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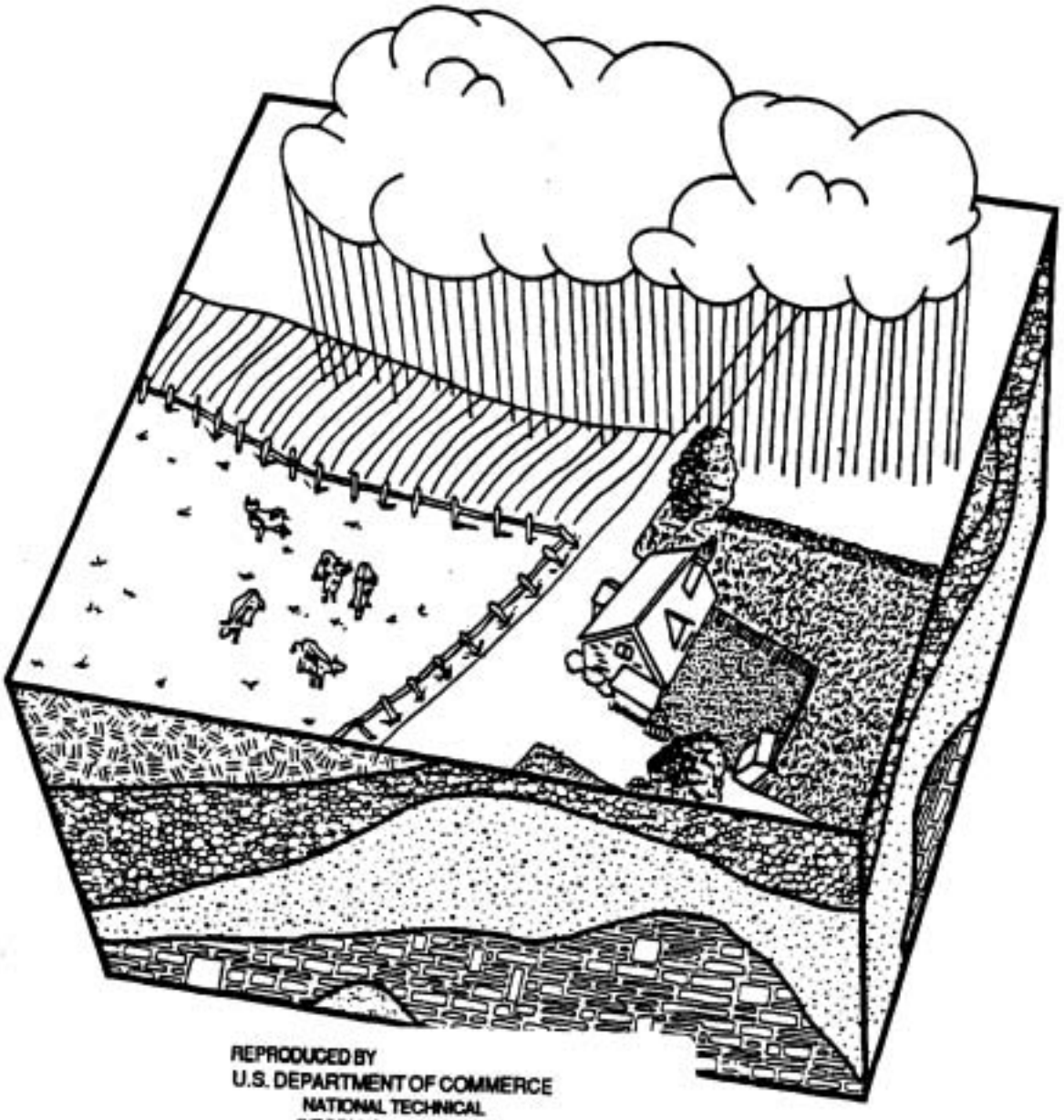
Environmental Fate and Effects Division Standard Evaluation Procedure

Terrestrial Field Dissipation



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16. Abstract (Limit: 200 words)

This Standard Evaluation Procedure (SEP) describes the procedures used by EPA to evaluate studies on the dissipation and movement of pesticide residues in the field. The SEP provides a data reviewer with important guidance in determining the acceptability of a terrestrial field dissipation study. Details of the proper study design are outlined and the relevance of each aspect of the study design pertin to pesticide degradation is explained. This information is to be used by the reviewe as guidance in determining study acceptability. The document outlines the general theory of pesticide degradation and provides an overview of the methods used for calculating pesticide degradation rates and half-lives. Important points to consider in assessing the data and in drawing a conclusion about the dissipation and movement of pesticide residues in the field are discussed.

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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;

- Hydrolysis half-life greater than about 25 weeks;
- Photolysis half-life greater than about 1 week; and
- 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

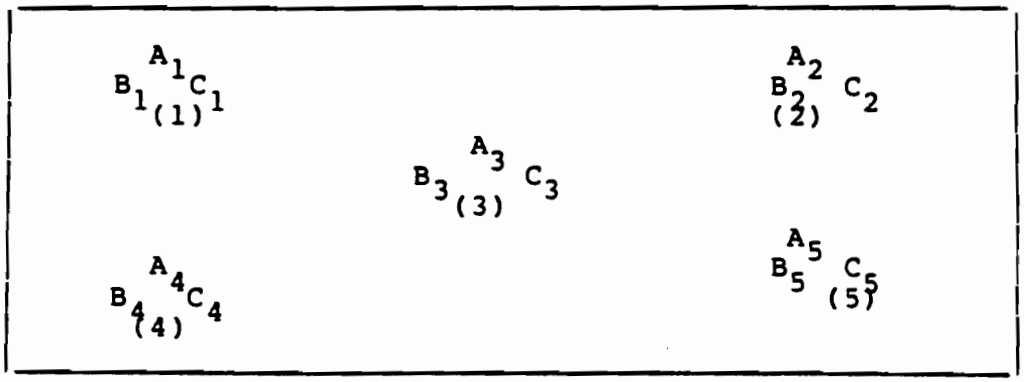
A study by Smith et al. suggests that 15 to 20 soil cores taken per sampling interval per test site will be adequate to determine pesticide residue concentrations, with an expected coefficient of variation for those residues of 50 to 100 percent, with a standard deviation (relative error) of ± 50 percent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

- o 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:

- o Field and vegetable crop uses: 18 months;

- Orchard crop and pastureland uses: 12 months;
- Domestic outdoor, park, ornamental, and turf uses: 4 months; and
- 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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HAZARD EVALUATION DIVISION

STANDARD EVALUATION PROCEDURE

SOIL COLUMN LEACHING STUDIES

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16. Abstract (Limit: 200 words)

The Standard Evaluation Procedure for the Soil Column Leaching Studies is a guidance document primarily intended for Agency reviewers and the regulated industry who evaluate toxicologic effects data specified in 40 CFR Part 158.124. The SEP is also intended to provide information to the general public indicating how the Agency evaluates these types of studies. As such, it is designed to supplement Subdivision N of the Pesticide Assessment Guidelines - Chemistry: Environmental Fate.

The SEP for Soil Column Leaching Studies is only one of a number of SEP's published by the National Technical Information Service as a supplement to Subdivision N of the Pesticide Assessment Guidelines.

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STANDARD EVALUATION PROCEDURE

PREAMBLE

This Standard Evaluation Procedure (SEP) is one of a set of guidance documents which explain the procedures used to evaluate environmental and human health effects data submitted to the Office of Pesticide Programs. The SEPs are designed to ensure comprehensive and consistent treatment of major scientific topics in these reviews and to provide interpretive policy guidance where appropriate. The Standard Evaluation Procedures will be used in conjunction with the appropriate Pesticide Assessment Guidelines and other Agency Guidelines. While the documents were developed to explain specifically the principles of scientific evaluation within the Office of Pesticide Programs, they may also be used by other offices in the Agency in the evaluation of studies and scientific data. The Standard Evaluation Procedures will also serve as valuable internal reference documents and will inform the public and regulated community of important considerations in the evaluation of test data for determining chemical hazards. I believe the SEPs will improve both the quality of science within EPA and, in conjunction with the Pesticide Assessment Guidelines, will lead to more effective use of both public and private resources.

John W. Melone

John W. Melone, Director
Hazard Evaluation Division

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SOIL COLUMN LEACHING STUDIES

I. INTRODUCTION

A. Objective of the Standard Evaluation Procedure

This Standard Evaluation Procedure (SEP) is to be used as an aid for Exposure Assessment Branch data reviewers in their evaluations of the soil column leaching studies submitted by registrants in support of pesticide registration.

Leaching and sorption/desorption tests are required by 40 CFR §158.130 in support of registration of each active ingredient in manufacturing-use products and in the pesticide end-use products formulated and intended for domestic outdoor use, greenhouse use, terrestrial noncrop use, forestry use, aquatic use, and aquatic uses involving direct discharge of treated water into outdoor aquatic sites.

Section 163-1 in the Subdivision N Guidelines[1] describes this study and provides a protocol for conducting it. Subdivision N Guidelines list options available for fulfilling this requirement for terrestrial noncrop uses, orchard crop uses, field crops, field-vegetable crop uses, and forestry uses. The mobility of the test substance and its degradation products in soil may be assessed by soil thin layer chromatography (soil TLC), soil column, or batch equilibrium (adsorption/desorption) testing.

When considered with other data required by 40 CFR §158.130, data on the mobility of pesticides are used by the reviewer to determine (1) the leaching potential of pesticides and their degradates through the soil profile at terrestrial sites, and (2) the potential mobility of pesticides and their degradation products to and dispersion in aquatic sites. Such movement may result in loss of usable land and water resources to man due to contamination of groundwater supplies, or cause habitat loss to wildlife.

B. General Theory of Leaching

The reviewer should be acquainted with the soil-water processes in the soil influencing pesticide mobility. The reviewer is directed to Appendix 1 for a brief description of these processes.

II. THE SUBMITTED STUDY

A. Purpose

The soil column leaching tests provide information on

(1) the leaching potential of pesticides and their degradates through the soil profile at terrestrial sites, and (2) the movement of pesticides and their degradates to and dispersion in aquatic sites. The soil column leaching study provides an estimate of pesticide mobility in soil for both the test chemical (parent compound) and aged residues.* The leaching test with the parent compound isolates pesticide mobility from many of the interactions of chemical and biological transformations, plant uptake, variations in soil moisture and temperature, etc..[2] All of these can influence the amount and depth of the chemical leached in the natural environment.[2] However, the aged residue leaching test provides for the assessment of the leaching potential of the soil degradation products resulting from the chemical and biological transformation of the parent compound.

Information gained from the leaching test can be applied to the design and conduct of the field dissipation study. Results obtained will be an estimate of field movement,[3] and will alert the registrant as to the depth at which soil samples will have to be taken.

B. Study Design

The registrant's report should contain (1) a stated goal of the study and (2) sufficient information on the test protocol (compound purity and type of compound used, complete characterization of soils, dose-level and method used) 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 study).

Types of information that the registrant should include in the report are 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 §158.130. Normally, the study is required to support registratrion of each active ingredient of an end-use product intended for domestic outdoor use, greenhouse use, terrestrial noncrop and crop use, and forestry use. Such data are also required to support each application for registration of a manufacturing-use product which may legally be used to make such an end-use product.

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* Aged residues are those degradation products formed in soil after the test chemical has been aged 30 days under aerobic conditions.

B. Read the Report

Reports of soil column leaching studies are first reviewed to determine if the following information is present:

° Is the compound purity, type of compound used and site(s) of radiolabeling (if used) specified? If radioisotopic techniques are used, the test should be conducted individually with the analytical grade for each active ingredient in the product. Complex molecules must be labeled in appropriate sites to allow each major component of the molecule to be monitored. If non-radioisotopic analytical techniques were used, the test should be conducted with the technical or purer grade of each active ingredient in the product.

° Were four different textured soils used? If only one soil type was used, is the pesticide use limited to that soil only? Did one of the soils used have an organic matter content less than or equal to one percent (sand or sandy loam, for example)? Was one of the soils the same as that used in the aerobic soil metabolism testing? For the testing of aged residues, was the soil used the same as that used in the aerobic soil metabolism study?

° Is complete characterization of soils included [pH, moisture capacity, percent organic matter, bulk density, cation exchange capacity, and textural composition (percent sand, silt and clay) and textural class]?

° Was the amount of test substance added to the soil equivalent to the highest recommended label rate for one application of the active ingredient? Is the treatment rate and method of treatment of the soil described? Is the treatment representative of the use rate?

° Are the methods which were used for quantitative and qualitative analyses described?

° Is a material balance reported?

The reviewer should determine if there are data gaps within the study. Failure to furnish all this information may result in rejection of the report. In cases where needed information is missing, the study report should be returned without review but with a detailed list of the deficiencies.

C. Prepare the Data Evaluation Record (DER)

After the reviewer has determined there are no data gaps which would cause the report to be rejected, the reviewer prepares

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

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

c. The material balance aids in determining the validity of the study. Does the report account for all or the major portion (90-95%) of the test chemical applied to the soil? If not, is a rationale presented to explain why not? Does the report account for an excess greater than 105-115% of the amount of chemical applied?

d. Are the quality control measures taken to ensure the integrity of the test described? Were logbooks and record-keeping procedures maintained? Were quality procedures maintained during sampling, storage, and analysis of soil samples? Were good laboratory practices followed? Was the soil used in the aged test maintained in such a manner that viable microbial populations were present?

2. Determine Study Acceptability

Were the stated goals of the study appropriate and clearly defined? Was the study conducted in a scientifically sound manner to accomplish those goals? If so, the reviewer then makes a determination as to the acceptability of the study and considers whether the study, either as it stands alone or in light of other studies (combined testing, surrogate studies, or waivers), supports the requested registration action.

From the information presented, can it be concluded as to whether unaged residues (parent compound) and the degradation products (aged residues) are mobile in soil and thereby have potential to contaminate groundwater? If residues reach surface water, will they associate with the soil or remain in the water phase?

The results of the test should provide an estimate of the mobility of the test material and answer the questions:

° Is the test chemical mobile in soil under the conditions of the test?

° Are soil degradates mobile in soil under the conditions of the test?

° Can the mobility of the test material or its degradates be predicted in the soil under field conditions?

If the study is deficient, a detailed description of the deficiencies and recommendations on how to rectify the deficiencies is prepared and included in the DER.

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

If the reviewer concludes either that (1) the test chemical or its degradates has a potential for groundwater contamination, or (2) there is a potential for dispersal in the aquatic environment, then the Toxicology and/or Ecological Effects Branches are notified.

4. Make Regulatory Determination

Based on the technical evaluation, the reviewer determines whether the study satisfies the data requirement for a mobility study.

A reliable prediction of the potential for ground water contamination is made as the reviewer considers the results of the study in light of the results of other environmental fate studies (hydrolysis, photodegradation, soil metabolism, other mobility studies, field dissipation). Results of other studies (physical chemical data such as vapor pressure or octanol/water partition coefficients, combined testing, surrogate studies) or waivers can also be considered here.

Factors that increase hydraulic conductivity will increase percolation and the potential for pesticide leaching.[3] Coarse textured or well-aggregated soil with high proportions of large pores should be fairly permeable whereas infiltration will be restricted in clay-rich and compacted soils.[3]

In addition to bulk, density, and texture of soils, other characteristics affect the downward movement of pesticides in soil. Adsorption of pesticides to soil is the major factor influencing the movement of the pesticide.[3] A very water soluble compound will not leach if it is irreversible adsorbed and compounds which are very insoluble in water will leach if they are not restricted by adsorption.[4] Soil characteristics which influence adsorption are soil organic matter, amount and type of clay present, field moisture capacity, surface area, soil pH, and cation exchange capacity (CEC).[2, 3, 15, 17]

APPENDIX 1

General Theory

The movement of a pesticide through soil bears on its potential to reach adjacent soil or ground water. Leaching of a pesticide in soil depends on water movement.[3] In some cases, herbicide persistence beyond a normal cropping season is reduced by higher amounts of natural or artificially applied water.[4] In part, this can be attributed to dissipation of the herbicide into lower soil horizons.

