (partially or completely), are altered in varying degrees and become part of the soil complex, or remain intact in the soil system. The parent compound or the degradation product(s) may also migrate to places other than the original point of application. The major purpose of a field dissipation study is to gain insight on transport and degradation processes of a pesticide over time in an actual use situation.

The important difference between a study addressing degradation and a study addressing field dissipation is that in field dissipation studies pesticide loss is a combined result of chemical (hydrolysis, photolysis, oxidation, and reduction) and biological (microbial) transformation processes as well as physi-cal migration processes (volatilization, runoff of soluble or sorbed residue, leaching of soluble residues, plant uptake, and drift), while degradation studies primarily examine chemical and biological transformation processes(4). A good field dissipation study should provide information on the vertical transport of the pesticide in the field.

The method of application is very important for physical transport considerations(2). For example, pesticide sprayed onto a developing crop canopy has the potential to drift from the site of application or be intercepted by the plant before a portion of the application reaches the soil. Soil samples taken immediately after application are important when the pesticide is applied in this manner in order to estimate the amount that reached the soil and became available for other dissipation processes. This initial amount of pesticide reaching the soil from application is known as the "source term." The source term can be assumed to be equal to the application rate when the pesticide is sprayed onto bare soil, unless the application is made from some distance from the bare soil (i.e., from an airplane) such that drift processes can transport residues from the site of application. The source term is 100 percent of application when the pesticide is either injected or incorporated. However, these methods of application can result in large spatial variation in residues and care must be taken when interpreting soil core results(2).

Physical processes which influence the dissipation of pesticide residues following application include volatilization, plant uptake, runoff and erosion, and diffusion and mass transport of residues in the soil and water(5,6,7). Volatilization refers to the gaseous loss of residues. Residues at or near the surface are most susceptible to volatilization, and moist conditions

increase this process. Although the volatilization rate generally is proportional to the vapor pressure of a pesticide, the vapor pressure alone is not a reliable predictor of the amount of pesticide that will be volatilized. Other properties of the chemical, especially water solubility, are correlated with volatilization rates. Volatilization is usually a very minor mode of pesticide dissipation if vapor pressure is less than 10^{-7} torr, water solubility is more than a few ppm, and the molecular weight is less than a few hundred(8). The importance of plants in pesticide dissipation varies with the type of pesticide and timing of application. For pesticides which are foliarly applied, a large fraction of the applied material is intercepted by the foliage and losses of pesticide due to photodecomposition and volatilization may be greater than when the pesticide is soil applied. Dissipation via plant uptake is low, and considered insignificant in comparison to other dissipation processes(9). Most often, plant uptake is lumped into general "soil degradation" estimates.

Runoff and erosion refer to the overland transport of solubilized residues or residues adsorbed to soil particles suspended in runoff water. Nearly all dissipation resulting from runoff occurs with pesticides within 1 or 2 cm of the soil surface. Therefore, injected, incorporated, or leached pesticide is generally unavailable to runoff(7). Pesticides applied below the surface may be more extensively leached since dissipation by the aforementioned processes is reduced and microbial degradation is usually reduced with greater depths in the soil profile.

Whether a pesticide will leach, runoff, or be lost via erosion is dependent upon both field and pesticide properties(5,10). Pesticides which have a low solubility and a high adsorption partition coefficient will tend to remain where they are applied, with generally a small percentage of loss possible (< 5% of application) on eroded soil. (K in mL/g is defined as C_s/C_w, where C_s is the concentration of solute (pesticide) adsorbed on the soil in ug/g and C_w is the equilibrium solution concentration in ug/mL in a soil-water complex). A more specific definition for the adsorption partition coefficient often used is K_d, which is the value of K when C_w equals 1 ug/mL. Pesticides with a high solubility and low K_d will move more easily in water, and are subject to more leaching and surface runoff.