Two general processes predominate in such movement, (1) diffusion and (2) mass transfer[2] (Note: Factors influencing movement, e.g., soil characteristics, will be discussed later.). Diffusion is the process by which the pesticide is transported as a result of random molecular motions caused by their thermal energy.[5] Mass transfer (flow) occurs as a result of external forces[5] acting on the pesticide.

Hamaker[6] noted that leaching through soil is a complex phenomenon with at least four elements:

1. "Soil adsorption which determines the underlying pattern;

2. Porous flow and diffusion which produce a dispersion of the chemical;

3. Adsorption dynamics which introduce a factor of hysteresis; and

4. Water infiltration and evaporation which determine the amount of water movement and hence, the observed amount of movement of a chemical."

The theoretical aspects of pesticide transport by soil-water movement have been well described.[7, 8, 9, 10, 11] Generally, pesticides entering the soil are leached in a vertical direction in the soil zone of aeration above the water table[12] with some lateral movement due to diffusion and dispersion. (Lateral movement may occur when the pesticide reaches a profile zone of water saturation and from capillary action near the boundary between dry and wetted soils).[2] [Movement of pesticides at the soil surface may occur by water (run-off) from sheet erosion and wind erosion.]

An equation describing water flow through soil is Darcy's law[5] and is expressed as:

$$v' = -ki \qquad (1)$$

where v' is the volume of water crossing per unit area perpendicular to the flow per unit time, k is the proportionality constant referred to as the hydraulic conductivity, and i represents the driving force which is the hydraulic head gradient. The reviewer is referred to many fine sources available which discuss Darcy's law.[13, 14]

The rate of soil-water infiltration and the magnitude of k depends on the relative distribution of large vs. small soil pores, the presence of abruptly discontinuous soil layers, and the initial soil moisture content.[2] Water will move in the direction of low to high matrix potential, i.e., from wet to dry soil. This explains why water (and dissolved chemicals) can move to the soil surface when a moist soil is drying out.[2]

The distribution of dissolved organic chemicals in soil water, as a function of time and depth, can also be described by chromatographic theory.[3] Here, the two major components of such movement are mass transfer and diffussion. Soil adsorption is the mechanism which is responsible for the pattern of movement of chemicals through soil.[6] Hence, movement downward decreases as adsorption increases. The adsorption of the chemical on the soil causes the moving front of the chemical to lag behind the moving front of the solvent.[6] This lag distance is known as "retardation."

It is noted,[6] however, that this chromatographic pattern is effected by flow through a porous medium which acts both to disperse and retard the chemical ("hydrodynamic dispersion"). Some of the liquid moves a greater distance through a more restricted passage or moves more slowly through smaller passages than that portion taking a more direct path.[6] Other factors effecting the chromatographic pattern include (1) a "frictional" effect (slow release by soil particles) when the chemical cannot get off the soil (desorb) fast enough, and (2) in the field, evapotransporation effects[6] - as the soil dries, there is an upward movement of water and chemical.

The effect of soil water content on diffusion is more complex than mass flow and depends on whether the chemical diffuses mainly in the vapor or solution phase.[9, 10] Movement by diffusion in water will be hindered by increasing bulk density[3] of the soil.

APPENDIX 2

Section 163-1 in the Subdivision N Guidelines describes this study and gives a protocol for conducting it. Also, Section 160-5 describes general reporting and evaluation requirements that should be included.

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. Name 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 identify the test substance and include the chemical name and purity of the active ingredient; molecular structure; manufacturer, and lot and sample number(s) of the test substance(s); and properties of the test substance(s) [including physical state and pH] if not reported elsewhere;

8. Description of the soil source and soil characteristics;

9. A detailed report in tabular form of the test data (Graphs can be included to expand on the data given in tabular form);

10. A complete discussion of the results of the study.

B. Detailed Discussion

1. The Test Substance

The chemical to be tested must be chemically pure. The use of radiolabeled compounds is preferred. Carbon-14 is usually used; ring labeling is preferred to side-chain labeling because the radioactivity is usually less easily removed from the central ring positions. If the molecule is complex and consists of moieties that are easily separated, then radiolabeling in more than one location of the compound may be necessary. In any case, the site of radiolabeling must be defined.

Use of radiolabeled chemicals rather than non-labeled ones allows: (1) the leaching process to be followed at a much lower concentration and (2) easier determination of mass (material) balance. If non-labeled compounds are used, the study must be conducted with the technical or purer grade of the active ingredient(s).

2. The Test Soil

The study should include, at a minimum, four soils, such as sand (agricultural), sandy loam, silt loam, clay, or clay-loam, each having a pH within the range of 4-8. However, if the pesticide is limited to use with one specific soil type, then only one soil may be used, but it should be representative of that specific soil type. At least one of the soils selected should have an organic matter content less than or equal to one percent (A sand or sandy loam soil is preferred.). One of the soils should be the soil used in the aerobic soil metabolism study. A field soil sample should be a subsample from the top layer of the field soil. The soil should be sifted through a 2 mm sieve.[19] Packed columns commonly use soil passing a 2-mm screen.[3] For the aged soil-pesticide test, the soil should be freshly taken from a typical use area or have been maintained in such a manner that it has viable microbial populations present at the time of initiation of the test. The soil should be stored in a clean, chemical-free environment. For the aging test, the pesticide is applied to the soil and incubated aerobically for 30 days before a subsample is taken and added to the top of the column. It is recommended that the incubation be done in a closed container and trapping solutions be used to trap any volatile degradation products formed during the incubation period. It should be aerated.

Information on the soil class, texture, pH, and percent organic matter is necessary to verify that the soil is representative of agricultural soils. If foreign soils are used, such data on soil class, textural classification, and crop use are needed to indicate its similarity to U.S. soils.

3. Test Procedures

a. Study Apparatus

The use of segmented columns (glass or metal) is convenient. The use of machined rings permits later separation and analysis of the individual segments.[3] The column diameter must be at least one inch.[20]

Numerous column methods have been reported.[2] However, the selection of the soil column method will depend on the specific needs of the investigator.

b. Preparation Of The Column

The soil column should be, at a minimum, 30 cm in height, consisting of the prepared soil described above. Two types of soil columns have been classified, "natural" and "handpacked."[18] The "natural" or undisturbed columns have been used rather infrequently. At least two methods for natural column retrieval have been used.[2] A metal column may be driven into the soil and the surrounding soil removed prior to careful removal of the column. Power drills have also been used to obtain the soil cores.[21] In either method, compaction of the core should be avoided.[2] A general problem with both undisturbed and packed columns is edge effects or "channel flow" (preferential solvent flow along the inner column wall). If it occurs, it can result in a somewhat greater apparent mobility of the added chemical than expected.[2]

In the preparation of "handpacked" columns, care must be exercised for uniform packing. Weighed, air-dried, soil is added slowly with column vibration. Soil bulk density should be measured and reported and should be the same for all columns of the same soil (One major weakness of using soil columns to study leaching is the possibility of nonreproducibile results, which can be caused by nonhomogenous packing.[3]). Review techniques on soil column packing are discussed by Weber and Peeper.[18]

The soil column should be pre-wetted and allowed to equilibrate.[20] The column can be eluded while either unsaturated (containing some airfilled voids) or saturated (total pore volume is filled with water). While an unsaturated column would be more typical of flow in the normal unsaturated zone of the upper soil profile[3] (except during heavy rainfall or irrigation), it has been shown that leaching under unsaturated conditions is less effective than under saturated conditions.[6] Therefore, conducting the study under saturated conditions (constant head) is preferred so that a worst case situation will be simulated.

5. The Treatment Rate

The amount of parent pesticide added should correspond to the highest recommended rate for a single application. In the unaged test, the unlabeled or radiolabeled parent pesticide is added uniformly to the top of the soil column via treated soil or in a minimum amount of solvent. In the aged test, a measured portion of the 30-day aged pesticide-soil mixture is placed on an untreated column where the untreated soil is the same as the aged soil. The soil surface should be covered after pesticide addition with a disc of glass-fiber filter paper, sintered glass, or glass wool to minimize disturbance of the soil and uniformily distribute water during leaching.

c. The Study Conditions

To simulate a worst-case, water-saturated condition, the column is eluted with a volume of water equal to 20 inches (50.8 cm) times the cross-sectional area of the column, preferably using 0.01-0.02 N calcium chloride solution.[20] During the test, the solution should be percolated through the column at a rate which maintains a constant head above the soil surface. The reviewer should recognize that this is not representative of field leaching conditions but when the final environmental exposure assessment is made, the conclusion concerning leaching will be tempered by the results of the field dissipation study.

Amounts of eluate used, effluent collected (after drainage has stopped), the 1/3 bar moisture content, and the infiltration rate (in/hr or cm/hr) are to be reported. If the pesticide photodegrades, the study should be done in the dark. If the pesticide is volatile, provision should be made to trap and analyze the volatiles.

If columns of a specific length are used which prevent eluate from percolating through the bottom of the column, then a tracer should be used in the study.[20] This will provide information on how far the water moved through the column in relation to how far the pesticide residues moved through the column.

d. Sample Collection

After leaching, the soil is removed from the column and is sectioned into five or more equal lengths by slicing the soil with a spatula. Each slice is analyzed to detect pesticide residues and their movement.[2] Analysis includes determination of (1) total residue content (parent plus degradation products), and (2) identity of residues. Care should be taken as the soil is extruded from non-segmented columns so that contamination is minimized and so that the column structure is maintained. The leachate solution is analyzed for total radioactive content and the radioactive compounds present are identified.

Soil samples should be analyzed as soon as possible after completion of the test. If samples are stored before analysis, it must be shown that the pesticide residues do not degrade under the storage conditions.

A distribution curve of the test substance and its products in the column should be determined by quantification of the test substance and its degradates in the soil segments and in the leachate.

Note: Currently, the Guidelines[1] state that for the soil column study, values of pesticide distribution relationships (K_d) should be reported for the test substance and its degradates using appropriate equations. The researcher should develop the values. At this time, however, the test will not be considered deficient if this relationship is not included in the test report since the K_d values provided by the equations vary by a factor of two or more.[20] The theoretical aspects of associating the pesticide distribution relationship and K_d have been reported.[2, 6]

APPENDIX 3

Analytical Data To Be Submitted by the Registrant

A. Analytical Procedures

1. Analytical methods

A full description of the analytical method(s) used in all steps of the analytical protocol must be submitted, including the following information:

- Name (and signature), title, organization, address, and telephone number of the person(s) responsible for the planning and supervision/monitoring and laboratory procedures/analyses;
- Analytical method(s) title/designation, date;
- Source of analytical method(s);
- Principles of the analytical procedure;
- The analytical method(s) detailing in step-wise fashion the procedures (extraction, clean-up, determination, calculation of the magnitude of the residue);
- Reagents or procedural steps requiring special precautions (to avoid safety or health hazards, explain);
- Identification of the chemical species determined;
- Modifications, if any, of the analytical methods(s);
- Extraction efficiency;
- 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];
- Interference(s), if any;
- Confirmatory techniques (e.g., other column packings, detectors, etc.);
- Date(s) samples taken, extracted and analyzed;

- Sample identification (coding and labeling information);
- Residue results (raw data, laboratory worksheets, step-wise 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);
- Statistical treatments (of raw data);
- Other (any and all additional information the registrant/researcher considers appropriate and relevant to provide a complete and thorough description of residue analytical methodology and means of calculating the residue results).

B. Method Validation

A full description of the method recovery validation procedures must be submitted and must include information on the following: the recovery level(s) of the test compounds from the soil (substrate) at various fortification level(s) using the residue analytical methodology; a validated sensitivity level; results of the study and any statistical tests applied; a step-wise presentation of the procedure for calculating percent recovery from the raw data; all the data/information necessary to idependently verify the results; summary of the data results; and 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: log books and/or record-keeping procedures, representative instrument printouts (chromatograms, spectra, etc.), sample coding, use of replicate samples and control blanks, use of written and validated analytical methodology for residue analyses, including modification(s) made, skilled laboratory personnel, well-equipped laboratory facility, minimal contamination, calibration and maintenance of instruments; and good laboratory practices in handling the test substance(s).

D. Residue Analyses

Reported results should include:

1. Total Soil Residues (Pre-Extraction)

When ^{14}C labeled parent compound is used, the subsamples of each soil slice will be combusted and $^{14}CO_2$ formed will be

trapped in appropriate solvents.

2. Extractable Soil Residues

Soil is extracted with appropriate solvents, filtered and reextracted if necessary. Exhaustive extraction methods are sometimes necessary when residues are not extracted by gentler means. The reviewer should determine that an appropriate extracting solvent system was used in the study.

3. Non-Extractable Residues (Post-Extraction)

The post-extracted soil is combusted in an oxidizer and the CO_2 formed is trapped in appropriate solvent.

4. Total Leachate Residue

Aliquots of the leachate are analyzed for presence of parent compound and degradation products.

These residue totals make up the material balance. The material balance summed should equal 100% of the amount of the test chemical applied. Thus, the material balance is a factor in determining the validity of the study. Studies wherein the material balance does not account for a large percentage (90-95%) or accounts for greater than 105% to 115% of the amount of test chemical applied may be invalid and not useful in satisfying the data requirement.

5. Identification of Metabolites

Residues occurring at a level of 0.01 ppm or greater at normal field application rates under the label treatment schedule should be identified when feasible. Thin-layer chromatography (TLC) of extracted residues with co-chromatography of known standards is adequate for qualitative identification. Autoradiography of TLC plates provides a record for locating any labeled degradation products. Gas chromatography coupled with mass spectroscopy (GC/MS) provides positive metabolite identification. Quantitative analysis can be either by LSC, LC, or GC. All analytical methods must be examined for their specificity, sensitivity and recovery.

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HAZARD EVALUATION DIVISION

STANDARD EVALUATION PROCEDURE

SOIL PHOTOLYSIS STUDIES

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16. Abstract (Limit: 200 words)

The Standard Evaluation Procedure for the Soil Photolysis Studies is a guidance document primarily intended for Agency reviewers and the regulated industry who evaluate data specified in 40 CFR Part 158.124. The SEP is also intended to provide information to the general public indicating how the Agency evaluates these types of studies. As such, it is designed to supplement Subdivision N of the Pesticide Assessment Guidelines - Chemistry: Environmental Fate.

The SEP for Soil Photolysis Studies is only one of a number of SEP's published by the National Technical Information Service as a supplement to Subdivision N of the Pesticide Assessment Guidelines.

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STANDARD EVALUATION PROCEDURE

PREAMBLE

This Standard Evaluation Procedure (SEP) is one of a set of guidance documents which explain the procedures used to evaluate environmental and human health effects data submitted to the Office of Pesticide Programs. The SEPs are designed to ensure comprehensive and consistent treatment of major scientific topics in these reviews and to provide interpretive policy guidance where appropriate. The Standard Evaluation Procedures will be used in conjunction with the appropriate Pesticide Assessment Guidelines and other Agency Guidelines. While the documents were developed to explain specifically the principles of scientific evaluation within the Office of Pesticide Programs, they may also be used by other offices in the Agency in the evaluation of studies and scientific data. The Standard Evaluation Procedures will also serve as valuable internal reference documents and will inform the public and regulated community of important considerations in the evaluation of test data for determining chemical hazards. I believe the SEPs will improve both the quality of science within EPA and, in conjunction with the Pesticide Assessment Guidelines, will lead to more effective use of both public and private resources.

John W. Melone

John W. Melone, Director
Hazard Evaluation Division

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SOIL PHOTOLYSIS STUDIES

I. INTRODUCTION

A. Objective

This Standard Evaluation Procedure (SEP) is to be used as an aid for Exposure Assessment Branch data reviewers in their evaluations of soil photolysis studies submitted by registrants in support of pesticide registration.

Title 40 Part 158.130[1] requires studies on photodegradation on soil to be conducted with each pesticide active ingredient used on terrestrial food crops, in orchard crops, and in forests. The data can be waived when the active ingredient is injected into the soil or entirely incorporated into the soil during application. This study is also required for a manufacturing-use product which may be used to formulate an end-use product for such uses.

B. General Theory

A general discussion of photochemical principles and of light sources appears in Appendix A (attached). Studies of the photolysis of pesticides on soil surfaces are needed in addition to those conducted in water since the pathways and ultimate products of pesticide degradation may differ significantly from those which occur in water. For example, a photoproduct formed on soil could react with the soil organic matter or be metabolized by soil microorganisms,[2] thus producing possibly unique degradation products.

II. THE SUBMITTED STUDY

A. Purpose

The purpose of these studies is to provide data on pesticide degradation rates and on the formation and decline of photoproducts on soil surfaces. Such data are required to support the registration of pesticides since pesticides are either: (1) intentionally applied to the soil surface, (2) remain on the soil surface due to incomplete soil incorporation[3] or, (3) reach the soil surface via drift[4,5] and/or runoff[6,7] from treated areas.

B. Study Design

The Subdivision N Guidelines[2] and the Data Submission Format Guidelines for Photolysis Studies[8] contain detailed information about what information must be supplied with the soil photolysis

study and under what conditions the study should be conducted. The registrant's report should contain the stated goal and sufficient information on the test protocol (compound purity and type of compound used; detailed description of light conditions; description of soil characteristics; sufficient description of sampling frequency) and the analytical protocol (description of methods used for quantitative, qualitative analyses and reports on the quality control procedures used to ensure the validity of the study).

Specific information that the registrant should include with the study is listed in Appendix B.

III. THE EVALUATION PROCESS

A. Determine the Need for the Study

For all data submitted as part of a registration action, the reviewer is to first determine whether the data is needed in support of the proposed use. The reviewer should also examine the proposed use pattern to determine if there are conditions that would support the selection of special test parameters (e.g., soil texture or organic matter content, incident light wavelength or intensity, or photoperiod) that would more closely approximate field conditions. If an initial look at the study reveals that the data supplied is not relevant and not needed to support the proposed registration action, then the reviewer should only mention in the review that the particular study was submitted but was not reviewed and why.

B. Read the Report

Read the soil photolysis report keeping the following broad issues in mind: (1) Are the goals appropriate; (2) Was the study conducted in a scientifically sound manner to meet those goals; (3) Was the experimental design, test substance and experimental procedures adequately described; and, (4) Are there data gaps that impede the review process or invalidate the study?

C. Prepare the Data Evaluation

The reviewer should now prepare the Data Evaluation Record (DER) according to the Standard Format for Preparation of Environmental Fate Reviews. Appendices B-D should be used in this process.

1. Write the Technical Evaluation

In the DER of the study, the reviewer is to record (1) whether the submitted study reliably defines the rate of soil photolysis of the a.i., and (2) the identity of the photoproducts present at > 10%. The identity of photoproducts present at < 10%

of the initial dose may be needed in cases where high concentrations of parent compound are applied to the soil.

2. Determine Study Acceptability

From the scientific point of view, the reviewer now determines if the study satisfies the soil photolysis data requirement in light of the proposed use.

3. Make Regulatory Determination

Based on the scientific results of the soil photolysis study, the reviewer now makes a statement on the impact the pesticide's photolytic fate will have on the environment such as persistence in soil.

4. Determine Need for Deferral/Referral to other HED Branches

If the parent compound or any of its degradation products are found to be stable to soil photolysis, then it may impact on ground water and/or nontarget organisms. Referral of this information should be made to the appropriate branches in HED.

APPENDIX A

GENERAL THEORY AND REFERENCES FOR EVALUATION OF SOIL PHOTOLYSIS STUDIES

Photolysis is the interaction of a compound with light in which bonds are broken as a result of the transfer of energy to those bonds.[9] While photolysis is viewed as a degradation process, compounds are not necessarily broken down into constituent parts or simpler compounds. Sunlight can transform the original compound into compounds of similar or even greater structural complexity.[10]

The energy transfer can occur in two ways: (1) directly from the light to the affected compound or (2) indirectly from the light to another compound which then transfers the light energy to the affected compound. The latter process is called sensitized energy transfer.[11]

The basic law of photochemistry states that only light which is absorbed can effect chemical change in a system.[12] The relationship of wavelength to the energy of one photon of radiation is derived from the following equations:

$$E = hv \; ; \quad v = c/\lambda \; ; \text{ therefore, } E = hc/\lambda$$

where E is the energy in ergs, v is the frequency in sec^{-1}, h is Planck's constant (6.6×10^{-27} erg sec), c is the velocity of the radiation in cm sec^{-1} and λ is the wavelength in centimeters.[9] Thus, the energy at any frequency can be calculated. Using this equation and comparing typical bond dissociation energies with energy levels associated with molecular transitions in different absorption regions, one finds that only electronic transitions from the UV/visible absorption region are energetic enough to lead to chemical reactions.[13] Since "the stratospheric ozone layer effectively prevents UV irradiation of less than 290 nm from reaching the ecosphere,"[13] the absorption region of interest is narrowed to 290-750 nm.[13]

APPENDIX B

INFORMATION SUBMITTED AS PART OF THE SOIL PHOTOLYSIS STUDY

1. The goals of the experiment.
2. Chemical name, common name, trade name, company designations and structures of both the active ingredient (a.i.) and the photolytic products.
3. Water solubility of the a.i..
4. Source and purity of the a.i..
5. Site of radiolabeling (if applicable).
6. Soil source, soil characteristics (type, pH, % sand, silt, clay, and organic matter, bulk density, moisture capacity) and if used for aerobic soil metabolism study.
7. Concentration of a.i. at which the study was conducted.
8. Description of experimental equipment (glassware, analytical equipment, artificial lighting arrangement, etc.).
9. Complete description of the analytical procedure (See Appendix D).
10. Test conditions (temperature, sterility, pH and darkness).
11. Method for adding the a.i. to the soil.
12. Means and technique of sampling and handling of sample.
13. Storage of samples (if applicable).
14. Rate of photolysis of the a.i. and the identity of the photolysis products.
15. For artificial light sources: the nature of the light source, its emission wavelength spectrum and intensity and their relationship to that of natural sunlight.
16. For sunlight sources: the latitude, time of year, atmospheric cover, and other major variables affecting incident light.
17. Method of calibrating and measuring the intensity of incident light.
18. The intensity of incident light and time of exposure with duration of dark and light periods.

19. Quality assurance. A complete description of the measures taken to insure the integrity of the study. This section should include: logbooks and/or record-keeping procedures; representative instrument printouts (chromatograms, spectra, etc.); sample coding; use of replicate samples and control blanks; use of written and validated analytical methodology, including modification(s) made; skilled laboratory personnel; well-equipped laboratory facility; use of high quality glassware, solvents, and test compounds; minimal contamination; calibration and maintenance of instruments; good laboratory practices in handling the test substance(s).

20. Contact for questions from the reviewer.

21. Raw data, sample chromatograms and sample calculations on how the photolysis rates were derived and how the photolysis products were identified.

22. Special problems with the study such as bound residues, etc.

APPENDIX C

CONSIDERATIONS IN REVIEWING SOIL PHOTOLYSIS STUDIES

1. Were the name and structure of the parent and photoproduct(s) provided?

2. Was the starting concentration high enough to permit the isolation and identification of photoproducts formed?

3. Were precautions taken to minimize losses through volatilization?

4. Were appropriate traps utilized to contain volatile products for analysis?

5. Was the radiolabel in a stable portion of the compound?

6. Were sufficient samples taken and at appropriate times during the study? Were adequate replicates made?

7. Did the study continue through at least 1 half-life or 30 days, whichever came first?

8. Was the pesticide applied to the soil in a uniform manner?

9. Were there controls, prepared and maintained as for the other samples except that they were kept in the dark?

10. For sunlight as the source, were the following given:

    - a record of the intensity of incident sunlight?
    - time of exposure?
    - latitude?
    - time of year?
    - atmospheric cover?
    - other major variables which affect incident light?

11. For artifical light as the source, were the following given:

    - description of the source?
    - intensity?
    - wavelength distribution? (emission spectrum)
    - time of exposure?
    - the relationship of the light intensity employed to that of natural sunlight?

12. Were filters used in the experimental apparatus to remove wavelengths below 290 nm?

13. Were photoproducts produced in > 10% yield identified?

14. Was there a good material balance?

15. Was a half-life estimate made for the parent compound?

16. Was there an impurity in the a.i. that would interfere with the analytical method?

17. Was the analytical method adequately described? Were statistics verifiable?

18. Were raw data and samples of analytical data sheets, chromatograms, calculations, etc. given?

19. Were control samples, prepared and handled the same as the pesticide treated study samples, run in each experiment?

APPENDIX D

TEST PARAMETERS INFLUENCING SOIL PHOTOLYSIS

1. Experimental Design

From the considerations of Appendix C, the reviewer must draw some conclusions about the influence of the experimental design on the validity of the study for the proposed use. Some questions the reviewer should answer are:

1. Was sunlight, if used, representative of the area of proposed use?

2. Did the emission wavelength spectrum of the artificial source, if used, simulate that of natural sunlight?

3. Was the pattern of light and dark given and was it reasonable for the proposed use pattern? (i.e., 12 hours of light/12 hours of dark per day; 16 hours of light/8 hours of dark per day; etc.)

4. Was the relationship of the intensity of the artificial sunlight used appropriate to that of natural sunlight in the area and for the time of the planned use?

5. Was a suitable method used for measuring the intensity of incident light?

Typical experimental procedures involve mixing the test substance with the soil and forming a thin film on a glass plate from a slurry (see for example ref. 14) or spraying the test substance on a pre-formed thin soil layer. To reduce error, a single, pesticide-fortified slurry should be used to coat the glass plates or, the untreated, pre-formed soil thin layers should be brought next to each other and be sprayed at the same time.

The amount of the test substance initially applied will depend on the analytical method, the proposed application rate, plus other factors. The initial concentration must clearly allow the isolation and identification of photoproducts formed and have representative results indicative of what would occur under use conditions. Samples periodically taken from the irradiated films are then analyzed for both the parent compound and any degradation products. Similar thin films held under identical conditions but kept in the dark serve as controls to demonstrate that any observed reactions are in fact photochemically driven.

2. Nature of Light and Factors Effecting the Incident Light

The light source used for sample irradiation may be either natural or simulated sunlight. If natural sunlight is used, a record of its intensity and wavelength distribution is required as well as the time of exposure, latitude, time of year, atmospheric cover, and other major variables which affect incident light. If an artificial light source is used, its intensity, wavelength distribution and the length of exposure are required as well as the relationship of the light intensity employed to that of natural sunlight. Samples should not be exposed to radiation below 290 nm, the cut off point of the solar spectrum at the earth's surface. If an artificial light source emits radiation below this level, suitable filters should be used.

The reviewer should be aware of seasonal differences in natural sunlight when evaluating photolysis data. The half-life of a pesticide can vary by a factor of three during exposure to spring versus summer natural sunlight.[15] Also, the results of a photolysis experiment under natural sunlight should not be extrapolated from one location to another because the intensity of solar ultraviolet radiation at the earth's surface is a function of latitude, season and elevation.[16] This is particularly true for the 300-320 nm region[16] which is a subset of the 290-450 nm region in which most photolysis reactions probably occur.[17]

Various kinds of glass absorb and transmit different wavelengths.[13] Therefore, the kind of glass (both in vessels and filters) should be specified and its transmissibility considered in evaluating the adequacy of the study. Also, the reference which gives the transmissibility of the glass should be current, as the glass manufacturing processes have changed with a concomitant change in transmissibility of glass batches.[18] Quartz is the glass of choice with borosilicate glass as an acceptable choice.[19] The reviewer should be aware that borosilicate glass varies with manufacturer.[19]

3. Radiolabeling

Use of radiolabeled pesticides as test materials provides easier and more reliable accountability of material balance than use of non-labeled material. Radiolabeling should be done in a stable portion of the molecule. Generally, tritium labeling is less reliable because of proton exchange with the medium. If the parent compound forms two or more significant photoproducts, it may be necessary to label the parent compound at more than one site in the molecule so that the degradation pathway may be more completely and easily followed. For a complete discussion of the use of radiolabeling in environmental fate studies submitted to EPA, see the SEP for Hydrolysis Studies.[20]

4. Mass Balance Considerations

All of the radioactivity used in the experiment must be accounted for to ensure that all the photoproducts have been detected and that the fate of all the starting material is traced. In particular, the study must demonstrate that no radioactivity is lost through volatilization. Therefore, traps must be used to monitor production of volatile photolysis products, such as carbon dioxide and humidified air should be drawn through the system. In addition, the temperature of the soil should be monitored and maintained at 20° to 30°C (as should the dark controls).

5. Soil Selection

The soil chosen should initially be pesticide free to eliminate interference during analysis. The soil chosen should also be taken from the surface of the field since sunlight does not penetrate soil; therefore, photolysis occurs at the surface. Also, soil at the surface is most rich in organic matter[21] of which a component, humic acid, has been shown to be a photosensitizer.[22] Using subsoil, therefore, in a photolysis study would not give results representative of photolysis at the surface.

The test soil used should be the same as one of those used in the aerobic soil metabolism study, so that direct comparisons can be made between microbial and photochemical pathways of degradation. If necessary, a variety of soils should be used which represent the likely range of soil types to be encountered under actual use.

6. Duration, Sampling and Identification of Photolysis Products

Sufficient data points should be taken to allow the estimation of the half-life for disappearance of the parent compound. In general, an irradiation regime equivalent to a thirty-day duration of the experiment (© 12-hour light:12-hour dark) is adequate. However, where photodegradation is a significant degradation pathway or where photoproducts of particular environmental or toxicological interest are formed, a longer duration of the experiment may be necessary to establish rates of reaction or structures of products. Taking four samples for analysis, with one sample taken at the half-life or at the conclusion of the 30-day test period has been recommended.[2] However, it is recognized that other sampling regimens (i.e., involving more frequent and additional sampling) may be necessary in some cases.

At each sampling interval, data to prepare a mass balance should be obtained. This requires simultaneous sampling and analysis of the soil and volatiles traps.

Degradation products produced in greater than about ten percent yield should be chemically identified. The structures of the photoproducts should be given and an overall degradation pathway provided. In some cases, it may be necessary to synthesize a particular photolysis product for further degradation studies. As a practical matter, if less than about 10% of the pesticide photodegrades within a thirty-day study period, the pesticide is usually considered photolytically stable in soil.

7. Analytical Method

A detailed description of the analyses used to determine the parent and photoproducts should be given. The following information should be included:

1. Name (and signature), title, organization, address, and telephone number of the person(s) responsible for the planning/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, other].

4. Principles of the analytical procedure [describe].

5. Non-Confidential Business Information (non-CBI) copy of the analytical method(s) detailing in stepwise fashion the procedures (extraction, clean-up, derivatization, determination, calculation of the magnitude of the compound(s)).

6. Reagents or procedural steps requiring special precautions [to avoid safety and health hazards, explain].

7. Identification of the chemical species determined.

8. Modifications, if any to the analytical method(s) [detail].

9. Extraction efficiency [if pertinent].

10. Instrumentation [make/model; type/specificity of detector(s); column(s) (packing materials, size); carrier gas(es); flow rate(s); temperature(s); voltage; limit of detection and sensitivity; calibration procedures; etc.].

11. Interference(s), if any [describe].

12. Confirmatory techniques [e.g., different column packing(s) or detector(s), etc.].

13. Sample identification [coding and labeling information; should be the same as - or cross-referenced to - the sample coding/labeling assigned at harvest].

14. Results [raw data; laboratory worksheets; stepwise calculation of levels; dilution factors; peak heights/areas; method correction factor(s) applied (e.g., storage stability and method validation recovery values); formula(e)/standard curve(s) used; amount found of total applied, and of individual component(s) (i.e., photoproducts); range of values; representative chromatograms, specta, etc. (as applicable) from control and treated samples; etc.].