Cohen et al.(11) listed the following pesticide properties which they found characteristic of some pesticides known to leach to ground water:

- Water solubility greater than 30 ppm;
- K_d less than 5.0, usually less than 1.0 or 2.0;
- K_{oc} (organic carbon partition coefficient) less than 300 to 500;
- Speciation - negatively charged (fully or partially) at ambient pH;

- o Hydrolysis half-life greater than about 25 weeks;
- o Photolysis half-life greater than about 1 week; and
- o Soil half-life greater than about 2 to 3 weeks.

These criteria were derived from an examination of the available environmental chemistry data on the pesticides alachlor, aldicarb (including sulfoxide and sulfone degradates), atrazine, bromacil, carbofuran, DBCP (1,2-dibromo-3-chloropropane), DCPA (dimethyl tetrachloroterephthalate), 1,2-dichloropropane, dinoseb, EDB (1,2-dibromoethane), oxamyl, and simazine. Cohen et al. set their criteria such that these pesticides, all of which were found in ground water at the time, each met most or all of them.

At this time, a larger number of pesticides have been detected in ground water. An examination of the larger data base, now available on the environmental chemistry of these pesticides detected in ground water, indicates that these criteria when used individually are poor predictors of potential groundwater contamination. For example, the solubility of the commonly used triazine herbicides varies widely, from 3 to 160 ppm. Triazine compounds have been found in ground water including those with solubilities lower than 30 ppm.

Perhaps the most important criteria used by Cohen et al. in examining leaching potential were the soil persistence and soil adsorption measurements. A pesticide must be sufficiently stable in the soil environment (persistent) and available for hydrologic transport (mobile) below the zone of active microbial degradation. Movement of pesticide residues to greater than or equal to 90 cm is considered a field indicator of a pesticide's potential to reach shallow ground water.

The rate of dissipation of pesticide residues by surface runoff is related to the same chemical characteristics. Whether a pesticide runs off or leaches is a function of formulation, application method, and soil and climatic factors. Factors which result in storm water leaching through the profile rather than running off the field include: "sandy" soil, low water holding capacity, little slope (< 2%), and a dense crop or plant residue cover. The reverse conditions (heavy clay soil, bare soil conditions, etc.) favor water running off the field. In general, storm events near the time of application are most likely to cause significant dissipation of residues via runoff. Residues will dissipate, adsorb and/or leach with time so that later storms will not have any residue available for transport in the top few centimeters. In the same way, recharge events near the time of application are most critical for leaching pesticides, since they may transport the pesticide below the zone of active microbial decay(7).

Numerous factors are known to influence degradation of pesticides in the soil environment, including the chemical nature

of the pesticide in combination with environmental factors. Laboratory studies (anaerobic and aerobic soil metabolism, hydrolysis, photolysis, etc.) help define the chemical reactivity of the pesticide and the rate of reaction under different conditions. Environmental factors of importance include soil pH, organic matter content, soil moisture, soil temperature, cation exchange capacity, and aeration(5). Since environmental conditions vary in both time and space, rates of degradation in the field also vary widely, being either slower or quicker than what is measured in the laboratory.

Under normal field conditions, aerobic microbes are predominantly responsible for the degradation of pesticide residues within the root zone (the few feet of soil below the surface). Under conditions of saturation (i.e., during flooding), however, the oxygen supply may be consumed and anaerobic organisms take precedence(12). In this condition, the rate of degradation may be similar to laboratory-determined anaerobic degradation. Additionally, if a pesticide shows a tendency to photodegrade, and the pesticide is applied to the canopy surface or to a bare soil surface, then photochemical degradation can become the major mode of degradation.