15. Statistical treatment(s) [describe test(s) applied to the raw data].

16. Quality assurance [control measures/precautions followed to ensure the fidelity of determinations, including logbooks and record-keeping procedures; representative instrument print-outs (chromatograms, spectra, etc.); sample coding; use of replicate samples and control blanks; use of written and validated analytical methodology for analyses, including modification(s) made; skilled laboratory personnel; well-equipped laboratory facility; use of high-quality glassware, solvents, and test compound(s); minimize contamination; calibration and maintenance of instrumentation; good laboratory practices.

17. Time required for analysis [to carry a sample completely through the analytical procedure, including the determinative step].

18. Other [any and all additional information the petitioner considers appropriate and relevant to provide a complete and thorough description of residue analytical methodology and the means of calculating the residue results].

8. Additional Considerations

Factors that affect the rate and products of photolysis on soils are not well understood at present.[19] Dr. Richard Zepp, research chemist, EPA-RTP, has suggested that based on limited studies the following factors appear to be very important and should be considered in this SEP. They are only raised now as points which need to be addressed.

1. Soils contain organic (humic) and mineral substances that strongly attenuate sunlight and that can photosensitize and/or quench light-induced transformations.[23] The net effect of the various photochemical influences of these soil components is difficult to predict quantitatively, because little research has been done in this area. It seems clear, however, that the light attenuation effect reduced the penetration of sunlight to no more

than about 1 mm. Variability in the extent of light attenuation is likely to be a major reason for lack of precision in the determination of pesticide photolysis rates.

2. Recent studies by Gohre and Miller[24] have shown that sunlight absorption by soils leads to production of singlet oxygen, a reactive, excited form of dioxygen. Singlet oxygen reacts rapidly with certain pesticides and also is known to react with natural substances to form other reactive oxidants such as peroxides. The likely precursors of singlet oxygen, soil components in their excited triplet states, are likely to be chemically reactive. This finding strongly indicates that sunlight-induced transformations of pesticides that do not even absorb sunlight may be significant on soil surfaces. This is consistent with earlier findings in field studies that certain cyclodiene insecticides such as aldrin are transformed on soils even though they are transparent to ground-level solar radiation. These indirect photoreactions could vary dramatically in rate constant and products from one soil to another.

3. As mentioned in section 1 of these comments, all of the solar radiation is absorbed in the top millimeter, and a substantial portion is transformed into thermal energy. Soil surfaces get very hot under sunlight and the heating may accelerate various nonphotochemical reactions of pesticides, e.g., hydrolysis, oxidation. Thus, if the soil is not cooled as in Hautala's[25] studies, thermal reactions are likely to make a significant contribution to pesticide loss in the soil, especially with hydrolyzable pesticides such as esters, ureas, carbamates, and phosphorothioates. It seems clear that soil temperature and its effects in thermal reactions are extremely important considerations in evaluating soil photolysis data.

4. Hautala's[25] studies showed that the moisture content of soils has an important effect on photolysis rates of certain pesticides and that the nature of the effect is altered in the presence of surfactants, substances that are often co-applied with active ingredients of pesticide formulations. These results also indicate that the mode of application of the pesticide to the soil may have important effects on photolysis rates, and that the photoreactions are described by first-order rate expressions.

5. Finally, the rate of loss may be influenced by physical processes such as sorption/desorption. Recent studies[26] with the hydrophobic, chlorinated-pesticide derivative, DDE, indicate that the photochemical behavior of a pesticide depends on the amount of time between application and the start of the irradiation.

Based on these comments, it has been suggested[19] that the reviewer place the heaviest weight on soil photolysis data obtained using soil from the actual location(s) where the pesticide will

be used. Also, the most meaningful data will be obtained when the pesticide is applied in the same way as in the field prior to photolysis.

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HAZARD EVALUATION DIVISION

STANDARD EVALUATION PROCEDURE

AEROBIC SOIL METABOLISM STUDIES

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15. Supplementary Notes

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16. Abstract (Limit: 200 words)

The Standard Evaluation Procedure for the Aerobic Soil Metabolism Studies is a guidance document primarily intended for Agency reviewers and the regulated industry who evaluate data specified in 40 CFR Part 158.124. The SEP is also intended to provide information to the general public indicating how the Agency evaluates these types of studies. As such, it is designed to supplement Subdivision N of the Pesticide Assessment Guidelines - Chemistry: Environmental Fate.

The SEP for Aerobic Soil Metabolism Studies is only one of a number of SEP's published by the National Technical Information Service as a supplement to Subdivision N of the Pesticide Assessment Guidelines.

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms

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(See ANSI-Z39.18) See instructions on Reverse OPTIONAL FORM 272 (4-77) (Formerly NTIS-35) Department of Commerce

STANDARD EVALUATION PROCEDURE

PREAMBLE

This Standard Evaluation Procedure (SEP) is one of a set of guidance documents which explain the procedures used to evaluate environmental and human health effects data submitted to the Office of Pesticide Programs. The SEPs are designed to ensure comprehensive and consistent treatment of major scientific topics in these reviews and to provide interpretive policy guidance where appropriate. The Standard Evaluation Procedures will be used in conjunction with the appropriate Pesticide Assessment Guidelines and other Agency Guidelines. While the documents were developed to explain specifically the principles of scientific evaluation within the Office of Pesticide Programs, they may also be used by other offices in the Agency in the evaluation of studies and scientific data. The Standard Evaluation Procedures will also serve as valuable internal reference documents and will inform the public and regulated community of important considerations in the evaluation of test data for determining chemical hazards. I believe the SEPs will improve both the quality of science within EPA and, in conjunction with the Pesticide Assessment Guidelines, will lead to more effective use of both public and private resources.

John W. Melone

John W. Melone, Director
Hazard Evaluation Division

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AEROBIC SOIL METABOLISM STUDIES

I. INTRODUCTION

A. Objective of the Standard Evaluation Procedure

This Standard Evaluation Procedure (SEP) is to be used as an aid for Exposure Assessment Branch data reviewers in their evaluations of the aerobic soil metabolism studies submitted by registrants in support of pesticide registration.

Aerobic soil metabolism studies are required by 40 CFR §158.130 in support of registration of an end-use product intended for terrestrial use or forestry 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 162-1 in the Subdivision N Guidelines describes this study and provides a protocol for conducting it.[1]

Data on the aerobic soil metabolism of pesticides are used by the Agency to determine the nature and extent of formation of pesticide degradation products to which rotational crops and nontarget organisms will be exposed, and to facilitate assessment of potential disposal problems and which will be available for leaching to ground water.

B. General Theory of Aerobic Soil Metabolism

The reviewer should be acquainted with the physico-chemical and microbial soil processes causing pesticides to degrade and dissipate in the soil environment. The reviewer is directed to Appendix 1 for a brief description of those soil processes.

II. THE SUBMITTED STUDY

A. Purpose

Aerobic soil metabolism studies should provide information on (1) the rate of degradation in soil; (2) identification of soil degradation products; (3) rate of formation and decline of the degradation products; and (4) a material balance. Information gained from this study is directly applied to designing and conducting field dissipation and accumulation studies. For example, it determines the degradation products one should analyze for in the field soil dissipation studies and to which degradation products rotational crops and nontarget organisms will be exposed.

B. Study Design

The registrant's report should contain (1) a stated goal of the study; and (2) sufficient information on the test protocol (compound purity and type of compound used; complete characterization of soils; dose level and method of inoculation of soil; sufficient description of sampling frequency) 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 study).

Types of information that the registrant should include in the report are 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 §158.130. Normally, the study is required to support registration of each active ingredient in pesticide products intended for terrestrial or forestry end-uses and for manufacturing-use products intended for use in formulating such end-use products.

B. Read the Report

Reports of aerobic soil metabolism studies are first reviewed to determine if the following information is present:

1. Are the compound purity and site(s) of radiolabeling specified? If radiolabeling is used, complex molecules must be labeled in appropriate sites to allow each major component of the molecule to be monitored.

2. Is the complete characterization of soil(s) included [pH, moisture capacity, percent organic matter, bulk density, cation exchange capacity, and textural composition (percent sand, silt and clay) and textural class]?

3. Is the treatment rate and method of treatment of the soil described?

4. Were soil treatments replicated and sampled frequently?

5. Are the methods used to determine material balance described?

6. Are the methods used for quantitative and qualitative analyses of the degraded compound and formation and decline of

the degradation products described?

7. Is the material balance determined?

8. Is the half-life calculated?

9. Are the raw data from which a half-life can be calculated included?

The reviewer should determine if there are data gaps within the study. Failure to provide adequate information may be sufficient for the reviewer to reject the study. In cases where considerable information is missing, the reviewer should make a detailed list of the deficiencies and omissions and not provide a detailed scientific review of the report at this time.

C. Prepare the Data Evaluation Record (DER)

After the reviewer has determined there are no data gaps which would cause the report to be rejected, the reviewer prepares a 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 protocol should provide adequate information as to how and under what conditions the study was conducted. Consult Appendix 2.

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

c. The material balance aids in determining the validity of the study. Is all or the major portion (90-95%) of the test chemical applied to the soil accounted for?

d. The rate of degradation of the test material provides a half-life estimate of the parent compound. It answers the questions:

   - Does the test material degrade?
   - Is it persistent in the soil environment?

   It also provides a measure of predicting the degradation rate under field conditions.

e. It is essential that the report provide the identity of the soil degradation products of the test substance in order to answer the following questions:

- To what does the test chemical degrade?
- How extensive is degradation? Does it mineralize to inorganic compounds (e.g., CO_2)?
- Which compounds can be expected to occur and should be looked for in the field dissipation studies?
- To which compounds will rotational crops and other nontarget organisms (e.g., aquatic organisms) be exposed?

f. The rate of formation and decline of degradation products provide a half-life estimate for the degradation products. This answers the questions:

- Are the degradation products persistent in the soil environment and thereby available for leaching to the water table?
- At what rate do they decline?

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

- Were logbooks and record-keeping procedures maintained?
- Were quality procedures maintained during sampling, storage, and analysis of soil samples? Were good laboratory practices followed?
- Was soil for testing maintained in a manner to maintain viable microbial populations?

h. A degradation scheme of the test compound and degradation products can suggest which mechanisms contributed to the degradation.

2. <u>Determine Study Acceptability</u>

Were the stated goals of the study appropriate and clearly defined? Was the study conducted in a scientifically sound manner to accomplish those goals? If so, the reviewer then makes a determination as to 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.

If the study is deficient, a detailed description of the deficiencies and recommendations on how to rectify the deficiencies is prepared and included in the DER.

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

If the reviewer concludes that (1) the test chemical or its degradates has/have a potential for reaching ground water due to its/their persistence, or (2) residues may occur in rotational crops due to their persistence, or (3) there may be exposure to other nontarget organisms due to persistence, then the Toxicology, Residue Chemistry, 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 an aerobic soil metabolism study as listed in 40 CFR §158.130.

APPENDIX 1

General Theory

Pesticide products reaching the soil may either decompose completely to inorganic compounds (e.g., CO_2), be altered in varying degrees and become part of the soil complex, or remain intact in the soil ecosystem. In all cases, residues may be available for uptake by rotational crops and exposure to non-target organisms. Degradation products may become important when their rate of formation exceeds their rate of decomposition.

Numerous factors are known to influence fate and behavior of pesticides in the soil system. These factors are basically either chemical (i.e, non-biological) or microbial (biological) degradation. Usually these two processes work in conjunction.[2,3] However, where the influence of one stops and the other begins is not well defined. The most complex process by which pesticides are degraded in soils involves microbial utilization of the pesticide as an energy source.[4] The aerobic soil metabolism study is designed to measure degradation of the test compound from biological degradation due to microorganisms in the soil complex and from the soil-associated physico-chemical processes.

Microorganisms comprise a large fraction of the living biomass in soil - up to 80% when soil algae are included.[5] However, they are not all active under the same conditions. Microbial degradation in soil has been viewed as a process in which organisms adapt to the chemical and use it as a preferred food source.[6] A variety of organisms which are capable of using pesticides as the sole energy source have been identified. It is reported that microbial species belonging to 16 genera of bacteria, 2 of actinomycetes and 13 of fungi have been identified as being able to degrade 20 of the commonly used herbicides.[7] It appears, however, that microbial degradation of most agricultural chemicals at low concentrations applied to soil occurs primarily via cometabolism by soil organisms using soil organic matter as their main source of energy.[6]

Soil microorganisms can decompose most synthetic organic soil additives as well as the natural soil organics, but there are some limitations. Some synthetic organic chemicals involve unusual molecular structures to which organisms may not be well adapted.[8] The action of organisms on organic compounds is primarily enzymatic. Enzymes are abundant in soil.[9] Microbial-associated chemical reactions can include hydrolysis, oxidation ring cleavage, and dehalogenation, all of which contribute to ultimate formation of CO_2 from the chemical in question. Where some microorganisms leave off in degradation of a chemical, others may begin. The reader is directed to additional literature on microbial activity in soil and on the biochemistry of living systems and their

components in soil (in particular, books edited by Gray and Parkinson[10] and McLaren and Peterson[11]).

There are numerous soil-associated physico-chemical reactions. Hydroxylation and oxidation are common soil chemical reactions.[4] Less is known of other mechanisms (reduction, isomerization, and free-radical reactions).

All the soil-associated chemical reactions are initiated through water acting as the medium of reaction, or reactant, or as both. These chemical reactions may be catalyzed by clay, metal oxides, metal ions, or extracellular enzymes.[4] The organic matter fraction of the soil can play a major role in the chemical degradation of pesticides in providing reactive functional groups[12, 13] as well as by retaining the molecule (adsorption) which allows these processes to take place.[14]

Both biodegradation and soil physico-chemical degradation are affected by soil pH. For example, microbial oxidation is most rapid between pH 6 and pH 8.[14] Soil water is seldom neutral and its pH range may vary from strongly acidic (pH 3) to strongly alkaline (pH 10.5).[15] A number of pesticides will hydrolyze rapidly under aqueous acidic and alkaline conditions that can be found in soil. For further information see the discussion in the Standard Evaluation Procedure for Hydrolysis Studies.

APPENDIX 2

Information to be Included in the Report

Section 162-1 in the Subdivision N Guidelines[1] describes this study and gives a protocol for conducting this study. Also, Section 160.5 in the Subdivision N Guidelines[1] describes general reporting and evaluation requirements for this study.

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 identify the test substance and include the chemical name and purity of active ingredient, molecular structure, manufacturer, and lot and sample number(s) of the test substance(s), and properties of the test substance(s) [including physical state, pH] if not reported elsewhere;

8. Description of the soil source and soil characteristics;

9. A detailed report in tabular form of the residue data from the treated soil (graphs are often included to expand on the data given in tabular form);

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

    a. Material balance;

    b. Degradation rate and half-life estimate of the parent;

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

d. Identity of residues occurring at levels of 0.01 ppm or greater;

e. Residue decline curves.

B. Detailed Discussion

1. The test substance.

The chemical to be tested must be chemically pure. The use of radiolabeled compounds is preferred. Carbon-14 is usually used; ring labeling is preferred to side-chain labeling since the radioactivity is usually less easily removed from the central ring positions. If the molecule is complex and consists of moieties that are easily separated, then radiolabeling in more than one position of the compound may be necessary.

Use of radiolabeled chemicals rather than non-labeled ones allows: (1) the degradation process to be followed at a much lower concentration and (2) easier determination of mass (material) balance. If non-radiolabeled compound is used, the study must be conducted with the technical or purer grade of the active ingredient(s).

Sometimes, initial concentrations of the test substance in soil exceeding the proposed use rate should be studied to permit measurement of the disappearance of the parent compound and identification of the major degradates formed.

2. The test soil.

The rate, type and degree of metabolism of the pesticide and its major degradates should be determined in a sandy loam or silt loam. A different soil may be used if representative of the soil at the intended sites. For example, celery is usually grown in a muck soil. Thus, to support such a use it may be necessary to conduct the study in muck soil. If the use covers a crop that is grown in various soil types with wide geographic distribution, then more than one soil type must be studied. For example, soybeans are grown in large geographical areas encompassing several distinct soil types. Here, it will be necessary to conduct the study in both a sandy loam and loamy clay soil.

There is no best way to collect and store soils for conducting this study.[16] The soil should be a collection of subsamples from the top layer of the field soil. The majority of the field microbial populations is located in the top layer of soil (the upper 14 centimeters).[17] This is the area where nutrient levels and oxygen availability are high.[18] The soil should not have received prior pesticide applications. If 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.[15]

As in most routine soil analyses,[19] the soil should be sifted through a 2 mm sieve. This removes extraneous debris which could adsorb the test compound thus affecting the results of the study. The soil should preferably be freshly acquired from a typical use area or have been maintained in such a manner that viable microbial populations are present in the soil. The soil should be stored in a clean, chemical-free environment. The soil may be dried to approximately 75% of the moisture level at 1/3 bar (Note: 1/3 (0.33) bar is a laboratory measure of the soil moisture at field capacity - the amount of water remaining in soil after excess water has been removed by force of gravity[16]). However, it is important the soil not become air-dry as that can adversely affect the microorganism populations present.[16]

Complete information on the soil class, textural characterization of the soil, soil pH, and percent organic matter is necessary to verify that the soil is representative of agricultural soils. Use of U.S. soils from typical use areas is preferred but if foreign soils are used, such data on soil class and textural classification are needed to indicate its similarity to U.S. agricultural soils from typical use areas. When foreign soils are used, additional studies conducted with U.S. soils and of sufficient duration will also be needed to provide assurance that any possible differences in microbial populations between the foreign and U.S. soils does not result in different patterns of degradation.

Since many reactions are pH sensitive, the nature of the soil pH reaction is an important consideration. The organic matter content is a measure of microbial viability, being the main energy source for soil microorganisms.

4. Test procedures.

a. Study apparatus.

The use of closed incubation systems, either flasks with side-arms[20] or positive air flow manifold systems,[21] are recommended for this study. They allow for determination of mass (material) balance. However, their use may be omitted if the parent compound is not volatile or if labeled CO_2 and/or other volatile metabolites are not formed. Collection of volatiles is necessary for the material balance and serves to indicate that the test material ultimately mineralizes to CO_2 or that other volatile organic compounds are formed. If the reviewer notes that an open system was used and the mass balance does not approximate 100% recovery, the reviewer can suspect that volatiles were formed but not

trapped. The reviewer should request clarification of this fact from the registrant, if not given.

b. Treatment rate.

The concentration of the test substance should be at levels sufficient to permit measurement of the disappearance of parent compound and identification of major degradation products. The dose should be at the highest proposed field use rate. Separate studies at higher doses (5 to 10X) may be necessary for identification of degradation products.

c. Study conditions.

Soil samples should be taken and replicated sufficiently to provide interpretable data for kinetic analysis. The soil study should include untreated controls. Treated soil should be maintained at a constant temperature between 18 and 30°C that is most representative of the use area. The recommended soil moisture content is at a level of 75 percent of 0.33 bar moisture. These are the soil moisture conditions most conducive to metabolism by aerobic microorganisms and is a compromise of the unlimited variety of combinations of temperature and moisture levels found in the natural environment.

One hundred percent of one-third (0.33) bar soil moisture represents the upper limit of soil moisture for aerobic microbial activity (equivalent to field moisture capacity). The 75% of 0.33 bar is a safe moisture level still within the optimum range.[16] It is probably a moisture level more prevalent in soil than 100% of 0.33 bar. If soil is maintained at another soil moisture level, this level should also be reported relative to the theoretical moisture content at 75% of 0.33 bar. However, the soil moisture level should be within 10-12% of the level at 75% of 0.33 bar moisture.

d. Duration of the study.

Reaction kinetics of decomposition of pesticides are concerned primarily with the decline in concentration of the pesticide over time.[4, 8, 23] However, the Guidelines[1] also require information on the degradation products. Therefore, data are collected until patterns of decline of the test substance and patterns of formation and decline of degradation products are established or for one year, whichever comes first for terrestrial crop and non-crop uses and forestry uses. When greenhouse and domestic outdoor uses are involved, data are collected through two half-lives of the test substance or to six months duration, whichever comes first. Data over these lengths of time are necessary for kinetic analyses.

e. Sample collection

The Guidelines[1] recommend sampling soil at pretreatment, immediately post-treatment, at 1, 3, 7, and 14 days, and at 1, 2, 3, 4, 6, 9, and 12 months post-treatment. To obtain sound kinetic data, it has been suggested that there should be at least six sampling points spread out over three half-lives of the chemical.[16] Others have suggested that the reaction should be followed for at least 1-1/2 half-lives if accurate rate constants are to be obtained.[8] Exact distribution will depend on rate of breakdown. However, an adequate number of samples should be collected in the beginning of the incubation in the event rapid degradation takes place.

If trapping solutions are used, they should be sampled when the soil is sampled.

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. Spiked samples should be maintained under identical conditions and extracted with treated samples unless preliminary data are available which show that additional degradation does not occur under the storage conditions.

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 (P.A.M), 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, etc.];

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

n. Sample identification (Coding and labeling information);

o. Residue results (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 (any and all 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 must include information on the following: the recovery level(s) of the test compounds from the soil (substrate) at various fortification level(s) using the residue analytical methodology; a validated method sensitivity level; results of the study and statistical tests applied; a stepwise presentation of the procedure for calculating percent recovery from the raw data; all the data/information necessary to independently verify the results; summary of data results; and 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: logbooks and/or record-keeping procedures; representative instrument printouts (chromatograms, spectra, etc.); sample coding; use of replicate samples and control blanks; use of written and validated analytical methodology for residue analyses, including modification(s) made; skilled laboratory personnel; well-equipped laboratory facility; use of high quality glassware, solvents, and test compounds; minimal contamination; calibration and maintenance of instruments; good laboratory practices in handling the test substance(s).

D. Residue Analysis

1. Samples should be subdivided and analyzed as follows:

a. Total soil residues

When ^{14}C labeled parent compound is used, the soil will be combusted in an oxidizer and CO_2 formed will be trapped in appropriate

solvents. This provides a preliminary material balance.

b. Extractable soil residues

Soil is extracted with appropriate solvents, filtered, and re-extracted if necessary. Exhaustive extraction methods are sometimes necessary when residues are not extracted by gentler means. The reviewer should determine that an appropriate extracting solvent was used in the study. The reader is directed to Chesters, et al.[23] for a general overview on the subject of pesticide extraction and analysis of soil without elaboration on specific procedures and to Hance and McKone[24] for specific procedures for herbicides.

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.

c. Non-extractable residues

The post-extracted soil is combusted in an oxidizer and the CO_2 formed is trapped in appropriate solvent. Non-extractable residues are those that may, at some later time, become available for uptake by rotational crops or for exposure to nontarget organisms. They are also a measure of the soil binding potential of the test chemical and degradation products.

These three residue totals - total volatile residues, total extractable residues and the non-extractable residues (expressed as percent of the total applied) - make up the material balance. The material balance summed should ideally equal 100% of the amount of test chemical applied. Thus, the material balance is a factor in determining the validity of the study. Studies wherein the material balance does not account for a large percentage (85-95%) or accounts for greater than 105-115% of the amount of test chemical applied may be invalid and not useful in satisfying the data requirement.

2. Identification of Metabolites

The Guidelines[1] require that residues occurring at a level of 0.01 ppm or greater at normal field application rates under the label treatment schedule should be identified when feasible. Thin-layer chromatography (TLC) of extracted residues with co-chromatography of known standards is adequate for tentative qualitative identification. Autoradiography of TLC plates provides a record for locating any labeled degradation products. Liquid chromatography (LC) or gas chromatography and mass spectroscopy (GLC/MS) analysis provides positive metabolite identification. Quantitative analysis can be either by LSC, LC or GLC. All analytical methods must be examined for their

specificity, sensitivity, and recovery.

Identification of metabolites is a major part of the aerobic soil metabolism study and involves most of the analytical resources. Metabolites found in the aerobic soil metabolism study are considered representative of those that will be found in the soil under actual field conditions although different levels may be found under field conditions. Knowing the identity of the degradation products aids in preparing a degradation scheme of the test chemical and analyzing the field soil samples.

3. Half-life Estimate

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 approach first-order kinetics at low concentrations and zero-order at high concentrations. Since pesticides are usually applied to soil at low concentrations and are often strongly sorbed, the rates of most chemicals should 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 velocity of the reaction.[25] However, rates tend to decrease with time more than would be expected which suggest sorptive forces are still active in the soil.[6] 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 first order is most commonly used since it is the simplest to use. Assuming first-order kinetics, the pesticide's half-life (the time required for the concentration to become equal to one-half of the original concentration) can be calculated. The dissipation of most pesticides from soils can be considered as following a first-order reaction[26] at least over

a portion of the degradation curve.[4, 8] It is reported that, overall, the reaction kinetics involved in decomposition of pesticides follow mostly the zero-, first-, and second-order reaction systems.[27] It is doubtful that any one single rate equation will ever be found which is applicable to all or most pesticides in soil.[4] The half-life estimate based on the kinetic analysis of the data generated in the aerobic metabolism study becomes a measure of persistence of pesticides under field conditions. However, it should be noted[25] that data summarized[8] show that the relationships imply that the proportion of the chemical degraded with time decreases as the concentration of the chemical decreases. The rate at which the last traces of a chemical disappears can be very slow.[25]

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HAZARD EVALUATION DIVISION

STANDARD EVALUATION PROCEDURE

AQUEOUS PHOTOLYSIS STUDIES

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15. Supplementary Notes

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16. Abstract (Limit: 200 words)

The Standard Evaluation Procedure for the Aqueous Photolysis Studies is a guidance document primarily intended for Agency reviewers and the regulated industry who evaluate data specified in 40 CFR Part 158.124. The SEP is also intended to provide information to the general public indicating how the Agency evaluates these types of studies. As such, it is designed to supplement Subdivision N of the Pesticide Assessment Guidelines - Chemistry: Environmental Fate.

The SEP for Aqueous Photolysis Studies is only one of a number of SEP's published by the National Technical Information Service as a supplement to Subdivision N of the Pesticide Assessment Guidelines.

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms

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STANDARD EVALUATION PROCEDURE

PREAMBLE

This Standard Evaluation Procedure (SEP) is one of a set of guidance documents which explain the procedures used to evaluate environmental and human health effects data submitted to the Office of Pesticide Programs. The SEPs are designed to ensure comprehensive and consistent treatment of major scientific topics in these reviews and to provide interpretive policy guidance where appropriate. The Standard Evaluation Procedures will be used in conjunction with the appropriate Pesticide Assessment Guidelines and other Agency Guidelines. While the documents were developed to explain specifically the principles of scientific evaluation within the Office of Pesticide Programs, they may also be used by other offices in the Agency in the evaluation of studies and scientific data. The Standard Evaluation Procedures will also serve as valuable internal reference documents and will inform the public and regulated community of important considerations in the evaluation of test data for determining chemical hazards. I believe the SEPs will improve both the quality of science within EPA and, in conjunction with the Pesticide Assessment Guidelines, will lead to more effective use of both public and private resources.

John W. Melone

John W. Melone, Director
Hazard Evaluation Division

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AQUEOUS PHOTOLYSIS STUDIES

I. INTRODUCTION

A. Objective

This Standard Evaluation Procedure (SEP) is to be used as an aid for Exposure Assessment Branch data reviewers in their evaluations of aqueous photolysis studies submitted by registrants in support of pesticide registration.

40 CFR Part §158.130[1] requires aqueous photolysis studies to be conducted with each pesticide active ingredient intended for any terrestrial use (except greenhouse and domestic outdoor use), aquatic use, or forestry use, or for any aquatic impact uses involving direct discharges of treated water into outdoor aquatic sites. This study is also required for a manufacturing-use product which may be used to formulate an end-use product for such uses.

B. General Theory

Pesticides can be applied directly to aquatic systems or can enter aquatic systems via leaching or runoff after terrestrial application. Upon entering aquatic systems, pesticides can undergo photolytic transformation by sunlight (photolysis). Therefore, data on rates of photolysis in water of the parent pesticide and its photodegradates are needed to establish the importance of this transformation process and the persistence characteristics of photoproducts formed.

A brief discussion of some basic photochemistry concepts is contained in Appendix A. The reviewer is referred to physical chemistry and photochemistry texts and many of the papers and books in the attached references for a more complete discussion of theory.

II. THE SUBMITTED STUDY

A. Purpose

The purpose of the study is to determine rates of aqueous photolysis of the pesticide ($t_{1/2}$) and identify photolytic products and rates of formation and decline of these products. The section in the Subdivision N Guidelines[2] which describes this study and provides sample protocol is 161-2.

B. Study Design

The Subdivision N Guidelines[2] and the Data Submission Format Guidelines for Photolysis Studies[3] contain detailed information about what information must be supplied with the aqueous photolysis study and under what conditions the study should be conducted. The registrant's report should contain the stated goal and sufficient information on the test protocol (compound purity and type of compound used; concentration of the compound in solution; detailed description of light conditions; sufficient description of sampling frequency) 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 study).

Specific information that the registrant should include with the study is listed in Appendix B.

III. THE EVALUATION PROCCESS

A. Determine the Need for the Study

For all data submitted as part of a registration action, the reviewer is to first determine whether the data is needed in support of the proposed use. If an initial look at the study reveals that the data supplied is not relevant and not needed to support the proposed registration action, then the reviewer should only mention in the review that the particular study was submitted but was not reviewed and why.

B. Read the Report

Read the aqueous photolysis report keeping the following broad issues in mind: (1) Are the goals appropriate, (2) Was the study conducted in a scientifically sound manner to meet those goals, (3) Were the experimental design, test substance and experimental procedures adequately described and, (4) Are there data gaps that impede the review process or invalidate the study?

C. Prepare the Data Evaluation

The reviewer should now prepare the Data Evaluation Record (DER) according to the Standard Format for Preparation of Environmental Fate Reviews. Appendices B-D should be used in this process.

1. Write the Technical Evaluation

In the DER of the study, the reviewer is to record (1) whether the submitted study reliably defines the rate of aqueous photolysis

of the a.i., and (2) the identity of the photoproducts present at > 10%. The identity of photoproducts present at < 10% of the initial dose may be needed in cases where high concentrations of parent compound are applied to or may be found in aqueous systems.

2. Determine Study Acceptability

From the scientific point of view, the reviewer now determines if the study satisfies the aqueous photolysis data requirement in light of the proposed use.

3. Make Regulatory Determination

Based on the scientific results of the aqueous photolysis study, the reviewer now makes a statement on the impact the photolytic fate of the pesticide will have on the environment, such as persistence in water.

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

If the parent compound or any of its degradation products are found to be stable to aqueous photolysis, then it may impact on ground water and/or aquatic organisms. Referral of this information should be made to the appropriate branches in HED after review of the other environmental fate studies.