Microorganisms, including heterotrophic bacteria, actinomycetes and fungi, and obligate and facultative photoautotrophic algae, comprise up to 80 percent of the living biomass in soil(13). Microbial populations are most concentrated in the upper few centimeters of soil and decline with depth in parallel with the decline in soil organic matter. Most pesticides degrade more slowly with increasing depth in the soil, presumbly largely because of decreased microbial metabolism. This does not necessarily mean, however, that microbial degradation of pesticides below the A or B soil horizon is inconsequential. Direct microscopic observation of soils provides evidence that many slow-growing organisms exist which cannot be cultured and studied further by traditional techniques, and which may be quite different in their metabolic characteristics from those organisms which have been identified. It is possible that some microorganisms existing below the root zone are more efficent utilizers of some pesticides as carbon energy sources and therefore substantially contribute to the degradation of these compounds even though they have a slow metabolic rate. Microbial degradation of pesticides will depend on what kind of organisms are present under the field conditions and the ability of these organisms to adapt to the chemical. In general, high organic matter, moist conditions (60 to 80 percent of the field capacity) and warm temperatures are favorable for microbes and enhance the microbial degradation of the pesticide. Other factors which influence microbial degradation include pH and cation exchange capacity. The reader is directed to the Standard Evaluation Procedures for Aerobic Soil Metabolism and Anaerobic Soil Metabolism for further information on the microbial degradation of pesticides.

Many pesticides are partially degraded in soil by nonbiological processes and some reactions can be brought about either by microbial enzymes or strictly by chemical reactions. Usually these two processes work in conjunction(14,15). The most complex process by which pesticides are degraded in soils involves microbial utilization of the pesticide as an energy source(16). It appears, however, that microbial degradation of most organic chemicals at low concentrations applied to soil occurs primarily via co-metabolism by soil organisms using soil organic matter as their main source of energy(16).

The method of application and the formulation can also affect the degradation in soil. For example, incorporation into soil can reduce volatilization (a physical process) as well as photodegradation (a chemical process). Pesticide formulations include dusts, wettable powders, granules, microcapsules, seed dressings, emulsions, miscible liquids, and solutions. In general, the more surface area available for decay processes, the more rapid will be the rate of degradation. The use of granules usually increases the persistence of pesticides, because the pesticide only becomes slowly available for microbial degradation, volatilization, etc. Emulsions tend to be more persistent as well. Wettable powders and dusts have the most surface area, and hence have the tendency to degrade the quickest of all formulations(17).

APPENDIX 2

Information to be Included in the Registrant's Report

Section 164-1 in the Subdivision N Guidelines describes the short-term field dissipation study and gives a protocol for conducting this study(1). Also, Section 160-5 in the Subdivision N Guidelines describes general reporting and evaluation requirements for this study(1).

A. Information to be Included

1. Dates on which the study began and ended;

2. Name and address of the laboratory or institution performing the test;

3. Location where the test was performed;

4. Names of the principal investigators;

5. Signatures of each of the senior personnel responsible for the study;

6. Certification by the registrant that the report is a complete and unaltered copy of the report provided by the testing facility;

7. The report should reference or identify the test substance, formulation statement, formulation category, and include the chemical name and purity of active ingredient, molecular structure, manufacturer and lot and sample number(s) (including physical state, solubility in water, vapor pressure, and pH) if not reported elsewhere;

8. Description of the test sites including soil characteristics (as a function of depth), the approximate water table location, area and field slope, previous pesticide/crop history;

9. Weather data on a daily basis including air temperature, precipitation (rain and snow), irrigation water, and soil temperature on an infrequent basis;

10. A detailed report in tabular form of the residue data from the treated soil (usually expressed as ppmW). Graphs are often included to expand on the data given in tabular form; and

11. A complete discussion of the results of the study which should include a discussion of the following:

a. Percent recovery for the analytical method (A);

b. Dissipation rate and half-life estimate of the parent, including regression analysis to indicate how well the dissipation rate is described by a first-order model;

c. Rate of formation and decline of the degradation products;

d. Identity of residues occurring at levels equal to or greater than 0.01 ppm or 10 percent of the application rate, whichever is lower. This is not dependent upon the toxicological significance of the pesticide residues;

e. Residue decline curves; and

f. Vertical mobility of parent compound and degradation products.

B. Detailed Discussion

1. The Test Substance

The test substance must be a typical end-use product. The test substance must also be a product whose formulation is typical of the formulation category to which the product belongs.

If the applicant's product is a manufacturing-use product that legally could be used to make an end-use product for which terrestrial field dissipation data are required, the test substance must be a product representative of the major formulation category which includes that end-use product. (If the manufacturing-use product is usually formulated into end-use products comprising two or more major formulation categories, a separate study must be performed with a typical end-use product for each such category.)

The pesticide product shall be applied at the maximum proposed use rate utilizing the same application method(s) as stated on the label.

2. The Test Sites

Field dissipation studies should be conducted in at least two different sites in the United States which are representative of the areas where the pesticide is expected to be used. For restricted use patterns where only one typical area is involved, data from two similar sites are needed. Studies at additional locations may be needed if the product is intended for a terrestrial crop use, and the sites of application vary appreciably in

climate or other pertinent characteristics. Therefore, a sufficient number of field dissipation test sites will be necessary as needed to represent all different uses. For each representative test site, a control and a cropped plot will be needed. The cropped plot should be treated with all applicable agricultural practices, e.g., irrigation, fertilizer, etc. In situations where a dense crop cover exists, and normal application procedures result in an insufficient amount of pesticide reaching the soil, a study using a bare soil plot may be necessary to determine the half-life of a parent compound and the patterns of formation and decline of degradates. Test sites which have not received prior pesticide application of the test pesticide are preferred. If the soil has received prior treatment of the same or similar type of compound, then the microbial enrichment or adaptation to that type of compound may have occurred. Subsequent pesticide applications may then degrade more rapidly(18).

The location of the test sites, slope, field area, location of water table, and complete information on the soil properties (textural characterization of soil, pH, and organic matter as a function of depth) should be provided.

A rain gauge should be installed as an integral part of every test site to determine if supplemental irrigation will be needed as the study progresses. Monthly rainfall averages based on 10-, 20-, or 40-year sets of data should be used to determine, if in any given month of the study, supplemental irrigation is needed to bring the natural rainfall up to the expected monthly average.

3. Test Procedures

a. Application

The test plots are prepared and maintained for the intended crop and/or noncrop uses in the same manner as for ordinary practices. The test substance should be applied using the method of application stated in the directions for use on the product label and at the highest rate recommended.

b. Sampling Scheme

The timing of sampling and number of sampling dates should be adequate to describe the degradation of the pesticide and the pattern of formation and decline of the degradates.

- Pesticides which are persistent and immobile need fewer sampling dates than pesticides which degrade quickly or are mobile. An appropriate sampling schedule for persistent and immobile pesticides (soil metabolism half-lives of 6 months to 1 year) would be monthly for 6 months near the beginning of the study, then bimonthly until

12 months, and quarterly until the termination of the study. For mobile and less persistent pesticides (half-lives of greater than 1 week to 6 months) sampling at weekly intervals for a month or more following application, and then biweekly for several months, then monthly sampling until the pesticide has dissipated, may be appropriate. The sampling schedule can be tailored to suit the degradation rate of the pesticide. The sampling schedule should be described and explained in a protocol prior to study initiation.

- For a pesticide with a very short half-life, less than 1 week, the sampling scheme may include samples on day 1, 3, 5, and then sampling emphasis should be directed toward the major degradate(s).