APPENDIX A

GENERAL THEORY AND REFERENCES FOR EVALUATING AQUEOUS PHOTOLYSIS STUDIES

Photolysis is the interaction of a compound with light in which bonds are broken as a result of the transfer of energy to those bonds.[4] While photolysis is viewed as a degradation process, compounds are not necessarily broken down into constituent parts or simpler compounds. Sunlight can transform the original compound into compounds of similar or even greater structural complexity.[5]

The energy transfer can occur in two ways: (1) directly from the light to the affected compound or (2) indirectly from the light to another compound which then transfers the light energy to the affected compound. The latter process is called sensitized energy transfer.[6]

The basic law of photochemistry states that only light which is absorbed can effect chemical change in a system.[7] The relationship of wavelength to the energy of one photon of radiation is derived from the following equations:

$$E = h\nu \; ; \quad \nu = c/\lambda \; ; \text{ therefore, } E = hc/\lambda$$

where E is the energy in ergs, ν is the frequency in $time^{-1}$, h is Planck's constant (6.6×10^{-27} erg sec), c is the velocity of the radiation in cm $time^{-1}$ and λ is the wavelength in cm.[4] Thus, the energy at any frequency can be calculated. Using this equation and comparing typical bond dissociation energies with energy levels associated with molecular transitions in different absorption regions, one finds that only electronic transitions from the UV/visible absorption region are energetic enough to lead to chemical reactions.[8] Since "the stratospheric ozone layer effectively prevents UV irradiation of less than 290 nm from reaching the ecosphere,"[8] the absorption region of interest is narrowed to 290-750 nm.[8]

APPENDIX B

INFORMATION SUBMITTED AS PART OF THE AQUEOUS PHOTOLYSIS STUDY

1. The goals of the experiment.
2. Chemical name, common name, trade name, company designations and structures of both the active ingredient (a.i.) and the photolytic products.
3. Water solubility of the a.i..
4. Source and purity of the a.i..
5. Site of radiolabeling (if applicable).
6. Source and purity of the water.
7. Concentration of a.i. at which the study was conducted.
8. Buffer solution(s) used and how it (they) was (were) prepared.
9. Description of experimental equipment (glassware, analytical equipment, artificial lighting arrangement, etc.).
10. Complete description of the analytical procedure (See Appendix D.).
11. Test conditions (temperature, sterility, pH and darkness).
12. Method for adding the a.i. to the buffer solution.
13. Means of sterilization.
14. Means and technique of sampling and handling of sample.
15. Storage of samples (if applicable).
16. Rate of photolysis of the a.i. and the identity of the photolysis products.
17. Cosolvent (if applicable).
18. For artificial light sources: the nature of the light source, its emission wavelength spectrum and intensity and their relationship to that of natural sunlight.
19. For sunlight sources: the latitude, time of year, atmospheric cover, and other major variables affecting incident light.

20. Method of calibrating and measuring the intensity of incident light.

21. The intensity of incident light and time of exposure with duration of dark and light periods.

22. Quality assurance. A complete description of the measures taken to insure the integrity of the study. This section should include: logbooks and/or record-keeping procedures; representative instrument printouts (chromatograms, spectra, etc.); sample coding; use of replicate samples and control blanks; use of written and validated analytical methodology, including modification(s) made; skilled laboratory personnel; well-equipped laboratory facility; use of high quality glassware, solvents, and test compounds; minimal contamination; calibration and maintenance of instruments; good laboratory practices in handling the test substance(s).

23. Contact for questions from the reviewer.

24. Raw data, sample chromatograms and sample calculations on how the photolysis rates were derived and how the photolysis products were identified.

25. Special problems with the study such as adhesion of a.i. to the test equipment, a.i. insoluble in water, emulsion formed, buffer catalysis, etc..

APPENDIX C

CONSIDERATIONS IN REVIEWING AQUEOUS PHOTOLYSIS STUDIES

1. Were the name and structure of the parent and photoproduct(s) provided?

2. Was the temperature controlled at 25 $\pm$ 1°C and monitored?

3. Was the cosolvent $\leq$ 1% by volume?

4. Was the cosolvent determined to be a non-photosensitizer?

5. Was the appropriate buffer type used?

6. Was the buffer at the appropriate concentration?

7. Was the starting concentration high enough to permit the isolation and identification of photoproducts formed?

8. Were precautions taken to minimize losses through volatilization?

9. Were appropriate traps utilized to contain volatile products for analysis?

10. Was a test made for the possible binding of the test compound to the surface of the reaction vessel?

11. Was the pH of greatest hydrolytic stability in the pH range of 5-9 used as determined by the hydrolysis study?

12. For compounds which are not hydrolytically stable in the pH range of 5-9, was the rate study done at pHs 5, 7 and 9 for compounds which reversibly ionize or protonate within the pH range of 5-9?

13. Was the study done under sterile conditions to minimize biological degradation?

14. Was the radiolabel in a stable portion of the compound?

15. Were sufficient samples taken and at appropriate times during the study? Were adequate replicates made?

16. Did the study continue through at least 1 half-life or 30 days, whichever came first?

17. Were there controls, prepared and maintained as for the other samples, except that they were kept in the dark?

18. For sunlight as the source, were the following given:

    - a record of the intensity of incident sunlight?
    - time of exposure?
    - latitude?
    - time of year?
    - atmospheric cover?
    - other major variables which affect incident light?

19. For artificial light as the source, were the following given:

    - description of the source?
    - intensity?
    - wavelength distribution? (emission spectrum)
    - time of exposure?
    - the relationship of the light intensity employed to that of natural sunlight?

20. Were filters used in the experimental apparatus to remove wavelengths below 290 nm?

21. Were photoproducts produced in >10% yield identified?

22. Was there a good material balance?

23. Was a half-life estimate made for the parent compound?

24. Was there an impurity in the a.i. that would interfere with the analytical method?

25. Was the analytical method adequately described? Were statistics verifiable?

26. Were raw data and samples of analytical data sheets, chromatograms, calculations, etc., given?

27. Were control samples, prepared and handled the same as the pesticide treated study samples, run in each experiment?

APPENDIX D

TEST PARAMETERS INFLUENCING AQUEOUS PHOTOLYSIS

1. Experimental Design

From the considerations of Appendix C, the reviewer must draw some conclusions about the influence of the experimental design on the validity of the study for the proposed use. Some questions the reviewer should answer are:

1. Was sunlight, if used, representative of the area of proposed use?

2. Did the emission wavelength spectrum of the artificial source, if used, simulate that of natural sunlight?

3. Was the pattern of light and dark given and was it reasonable for the proposed use pattern (i.e., 12 hours of light/12 hours of dark per day; 16 hours of light/8 hours of dark per day, etc.)?

4. Was the relationship of the intensity of the artificial sunlight used appropriate to that of natural sunlight in the area and for the time of the planned use?

5. Was a suitable method used for measuring the intensity of incident light?

Other aspects of the experimental design which influence the aqueous photolysis study are concentration, sterile conditions, and competing natural processes.

Since experience has shown that photolysis proceeds by first-order or pseudo first-order kinetics at high doses,[9] the starting concentration of the pesticide in the aqueous photolysis study need not be at the expected low environmental levels but may be at a high enough level to define the reaction kinetics and permit the isolation and identification of the photoproducts formed.

The study should be conducted under sterile conditions to eliminate biological metabolism and at a pH between 5 and 9 of maximum hydrolytic stability to minimize hydrolysis. In the case of compounds which reversibly ionize or protonate within the pH range of environmental concern (pH 5-9), aqueous photolysis rate determination studies should be conducted at pHs 5, 7, and 9.

Photolysis competes in nature with both biological metabolism and hydrolysis.[4] Under actual environmental conditions, one process may predominate over the others. The reviewer must be aware that photoproducts produced in a laboratory aqueous photolysis study may not be found in water in the environment[4] if hydrolysis or metabolism is the major pathway of environmental degradation.

2. Buffers

See the discussion of buffers in the hydrolysis SEP for consideration of choice and concentration.

Cosolvents have been used in aqueous photolysis studies to increase the solubility of pesticides with low water solubilities.[10, 11] Preferably, cosolvents should be used only when absolutely necessary to solubilize water-insoluble pesticides bringing them to a starting concentration sufficient to allow the study to proceed. The cosolvent should not exceed 1% by volume and should not act as a photosensitizer. Cosolvents should not be photosensitizers, nor should they absorb light in the range of concern. Methanol and acetonitrile are the preferable cosolvents for aqueous photolysis.[12]

3. Nature of Light and Factors Affecting the Incident Light

The reviewer should be aware that photolysis rate constants and half-lives in the environment will vary with weather conditions and with time of year[6] as well as with latitude and atmospheric conditions[7] (See Figures 1 and 2 showing the effects of season and latitude on the intensity of short and long wavelength sunlight.[7]). Therefore, when artificial light is used, the spectra should be similar to that of natural sunlight at a typical use site. The inclusion of the absorption spectrum of the test compound can aid the reviewer in deciding if the appropriate light source has been used.

Various kinds of glass absorb and transmit different wavelengths.[8] Therefore, the kind of glass (both in vessels and filters) should be specified and its transmissibility considered in evaluating the adequacy of the study. Also, the reference which gives the transmissibility of the glass should be current, as the glass manufacturing processes have changed with a concomitant change in transmissibility of glass batches.[13] Quartz is the glass of choice;[12] borosilicate glass is acceptable to some[12] but not others;[12a] therefore, its transmissibility should be defined. The reviewer should also be aware that borosilicate glass varies with manufacturer.[12]

4. Radiolabeling

Use of radiolabeled pesticide provides easier accountability of material balance as well as easier identification of degradation products than use of non-radiolabeled starting material. If radiolabeling is done, it should be in a stable portion of the molecule. For a more complete discussion of the use of radiolabeling in studies submitted to EAB see the Standard Evaluation Procedure for Hydrolysis.

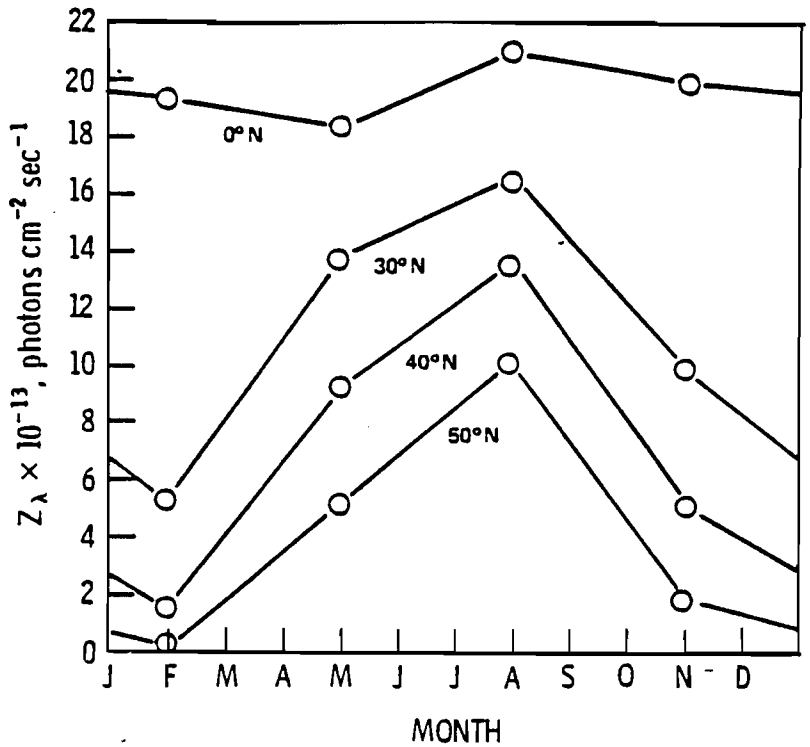

Fig. 1 Dependence of short-wavelength solar uv irradiance ppon season and latitude

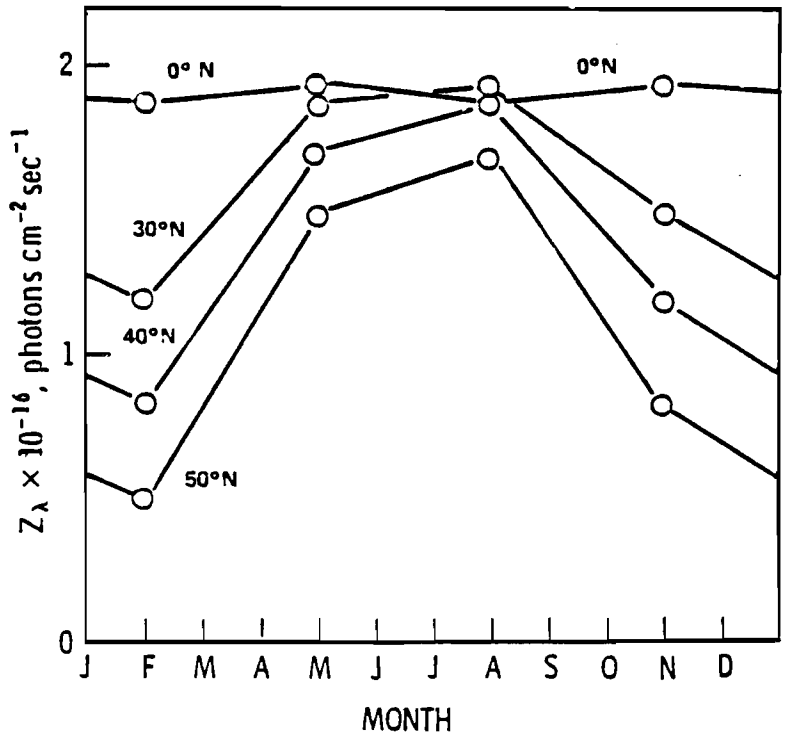

Fig. 2 Dependence of long-wavelength solar uv irradiance upon season and latitude

5. Mass Balance

All of the radioactivity used in the experiment must be accounted for to ensure that all the photolysis products have been detected and that the fate of all of the starting material is understood. The reviewer must be able to ascertain that the data on the mass balance are adequate. Generally the study results should account for $\geq$ 95% of the starting mass (as represented by the radioactivity when employed). An explanation should accompany any study which is not able to account for at least 95% of the starting mass.

Care must be taken to ensure that no products are lost due to volatilization. Therefore, traps should be used to monitor the possible production of volatile photolysis products. Also, consider possible binding of the pesticide to the surface of the test equipment which can occur unexpectedly, resulting in an unaccountable loss of mass and possible invalidation of the study.

6. Photosensitization

Although the Subdivision N Guidelines[1] provide for a "supplemental rate and photoproduct identification study" which "may also be carried out in the presence of a photosensitizer," the reviewer should request a photosensitized study for each pesticide, since most, if not all, natural waters contain photosensitizers.[14, 15, 16] Any pesticide reaching natural water is likely to encounter a photosensitizer.

7. Duration/Sampling

A study duration of 30 days is usually sufficient to establish whether a compound will be resistant to photolysis. As a practical matter, if less than about 10% of the pesticide photolyzes within 30 days, the pesticide will be considered photolytically stable in water.

Generally, aqueous photolysis studies of 30 days duration will suffice, since dilution in the environment is likely to reduce any concerns by that time. However, in cases in which dilution is not likely to occur at a significant rate; e.g., ditch bank empoundments, ponds, etc., then consideration must be given to experiments of longer duration.

Samples should be taken for analysis at four or more time intervals with at least one sample made after one half-life or at 30 days of natural sunlight (about 12 hours of light/12 hours of dark per day) whichever comes first. The number and timing of the samples will depend on the half-life of the compound and should define the pattern of decline of the pesticide undergoing photolysis.

8. Analytical Method

A detailed description of the analyses used to determine the parent and photoproducts should be given. The following information should be included:

1. Name (and signature), title, organization, address, and telephone number of the person(s) responsible for the planning/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, other].

4. Principles of the analytical procedure [describe].

5. Non-Confidential Business Information (non-CBI) copy of the analytical method(s) detailing in step-wise fashion the procedures (extraction, clean-up, derivatization, determination, calculation of the magnitude of the compound(s)).

6. Reagents or procedural steps requiring special precautions [to avoid safety and health hazards, explain].

7. Identification of the chemical species determined.

8. Modifications, if any, to the analytical method(s) [detail].

9. Extraction efficiency [if pertinent].

10. Instrumentation [make/model; type/specificity of detector(s); column(s) (packing materials, size); carrier gas(es); flow rate(s); temperature(s); voltage; limit of detection and sensitivity; calibration procedures; etc.].

11. Interference(s), if any [describe].

12. Confirmatory techniques [e.g., different column packing(s) or detector(s), etc.].

13. Sample identification [coding and labeling information; should be the same as - or cross-referenced to - the sample coding/labeling assigned at harvest].

14. Results [raw data; laboratory worksheets; step-wise calculation of levels; dilution factors; peak heights/areas; method correction factor(s) applied (e.g., storage stability and method validation recovery values); formula(e)/standard curve(s)

used; amount found of total applied, and of individual component(s) (i.e., photoproducts); range of values; representative chromatograms, spectra, etc. (as applicable) from control and treated samples; etc.].

15. Statistical treatment(s) [describe test(s) applied to the raw data].

16. Quality assurance [control measures/precautions followed to ensure the fidelity of determinations, including logbooks and record-keeping procedures; representative instrument print-outs (chromatograms, spectra, etc.); sample coding; use of replicate samples and control blanks; use of written and validated analytical methodology for analyses, including modification(s) made; skilled laboratory personnel; well-equipped laboratory facility; use of high-quality glassware, solvents, and test compound(s); minimize contamination; calibration and maintenance of instrumentation; good laboratory practices.

17. Time required for analysis [to carry a sample completely through the analytical procedure, including the determinative step].

18. Other [any and all additional information the registrant considers appropriate and relevant to provide a complete and thorough description of residue analytical methodology and the means of calculating the residue results].

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HAZARD EVALUATION DIVISION

STANDARD EVALUATION PROCEDURE

HYDROLYSIS STUDIES

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16. Abstract (Limit: 200 words)

The Standard Evaluation Procedure for the Hydrolysis Studies is a guidance document primarily intended for Agency reviewers and the regulated industry who evaluate data specified in 40 CFR Part 158.124. The SEP is also intended to provide information to the general public indicating how the Agency evaluates these types of studies. As such, it is designed to supplement Subdivision N of the Pesticide Assessment Guidelines - Chemistry: Environmental Fate.

The SEP for Hydrolysis Studies is only one of a number of SEP's published by the National Technical Information Service as a supplement to Subdivision N of the Pesticide Assessment Guidelines.

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John W. Melone

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I. INTRODUCTION

A. Objective

This Standard Evaluation Procedure (SEP) is to be used as an aid for data reviewers in the Exposure Assessment Branch while reviewing hydrolysis studies submitted by registrants in support of pesticide registration.

40 CFR Part §158.130 requires hydrolysis studies to be conducted with each pesticide active ingredient intended for use outdoors. The section in the Subdivision N Guidelines which describes this study and provides sample protocol is 161-2. Section 160-5 of the Guidelines gives general guidance on the reporting of data.

B. General Theory

Since outdoor-use pesticides can be applied directly to aquatic systems or can enter aquatic systems via leaching or runoff after terrestrial application, knowledge of the hydrolytic fate of pesticides is critical to understanding the overall fate of pesticides in the environment.

Hydrolysis refers to the reaction of a compound with water during which bonds in the compound are broken and a net exchange between some group X on the compound with OH of water at the reaction center occurs. For background information and theory on the hydrolysis reaction, refer to Appendix A.

II. THE SUBMITTED STUDY

A. Purpose

The hydrolysis study is to be designed and conducted in such a way as to reliably provide the rate of hydrolysis of the parent compound, rates of formation and decline of hydrolysis products, and the identity of the hydrolysis products.

B. Study Design

The submitted hydrolysis study should provide sufficient information on experimental design, the test substance and the experimental procedures. For a list of the information to be included in the submitted hydrolysis study, refer to Appendix B.

III. THE EVALUATION PROCESS

A. Determine the Need for the Study

For all data submitted as part of a registration action, the reviewer is to first determine whether the data is needed in support of the proposed use. If an initial look at the study reveals that the data supplied is not relevant and not needed to support the proposed registration action, then the reviewer should only mention in the review that the particular study was submitted but was not reviewed in detail and why.

Hydrolysis data is needed for all outdoor use pesticides; therefore, the hydrolysis study will always be reviewed in detail except in cases where the submitted study provides only hydrolysis information already known from the earlier review of other hydrolysis studies.

B. Read the Report

Read the hydrolysis report keeping the following broad issues in mind: (1) Are the goals appropriate, (2) Was the study conducted in a scientifically sound manner to meet those goals, (3) Were the experimental design, test substance and experimental procedures adequately described and, (4) Are there data gaps that impede the review process or invalidate the study?

When reading the study, the reviewer should note whether all necessary descriptive information has been supplied in the report. Some descriptive information is so critical to the review process, such as the temperature at which the study was run, that its absence can result in not allowing the review to proceed while the absence of some information, such as loss of a single sample, will only minimally affect the review process.

C. Prepare the Data Evaluation Record

The reviewer should now prepare the Data Evaluation Record (DER) according to the Standard Format for Preparation of Environmental Fate Reviews. Appendices B-D should be used in this process.

1. Write the Technical Evaluation

In the DER of the study, the reviewer is to record (1) whether the submitted study reliably defines the rate of hydrolysis of the a.i., (2) the rates of formation and decline of the hydrolysis products and (3) the identity of the hydrolysis products.

2. Determine Study Acceptability

From the scientific point of view, the reviewer now determines if the study satisfies the hydrolysis data requirement in light

of the proposed use.

3. Preparations for Making the Final Regulatory Determination

Based on the scientific results of the hydrolysis study, the reviewer now makes a statement on the possible impact the pesticide could have on the environment such as in ground water and/or surface water due to its hydrolytic persistence. This statement will be considered with similar statements from the review of the other environmental fate studies in making the final regulatory determination.

4. Determine Need for Deferral/Referral to other HED Branches

If the parent compound or any of its degradation products are found to be stable to hydrolysis, then it may impact on ground water and/or aquatic organisms. Referral of this information and other information relating to impact on ground water should be made to the appropriate branches in HED.

APPENDIX A

GENERAL THEORY AND REFERENCES FOR EVALUATING HYDROLYSIS STUDIES

In the hydrolysis of organic pesticides, a carbon-oxygen bond is often broken although carbon bonds with nitrogen, sulfur, and halogens can also be broken during hydrolysis.[1] Also, phosphorus-oxygen and phosphorus-sulfur bonds are susceptible to hydrolysis.[2]

Pesticides and water can react through several different mechanisms; however, the physico-chemical hydrolysis reactions that occur under conditions typically found in the environment (i.e., pH 5-9 and temperatures of 15-35°C) are usually either the substitution nucleophilic (S_N1 and S_N2) reactions[3] or ester hydrolysis.[4] In addition, an elimination (E_2) mechanism has been found to be responsible for the hydrolysis of dibromochloropropane (DBCP) under environmental-like conditions.[5] For an in-depth discussion of these mechanisms and more information on hydrolysis, the reviewer is referred to the excellent texts available.[6, 7, 8]

APPENDIX B

INFORMATION SUBMITTED AS PART OF THE HYDROLYSIS STUDY

The goals of the experiment.

Chemical name, common name, trade name, company designations and structures of both the a.i. and the hydrolysis products.

Water solubility of the a.i..

Source and purity of the a.i..

Site of radiolabeling (if applicable).

Source and purity of the water.

Concentration of a.i. at which the study was conducted.

Buffer solutions used and how they were prepared.

Description of experimental equipment (glassware, analytical equipment, etc.).

Complete description of the analytical procedure.

Name and signature, title, organization, address and telephone number of the persons responsible for all aspects of the laboratory procedures and analytical work.

The title, date of development and source of the analytical method (company developed, taken from the literature, etc.)

A description of the principles of the analytical method.

A copy of the method containing all steps of the procedure in detail. Especially describe those steps involving special precautions (to avoid safety or health hazards, etc.; explain). Describe any modifications made to the method.

Extraction efficiency.

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

Interferences (if any).

Confirmatory techniques used.

Statistical treatment of data.

Other appropriate and relevant information needed to provide a thorough and complete description of the analytical methodology and the means of determining the results of the study.

Conditions of test solution (temperature, sterility, pH and darkness).

Method for adding the a.i. to the buffer solution.

Means of sterilization.

Means and technique of sampling and handling of the sample.

Storage of samples (if applicable).

Tables of results (raw data, sample calculations of concentration of analytes, correction factors applied, etc.).

Rate of hydrolysis of the a.i., rates of formation and decline of hydrolysis products and the identity of the hydrolysis products.

Cosolvent (if applicable).

Quality assurance - A complete description of the measures taken to ensure the integrity of the study such as logbooks, record-keeping procedures, sample chromatograms, sample coding, skilled personnel, use of high quality glassware/compounds/solvents, calibration and maintenance of instruments, etc.).

Contact for questions from the reviewer.

Raw data, sample chromatograms and sample calculations on how the hydrolysis rates were derived and how the hydrolysis products were identified. Also, method validation and recovery data.

Special problems with the study such as adhesion of a.i. to the test equipment, a.i. insoluble in water, emulsion formed, buffer catalysis, etc..

APPENDIX C

CONSIDERATIONS IN REVIEWING HYDROLYSIS STUDIES

Were the stated goals of the study appropriate and clearly defined? Was the study conducted in a scientifically sound manner to accomplish those goals?

Has the name and structure of the a.i. been provided?

Did the starting concentration exceed the water solubility?

Was the starting concentration too high?

Were there impurities in the a.i. that would interfere with the analytical method?

Was the site of radiolabeling in a stable portion of the a.i.? Was an appropriate isotope used?

Were the buffer solutions adequately described?

Did the pH of the buffer solutions change during the study?

Were sterile conditions maintained? Could microbial degradation affect the study?

Was the analytical procedure adequately described? Were raw data, sample chromatograms and sample calculations provided? Were the statistics verifiable?

Was the study conducted at an appropriate temperature and at suitable pHs? Was the temperature maintained? Did the pH change during the experiment? Does the use pattern dictate that the study be run under conditions outside of those recommended by the Subdivision N Guidelines (Refer to Appendix D)?

If the study was conducted while exposed to light, does photolysis contribute to degradation?

If cosolvent(s) were used, did they affect the degradation rate? Will another study be needed using less cosolvent to determine this?

Were there buffer catalysis effects?

Was there a good mass balance? If not, was the loss of material accounted for? Is the study invalid due to unaccounted for material?

Was the study conducted long enough?

Were samples taken frequently enough to establish the kinetics? Were replicates taken? Was the study of sufficient duration (Refer to Appendix D)?

Were samples stored between the time of sampling and analysis? How long? Were the conditions of storage described? Are the a.i. and its hydrolysis products stable under the storage conditions? If stored, how were the samples prepared for analysis upon removal from storage?

Was the test solution sampled immediately after addition of the a.i.?

Were appropriate solvents used for extraction/partitioning?

Is the study of such low quality or are there so many questions that you would recommend there be a lab audit?

Were the reported method sensitivity and limit of detection appropriate?

Were the kinetics of the study determined correctly?

Are the results of the study supported by the results of similar studies? Refuted by the results of similar studies?

Would residues of the a.i. and/or its hydrolysis products persist in ground water?

Was the study conducted with good quality control procedures? If applicable, determine if additional hydrolysis data are needed (such as a long-term hydrolysis study) even though the data requirement may be satisfied. Does the hydrolytic fate of the compound pose special problems or questions affecting other environmental fate studies or studies of importance to other HED branches? (For example, does a significant hydrolysis product form which should be highlighted in the review and perhaps be referred to the Toxicology or Ecological Effects branches?) Do data submitted as part of other environmental fate studies (such as the dark control of the photolysis study) support or refute the results of the hydrolysis study? Should a time limitation be imposed for submitting additional hydrolysis data?

Does the study support the proposed use?

See Appendix D for an explanation of the significance of some of the test parameters influencing hydrolysis.

APPENDIX D

TEST PARAMETERS INFLUENCING HYDROLYSIS

pH, Temperature, Light Conditions, and Initial Concentration

The Agency has received and reviewed pesticide hydrolysis studies at every pH between 1 and 14 and at temperatures between 5 and 100°C. However, applied pesticides usually do not encounter a pH outside the range of 5-9. Likewise, temperatures during the time of use of most pesticides do not usually vary outside of the 15-35°C range. Therefore, a hydrolysis study conducted at 25°C and pHs of 5, 7, and 9 would, in most cases, be adequate to describe the hydrolytic fate of the pesticide under ordinary use conditions. The temperature of the reaction should be precisely controlled since an uncertainty of ± 1°C in temperature roughly corresponds to a change of ± 10% in the rate (k_T).[3] Environmental temperatures of surface aqueous systems vary much more than 1°C on a monthly or even a daily basis. However, duplicating this natural fluctuation in temperature in the lab would not be practical. On the other hand, the temperature of deeper ground water has been found to be relatively constant.[9]

Some researchers prefer to conduct hydrolysis at temperatures between 50 and 80°C to speed up the reaction and then determine the rate constant at 25°C using the Arrhenius equation:

$$k = Ae^{-E_A/RT}$$

where: k is the rate constant ($time^{-1}$);

E_A is the Arrhenius activation energy (kcal/mol);

R is the gas constant (1.987 cal/deg·mol);

T is the temperature (°K); and

A is a pre-exponential factor with the same units as k.

However, it is probably prudent to regard rate data obtained by extrapolation as order-of-magnitude estimates[3] and to request that hydrolysis studies be conducted at 25°C.

There are some pesticide use conditions, both agricultural and non-agricultural, that would result in pesticide usage out-

side the pH and/or temperature ranges noted above. For example, pesticides may be used in acidic environments (e.g., azaleas whose optimum soil pH is as low as 4.5,[10] highbush blueberries which grow in soils with pH as low as 4.0,[11] paper mills with pHs of 4.3 and 11.0,[12] and in mosquito breeding areas where the pH may be 3.6[13]) or at temperatures significantly above or below 25°C (e.g., paper mills and oil production fields where pesticides are added to solutions of temperatures 44-63°C[12] and 0-76°C,[14] respectively). Use of pesticides under these special situations should be supported with hydrolysis experiments conducted under these unique conditions of pH and temperature.

Since photolysis of organic compounds can occur under normal laboratory lighting conditions[15], the hydrolysis study should be conducted in darkness thereby eliminating photochemical mechanisms of degradation.

It is also important to periodically check the pH of the buffered test solution to be sure the desired pH is being maintained.

The hydrolysis study should be conducted at a starting concentration approximating the maximum concentration at which the pesticide might be expected to be found in the aquatic environment (although the Guidelines[16] allow a maximum starting concentration of 250 ppm). This is usually around 100 parts per billion for ground water contaminants[17] and for compounds partitioning into the soil water after terrestrial application to 1-20 parts per million for compounds applied to aquatic surface systems for the control of aquatic pests. Therefore, typical starting concentrations are 0.1-20 parts per million.

Levels of some pesticides may be found in aquatic systems at concentrations much less than the starting concentration of the pesticide in the hydrolysis study and there may be concern that the hydrolysis data may, therefore, not be indicative of hydrolysis that would occur in the environment. However, it has been generally observed that the rate of aqueous hydrolysis of organic compounds is first-order in the concentration of the solute and the rate of disappearance of the solute is directly proportional to its concentration,[3] as expressed by the equation:

$$\frac{-d[RX]}{dt} = k_T[RX]$$

where: [RX] = concentration of the solute; and

k_T = the hydrolysis rate constant.

Since rate processes found to be simple at high concentrations remain simple at lower starting concentrations,[18] conclu-

sions derived from hydrolysis studies conducted at concentrations recommended by the Guidelines[16] should be valid for hydrolysis occurring at the lower expected environmental concentrations.

However, there have been cases where different rates of hydrolysis have been observed for the same compound with the only variable being the starting concentration. Such differences in rate might be due to adsorption onto the surface of the reaction flask or to catalysis effects[19] resulting from the necessity to use a higher buffer concentration with a high starting concentration of the parent material.

The reviewer should verify that the reported inital concentration does not exceed its water solubility.

Radiolabeling

Use of a radiolabeled pesticide provides easier accountability of material balance and an easier identification of degradation products than use of non-radiolabeled starting material. Generally, lower starting concentrations can be used due to the higher sensitivity of radio detectors over conventional analytical methods.

Carbon atoms are the most convenient atoms to tag in the starting material due to the 5,730 year half-life[20] and relative ease of handling of ^{14}C material. However, some aldicarb studies using ^{35}S, which has an 88 day half-life,[20] have been successfully done.[21] Although many pesticides contain chlorine, and ^{36}Cl has a 3.1×10^5 year half-life,[20] use of ^{36}Cl to radiolabel pesticides is not done due to its high expense and the additional safety procedures needed.[22] Although ^{32}P has been used for metabolism studies of organo-phosphorus pesticides, it is generally not used for hydrolysis studies due to its relatively short half-life of 14.3 days.[20] Tritium (^{3}H), with a half-life of 12.3 years,[21] has been used successfully to tag pesticides for use in environmental fate studies. However, the registrant must show that proton exchange will not interfere with the experiment.