c. Number and Compositing of Soil Samples

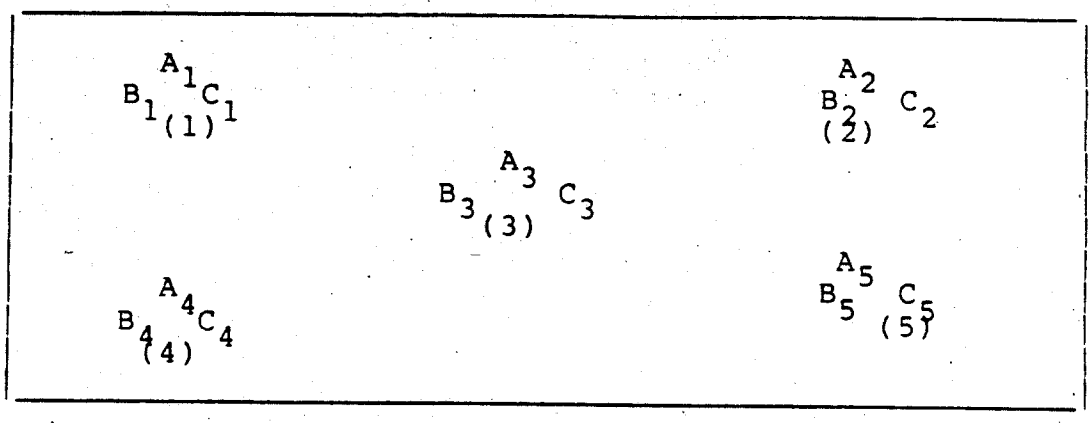
A study by Smith et al. suggests that 15 to 20 soil cores taken per sampling interval per test site will be adequate to determine pesticide residue concentrations, with an expected coefficient of variation for those residues of 50 to 100 percent, with a standard deviation (relative error) of ± 50 percent around the mean(19,20).

- For a small field plot approximately 15 meters square (225 m^2) a minimum of 15 soil cores per field plot (or application site) per sampling interval after pretreatment per sampling depth increment must be taken. A one time sampling of 15 soil cores is recommended at pretreatment.

- For a field plot as typically used in field dissipation studies, 15 soil cores per sampling interval per 15 cm depth increment are adequate to characterize the pesticide residues in the field. Individual depth increments from these 15 cores may be composited to a smaller subset of samples for analysis.

  For example, for each depth increment, three composite samples consisting of five cores each are acceptable. However, all cores should not be composited to one sample for analysis. The Agency finds it necessary to have some idea of the variation in the concentrations of pesticide residues in the field for determining a half-life range.

Samples may be composited as follows: All A cores (A_1, A_2, A_3, etc.) and all B cores (B_1, B_2, B_3, etc.) and all C cores (C_1, C_2, C_3, etc.) are pooled, homogenized and subsamples analyzed. A minimum of three composited samples must be available for analysis in any plot for any time increment. The figure below is illustrative; other sample collection schemes are possible.



d. Soil Sampling Depths

Soil from the test areas should be sampled following treatment for the purpose of ascertaining the extent of pesticide dissipation.

Preapplication Sampling

- Soil cores should be taken to a minimum depth of 90 cm. (Modifications may apply on a case-by-case basis. All modifications must be detailed in an approved protocol prior to study initiation.)

- Soil samples serving as test controls should be obtained from the intended application sites immediately prior to application of the test substance and, if possible, from adjacent untreated areas to check for any background residues of pesticide in the soil. A single pretreatment sample consisting of 15 soil cores each taken to 90 cm should be taken and analyzed from the intended application sites to establish the presence or absence of residues, and for soil characterization down to 90 cm before study initiation. The 15 soil cores may be composited in increments greater than 15 cm down to 1 sample for analysis.

Postapplication Sampling

- Samples must be taken immediately following each application. Therefore, when multiple applications are made, immediate postapplication samples should be taken after every application. Depending on the length of time between application intervals, the exact sampling depth and schedule for immediate postapplication samples may be negotiated. Samples taken immediately postapplication should be sampled to 15 to 30 cm. A shallower sampling depth is considered adequate immediately after application, as long as no significant rainfall or irrigation events have occurred between the application and the sampling. Immediate postapplication samples should be taken the day of the application (day zero). However, if the pesticide is soil-incorporated beneath 15 to 30 cm, the immediate postapplication sample must be taken to the depth of incorporation. Initial shallower sampling may reduce the possibility of contaminating deeper soil layers during the sampling process with high levels of pesticide residues.

- For all samples collected after the immediate postapplication samples, soil samples will be consistently taken to a depth of 90 cm. The soil cores will be divided or taken in the following increments: 0 to 15 cm (plow/disc depth) and then in additional 15 cm increments to a minimum depth of 90 cm for each sampling interval.

e. Field Study Design

The use of a grid or regularly-spaced pattern to define possible sampling points within a test plot is recommended. The actual grid points selected may be chosen randomly at the center of grid sections, at grid intersection points, or at opposite corners of grid sections. Instructions on setting up regularly-spaced sampling patterns using subplots within a field and collecting cores within the subplots for compositing are available in the open literature(20,21). Random number routines may be used to select sampling points(22).

f. Analysis Regime

- The single pretreatment sample consisting of 15 soil cores collected before pesticide application will be analyzed throughout the 90 cm depth to establish the background conditions for the

field plots and to characterize the soil profile. The one time sampling is necessary to determine the presence or absence of residues and establish background conditions.

- Day zero samples taken immediately after final pesticide application should be collected and analyzed to a 15 to 30 cm depth to establish day zero conditions in the field. When multiple applications are made, all immediate post-application samples prior to the final application, must be sampled and analyzed to a 15 to 30 cm depth. Sampling and analysis depths should be discussed in a protocol for Agency approval prior to study initiation. (If the pesticide is incorporated into the soil, soils must be sampled to a depth which allows for the injection depth.)

- All samples taken after the immediate postapplication sample must be collected down to 90 cm in 15 cm increments, and each set of 15 cm increments may be composited into subgroups for a minimum of three composites for analysis as previously explained. Increments may be frozen and stored and analyzed sequentially as residues are detected in successively deeper soil increments. Increments must be analyzed to a minimum depth of 30 cm (two successive 0 to 15 cm increments) below the deepest increment in which residues are found.

- The parent and major degradates as identified from aerobic soil metabolism studies should be tracked in the field dissipation study. Any degradate identified in the aerobic soil metabolism study at greater than or equal to 0.01 ppm (10 ppb) or 10 percent of the application rate, whichever is lower, should be tracked in the field dissipation studies. The 0.01 ppm and 10 percent of application rate levels are intended as goals to be met or surpassed. A registrant will not be penalized for not being able to meet the 0.01 ppm goal because of limitations with the analytical method. However, the registrant is expected to try to reach these goals. There are new compounds in use that are applied at use rates less than 10 ppb. Because of possible toxic effects on humans and the environment, the ability to detect these low use compounds and their degradates becomes necessary.

- Important evidence that sampling has not gone deep enough include:

  - Significant concentrations at the lowest depth of sampling; and

  - A significant amount of time between sampling dates (≥ 1 month) and prior information indicating that the pesticide and/or its degradation products may be leachers.

Soil samples should be analyzed as soon as possible after being taken. If samples are stored before extraction and analysis, it must be shown that the pesticide residues will not degrade under the storage conditions. Freezing the soil samples at or lower than 0 degrees C (preferably -18 degrees C) as soon as possible after collection until analysis is an acceptable means of storage. (A temperature of 0 degrees C) it is given as a set standard unless the registrant can show that there was no degradation at a higher temperature through a storage stability study. Storage stability must be determined using pesticide-fortified samples stored for as long as test samples are stored before residue analysis (see below).

g. Storage Stability

It is recommended that a number of soil samples from the various depth increments be field spiked with the pesticide in order to ascertain the storage stability of the pesticide and degradates during transport for the longest storage period.

A storage stability study is required as a part of the field dissipation studies. Field soil should be spiked in the lab and kept under storage conditions identical to those used for the field samples. The storage stability study should indicate if the pesticide is degrading during storage. Periodically, a storage sample should be removed and analyzed for this purpose. Storage stability samples should be kept for analysis for as long a period as the field samples are held under storage prior to analysis.

h. Test Duration

Reaction kinetics of dissipation of pesticides are concerned primarily with the decline in concentration of the pesticide over time(5,22,23). However, the Guidelines(1) also require information on the degradation products. Therefore, residue data should be collected until patterns of decline of the active ingredient of the test substance and patterns of formation and decline of degradation products are established in soil or to the time periods specified below, whichever comes first:

- Field and vegetable crop uses: 18 months;

- o Orchard crop and pastureland uses: 12 months;
- o Domestic outdoor, park, ornamental, and turf uses: 4 months; and
- o Rights-of-way, shelter belts, and related uses: 2 months.

i. Triggering Ground-Water Monitoring Studies

If the pesticide is shown to have a potential of moving into or is detected in the 75 to 90 cm increment, a ground-water monitoring study may be required. The following points should be considered when assessing the significance of any finding of residues at 75 to 90 cm:

1) Is the detection consistent with trends observed at earlier times in the experiment and with behavior exhibited at other sites (after allowing for differences in soil type and precipitation intensity)?

2) Is the apparent mobility consistent with laboratory measurements of the soil-water partition coefficient for the pesticide on similar soils?

3) Can sample contamination (as a result of coring or analytical procedures) be eliminated as a potential cause of detection?

The toxicological significance of pesticide residues present at the 75 to 90 cm depth in the soil profile will not play a role in determining if further small-scale prospective or retrospective ground-water monitoring studies are warranted.

j. Triggering Surface-Water Monitoring Studies

If the pesticide is shown to have a potential of moving from the site of application into surface waters, a surface-water monitoring study may be required. [Note: the exact criteria for surface-water monitoring studies have not been established.]

APPENDIX 3

Analytical Data to be Submitted by the Registrant

A. Analytical Procedures

1. Analytical Methods

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

a. Name (and signature), title, organization, address and telephone number of the person(s) responsible for the planning and supervision/monitoring and laboratory procedures/analyses;

b. Analytical method(s) title/designation/date;

c. Source of analytical method(s) [e.g., Pesticide Analytical Manual (PAM), Vol. II, scientific literature, company reports);

d. Principles of the analytical procedure (description);

e. Copy of the analytical method(s) detailing in stepwise fashion the procedures (extraction, clean-up, derivatization, determination, calculation of the magnitude of the residue);

f. Reagents or procedural steps requiring special precautions (to avoid safety or health hazards, explain);

g. Identification of the chemical species determined;

h. Describe modifications, if any, of the analytical method(s);

i. Extraction efficiency;

j. Instrumentation [make/model, type/specificity of detectors, column(s) packing materials, size, gas carrier, flow rates, temperatures, limit of detection and sensitivity, calibration procedures, etc.;

k. Interference(s), if any;

l. Confirmatory techniques [e.g., other column packings, detectors, mass spectrometry, nmr, etc.];

m. Date(s) of sample taking, extraction and residue analyses;

n. Sample identification [coding and labeling information];

o. 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 found of "total" residues and of individual components if of special concern, range of residue values, representative chromatograms, spectra of control and treated samples)];

p. Statistical treatments of raw data;

q. Other additional information the registrant/researcher considers appropriate and relevant to provide a complete and thorough description of residue analytical methodology and the means of calculating the residue results.

B. Method Validation

A full description of the method recovery validation procedures must be submitted and include information on the following:

1. The 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 tests applied, 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 data results; and

6. Conclusions drawn from the data results.

C. Quality Assurance

A complete description of the measures taken to ensure the integrity of the test and analytical protocols should include information on the following:

1. Logbooks and/or recordkeeping procedures; representative instrument printouts (chromatograms, spectra, 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 modification(s) 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; and

9. Good laboratory practices in handling the test substance(s).

D. Residue Analysis

1. Extraction of Soil Residues

Soil samples from each depth increment should be subdivided and extracted with appropriate solvents, filtered, and reextracted if necessary. Exhaustive extraction methods are sometimes necessary. The reviewer should determine that an appropriate extracting solvent was used in the study. The reader is directed to Chesters, et al.(24) for a general overview on the subject of pesticide extraction and analysis of soil without elaboration on specific procedures and to Hance and McKone for specific procedures for herbicides(25). Extractable residues are considered as those being immediately available for uptake by rotational crops, exposure to nontarget organisms, and for leaching into the ground water. They are also available for further degradation.

2. Qualitative Identification of the Extracted Residues

Thin-layer chromatography (TLC) of extracted residues with cochromatography of known standards (identified as degradation products from the laboratory soil metabolism studies), preferably in more than two solvent systems, is adequate for tentative qualitative identification. Other spectroscopical analysis such as gas chromatography/mass spectrometry (GC/MS) may be needed for positive identification.

3. Quantitative Analysis of Residues

Quantitative analysis of the extracted residues can be done either by GC or high performance liquid chromatography (HPLC). All analytical methods must be examined for their specificity, sensitivity, and recovery.

E. Persistence and Mobility

1. Field Mobility Determination

Based on the residue analysis in soil increments, the extent of leaching and potential for ground water contamination of the test material or its degradation product(s) is examined. A qualitative judgment can be made on the mobility of the parent and degradation products based on criteria described earlier (solubility, K_d, etc.) and this judgment is compared with results of the field dissipation study, i.e., how much pesticide leached below the treated zone, how fast it leached, and how far it leached? Movement of residues to the 75-90 cm depth is an immediate indicator of potential to reach shallow ground water in the absence of other data. Field data which indicate leaching in combination with laboratory data indicating mobility and persistence are sufficient grounds to conclude that the pesticide and/or its degradation products have the potential to contaminate ground water.

2. Half-Life Estimation

Although dissipation of pesticides under field conditions is not only due to loss by degradation but also due to loss by other means (e.g., volatilization, runoff, etc.), first-order degradation rate equations are useful for describing approximately the rate of dissipation of pesticides. Caution must be used, however, since dissipation can be misunderstood and thought of as disappearance. In fact, the disappearance of residues from soil can mean appearance in another media, such as ground or surface water or air.

As mentioned earlier, the reaction kinetics of pesticide degradation in soil are concerned primarily with the decline in concentration of the pesticide with time. For pesticides that are not strongly sorbed to soil, rates of degradation often approach first-order kinetics at low concentrations and zero-order at high concentrations. At field application rates, the degradation rates of most pesticides approach first-order kinetics. That is, the concentration of the pesticide in soil (which is usually low compared to the other reacting materials in soil) determines the rate of the reaction(26). However, rates tend to decrease with time more than would be expected which suggest adsorptive forces are still active in the soil(16). The rate of loss is proportional to its concentration in the soil and can be expressed by the equation:

$$-\frac{dc}{dt} = Kc^n \qquad (1)$$

where c = the concentration of the pesticide, K = the rate constant, t = time, and n is the order of the reaction. For first-order kinetics, n = 1, therefore,

$$-\frac{dc}{dt} = Kc \qquad (2)$$

where c is the amount of pesticide present in soil at time t. Here, the first-order reaction means that the disappearance of the pesticide is proportional to the amount left in the soil.

The dissipation of most pesticides from soils can be considered as following a first-order reaction at least over a portion of the degradation curve (5,19,24). It is reported that, overall, the reaction kinetics involved in decomposition of pesticides follow mostly the zero-, first-, and second-order reaction systems (26). However, it is doubtful that any one single rate equation will ever be found which is applicable to all or most pesticides in soil (5). Data summarized show that the relationships imply that the proportion of the chemical degraded with time decreases as the concentration of the chemical decreases (24). The rate at which the last traces of a chemical disappears can be very slow (27).

With these caveats, the first-order rate of reaction can be determined as:

$$K = (-\ln(c/c_o))/t \qquad (3)$$

where c = soil concentration at time t, c_o = initial concentration immediately following application, t = time in days.

The half-life, $t_{1/2}$, that is, when C = Co/2, can then easily be determined as:

$$t_{1/2} = 0.693/K \qquad (4)$$

where K = reaction rate, day^{-1}, as determined by Equation (4).

The reviewer should use judgment when applying this equation, since each date on which soil residues were determined would imply a different half-life. Computer programs are available which fit all the residue data to a first-order rate equation. If possible, these should be used to determine a reaction rate which best fits all the data available.

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