Radiolabeling should be done in a stable position of the molecule. Tagging a carbon that would be rapidly released as $^{14}CO_2$ would not be appropriate. Also, if the molecule breaks into two or more significant fragments, it may be necessary to label the parent compound in more than one site so that the hydrolytic fate of each fragment may be followed.

Mass Balance

All (> 95%) of the radioactivity used in the experiment should be accounted for to ensure that all the hydrolysis products have been quantified and that the fate of all of the starting material is understood. The reviewer must be able to ascertain that the

data on the mass balance are adequate. Traps to monitor possible production of volatile hydrolysis products must be used. Also, binding of pesticide to the surface of the test equipment should be considered. This binding can unexpectedly occur resulting in what would appear to be unaccounted mass thus invalidating the study.

Duration/Sampling

Sampling must be conducted for a period of time sufficient to define the rate of decline of the pesticide as well as the rate of appearance and decline of the degradation products. It is desirable that samples be taken over two half-lives to ensure that any deviations from the presumed first-order linearity are detectable.[3]

Since the Agency frequently uses the hydrolysis reaction rate with models for estimation of a pesticide's environmental concentration, accurate rate data are needed.[19] It is recognized that environmental variables which can affect the hydrolysis rate vary dramatically and this fact tempers the need for highly accurate rate data. Therefore, a sampling regimen which approaches the following and includes sampling immediately after addition of the pesticide to the buffer solution would provide sufficient precision.

> "Take a minimum of six regularly spaced, duplicate samples all taken between 20% and 70% hydrolysis with ± 4% precision. When only 20-30% hydrolysis occurs in the first several weeks, then 15-20 samples should be taken between 10-30% hydrolysis."[23]

A study duration of 30 days is usually sufficient to establish whether a compound will be resistant to hydrolysis. As a practical matter, if less than about 10% of the pesticide hydrolyzes within 30 days, the pesticide will be considered to be hydrolytically stable.

Generally, hydrolysis studies of 30 days duration will suffice, since dilution in the environment is likely to reduce any concerns by that time. However, in cases in which dilution is not likely to occur at a significant rate; e.g., ditch bank empoundments, ponds, ground water, etc., consideration must be given to experiments of longer duration.

Cosolvents

The solvent composition chosen can affect both the rate of the hydrolysis reaction and the products formed.[24] Use of a 100% aqueous system is ideal but a cosolvent concentration of $\leq$ 1% (of the common organic solvents) will not significantly

impact on the reaction. Preferably, cosolvents should be used only when absolutely necessary to solubilize water-insoluble pesticides to a starting concentration sufficient to allow the study to proceed.

Buffers and Catalysis Effects

Buffers should be used at the lowest concentration possible due to possible catalysis effects. In general base catalysis, the basic component of the buffer attracts a proton from water molecules, polarizing the water molecules thereby increasing their nucleophilicity and resulting in more hydrolysis.[25] In general acid catalysis, the acidic component of the buffer attracts the leaving anion of the pesticide, thereby polarizing the pesticide and causing greater attraction for hydroxyl groups at the partial positive site.

To minimize buffer effects, it is recommended that borate or acetate buffers rather than phosphate buffers be used whenever possible.[18] Also, since the starting concentration of pesticide is less than 10^{-4}M, the buffers may be used at 0.01M concentrations to keep the pH constant, concentrations which largely reduce the likelihood of buffer effects.[18]

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PESTICIDE ASSESSMENT GUIDELINES

SUBDIVISION N

CHEMISTRY:

ENVIRONMENTAL FATE

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16. Abstract (Limit: 200 words)

This document, Subdivision N, is intended to support 40 CFR 158 requirements for data for the registration of pesticides. Subdivision N describes the Agency's requirements for data on the degradation, metabolism, mobility, dissipation, and accumulation of pesticide chemicals in the environment. These data will be used to identify and assess the potential hazards associated with the uses of a pesticide.

Subdivision N constitutes one volume of a twelve-part FIFRA guideline series published by the National Technical Information service.

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b. Identifiers/Open-Ended Terms

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c. COSATI Field/Group

18. Availability Statement

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20. Security Class (This Page)

(See ANSI-Z39.18) See Instructions on Reverse OPTIONAL FORM 272 (4-77) (Formerly NTIS-35) Department of Commerce

Foreword

Subdivision N describes protocols which may be used to perform environmental fate testing to support the registration of pesticides under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). It is a non-regulatory companion to 40 CFR Part 158, Data Requirements for Registration. A public meeting was held in July, 1982 to accept comments on the FIFRA guidelines. Because of the importance of the issues raised in the Subdivision N comments, a review committee comprised of representatives of industry, environmental groups and academia read and approved the Agency revision. This guideline refers to requirements established in 40 CFR Part 158 so that this document can be read as a complete package and so that the protocols may be explained in their proper context.

Subdivision N

ENVIRONMENTAL FATE

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I. ORGANIZATION AND PHILOSOPHY

A. Purpose

The data generated by the environmental fate studies described in these guidelines are used by the Agency, along with other data, to assess the hazards posed by use of a pesticide product, in order to determine whether the product should be registered. In particular, the Agency needs these data to assess:

(1) Direct consequences to man through exposure to pesticide residues remaining after application, either upon reentering treated areas or from consuming inadvertently-contaminated food;

(2) Indirect consequences to man from the presence of widely distributed and persistent pesticide residues in the environment which may result in loss of usable land, water, and wildlife resources; and

(3) Potential environmental exposure of other nontarget organisms such as fish and wildlife to pesticide residues.

Another specific purpose of the environmental fate data requirements is to help registration applicants and the Agency estimate expected environmental concentrations of pesticides in specific habitats where endangered species or other populations at risk are found.

Pesticides can be introduced into the environment by application to water, soil, and air. Following introduction to any of these media, pesticides may be transported from one medium to another by processes that are partly influenced by the chemical characteristics of the pesticide. Transport is also influenced by physical forces in the environment such as meteorological conditions, flow of surface water, location and flow of ground water, tidal action, and topographic characteristics. The physical and chemical characteristics of soil, sediments, particulates, and water also influence the transport and fate of pesticides.

No single test scheme can predict precisely the length of time a pesticide will remain in one particular location, or by what mechanism and at what rate it will be transported, transformed, or degraded. A test sequence at best can provide data which a skilled evaluator can integrate with other information to provide a rough estimate of the concentration of the pesticide and a tentative conclusion about its persistence or rate of disappearance. On the basis of such conclusions, the evaluator can often rule out the

possibility of a pesticide entering certain environments at a concentration that presents a significant risk to man and/or nontarget organisms. On the other hand, the pesticide may enter certain environments at a concentration that would present a significant risk. In these situations, field monitoring studies may provide the information necessary to evaluate the significance of the risk to nontarget organisms.

B. Approach

Proposed rule, 40 CFR Part 158, specifies the kind of data and information that must be submitted to EPA to support the registration of each pesticide under the Federal Insecticide, Fungicide and Rodenticide Act. The Agency intends to promulgate Part 158 as a final rule during 1983. This subdivision provides detailed information that should be included in a test report.

The guidelines also describe circumstances under which an applicant should consult with the Agency before initiating a test. In addition, the references specified in these guidelines provide useful information for designing test protocols and, in some cases, examples for acceptable protocols for conducting the required testing.

The sections of this subdivision of the guidelines have been reorganized since they were proposed as rulemaking in 1978. The following description of the section series, complete with new numbers and the corresponding numbering system as proposed July 10, 1978, will explain this reorganization.

Section 160-1 "General Information" (formerly § 163.62-1 "Purpose: Hazard Evaluation" and § 163.62-3 "Scope and Requirements") describes the purpose of the prescribed environmental fate studies as they relate to environmental hazard assessment. Two tables have been included which summarize the basic Part 158 environmental fate data requirements as they relate to intended use patterns of a pesticide.

Section 160-2 "Definitions" (formerly § 163.62-2) contains definitions of terms used in this subdivision.

Section 160-3 "Use Patterns" (formerly § 163.62-6 "Use Patterns Associated With Data Requirements") categorizes use patterns of pesticides intended for outdoor application.

Section 160-4 "General Test Standards" (formerly § 163.62-4 "Basic Standards for Testing") provides a discussion of the general requirements for test design and test substances applicable to most tests.

Section 160-5 "Reporting and Evaluation of Data" (formerly § 163.62-5 "Reporting of Data") provides reporting requirements that apply to most or all studies.

Section series 161 through 165 (formerly §§ 163.62-7 through 163.62-11) contain specific provisions pertaining to each of the studies required to support the registration of manufacturing-use and end-use products. Each of the five sections series pertains to a single test or related group of tests.

Thus, §§ 161-1 through -4 (formerly § 163.62-7 "Data Requirements: Degradation") relate to physicochemical degradation of pesticides in the environment and describe data requirements for studies of hydrolysis and photodegradation in soil, water, and air. Pesticides introduced into water in the environment may undergo hydrolysis (degradation of the pesticide as a result of interaction with water) and be transformed into new chemicals with properties different from their precursors. The extent to which this process occurs in water can be determined from quantitative data on rate of hydrolysis and half-life determinations. Pesticides introduced into water in the environment can also undergo transformation by photolysis (breakdown by sunlight) into new chemicals with different properties than the original chemical. In certain circumstances, photolysis can also be a major route of degradation of pesticide residues on soil or in the vapor phase. Data on rate of photolysis and halflives establish the importance of photolysis in sunlight as a dominant process in the transformation of pesticides in water. The data generated from both hydrolysis and photolysis studies are then used to determine rate of degradation of the pesticide and identification of pesticide residues which may adversely affect nontarget organisms in the environment.

Sections 162-1 through -4 (formerly §163.62-8 "Data Requirements: Metabolism") describe the Agency's requirements for data related to metabolism which will be used to assess the persistence of a pesticide in a natural environment. These data requirements concern aerobic (in the presence of oxygen) and anaerobic (without oxygen) soil metabolism, and aerobic and anaerobic aquatic metabolism. The data generated from the metabolism studies described in this section are essential to determining the nature and availability of pesticide residues to rotational crops and to aiding in the assessment of environmental hazards related to the persistence of a pesticide in the environment after its disposal.

Sections 163-1 through -3 (formerly § 163.62-9 "Data Requirements: Mobility") describe the data requirements related to pesticide mobility. The data generated from the studies required in §§ 1631 through -3 provide information regarding pesticide transport and are used to assess potential environmental hazards related to contamination of human and animal food, loss of usable land and water resources to man through contamination of water (including

ground water), and habitat loss to wildlife resulting from pesticide residue movement or transport in the environment.

These data requirements pertain to leaching, adsorption/desorption, and volatility of pesticides, and provide information both as to the mode of transport and eventual destination of the pesticide. For example, a pesticide with a high vapor pressure relative to its sorptive tendency (i.e., water solubility, soil absorptivity) is likely to volatilize from the medium where it was applied. A pesticide with a low vapor pressure and relatively high water solubility, in contrast, is more likely to leach through the soil. Volatile chemicals are prime candidates for photolysis, and therefore may cause the presence of photo-oxidants in the air (atmosphere) or otherwise contribute to adverse atmospheric effects. However, nonvolatile chemicals will either bind to the soil or leach, depending on their affinity for particular surfaces and their water solubility. Pesticides that adsorb tightly are generally less subject to environmental transport in the gaseous phase or in solution and may accumulate in the soil. Substances which are not tightly adsorbed, however, can be transported through soils to aquatic systems and to the atmosphere.

Sections 164-1 through -6 (formerly § 163.62-10 "Data Requirements: Field Dissipation") establish requirements for data from terrestrial, aquatic, aquatic impact, and forestry field dissipation studies. A pesticide combination and tank mix dissipation study and a long term field dissipation study may also be required under certain situations. The data generated from the studies described in these sections are used to assess the potential environmental hazards (under actual field use conditions) related to reentry into treated areas, hazards from residues in rotational crops and other food sources, and the loss of land and water resources.

Sections 165-1 through -5 (formerly § 163.62-11 "Data Requirements: ccumulation") describe data requirements for accumulation studies. These studies deal with pesticide residue uptake and accumulation in rotational crops, irrigated crops, and fish. The data generated from these studies are used as part of an assessment of the potential adverse effects of these residues on nontarget organisms. These data also reveal pesticide levels in food supplies that originate from wild sources or from rotational crops. Rotational crop studies are necessary to establish realistic crop rotation restrictions (time from application to time when crops can be rotated) and to determine if tolerances may be needed for residues on such crops. Data from irrigated crop studies are used to determine the amount of pesticide residue taken up by representative crops from irrigation water transported from some other pesticide-treated area. These studies will allow the Agency to establish label restrictions regarding application of pesticides in sites where the residues can transport to irrigated crops.

These data will also provide information that will aid the Agency in establishing any corresponding tolerances that would be needed for residues on such crops. Data from pesticide accumulation studies in fish are used to establish label restrictions (e.g., to prevent applications in certain sites so that there will be minimal residues entering edible fish or shellfish such as catfish or crayfish inhabiting rice fields). These residue data will also be used to determine if any tolerance or action levels are needed for residues in aquatic animals eaten by humans.

Proposed §§ 163.62-12 "Data Requirements: Reentry" and 163.62-13 "Data Requirements: Disposal and Storage" were reserved in the 1978 proposed guidelines. Data requirements for reentry are now treated in Subdivision K of these guidelines; disposal and storage data requirements will be treated in Subdivision P (reserved).

References that appeared in the Appendix to the 1978 proposed guidelines have been carefully scrutinized for adequacy and usefulness. Some were deleted and several new references have been added. All references now include explanatory annotations which better describe the usefulness of each cited reference to the registrant. In the revised guidelines the references have been grouped according to subject matter and relocated at the end of each section.

A listing of current sections and paragraphs in Subdivision N and the equivalent former sections and paragraphs in the environmental chemistry portion of Subpart D in the 1978 proposed guidelines appears in Table 1.

Table 1. Location of current and proposed guidelines.

Subject	Current	Proposed
GENERAL INFORMATION AND REQUIREMENTS		
Purpose and scope of data requirements	160-1(a)	163.62-3
Application of requirements	-1(b)	.....
Approach of subdivision (subpart)	-1(c)	-3(a)
Summary tables	-1(d)	-3(a)
Organization and content of sections	-1(e)	-3(b)
Definitions	160-2	163.62-2
Use patterns	160-3	163.62-6
General	-3(a)	163.62-6
Terrestrial uses	-3(b)	-6(a)
Aquatic uses	-3(c)	-6(b)
Aquatic impact uses	-3(d)	-6(c)
Forestry	-3(e)	-6(d)
General test standards	160-4	163.62-4
Overview	-4(a)	.....
Personnel	-4(b)	-4(a)
Test controls	-4(c)	-4(b)
Test substance	-4(d)	-4(c)
Field studies	-4(e)	-4(d)
Inter-relationship between studies with respect to soil type	-4(f)	.....
Reporting and evaluation of data	160-5	163.62-5
Overview	-5(a)	.....
Nature of submission	-5(b)	-5(a)
Content	-5(c)	-5(b),(c)
Content (data evaluation)	-5(c)(10)	163.62-1(a),(b)
DEGRADATION STUDIES		
General	.....	163.62-7(a)
Hydrolysis studies	161-1	-7(b)
Photodegradation studies in water	-2	-7(c)
Photodegradation studies in soil	-3	-7(c)
Photodegradation studies in air	-4	-7(c)
METABOLISM STUDIES		
General	.....	163.62-8(a)
Aerobic soil metabolism studies	162-1	-8(b)

Table 1. (continued)

Anaerobic soil metabolism studies	-2	-8(c)
Anaerobic aquatic metabolism studies	-3	-8(d)
Aerobic aquatic metabolism studies	-4	-8(e)
Microbial metabolism	.....	-8(f)
General	.....	-8(f)(1)
Effects of microbes on pesticides	.....	-8(f)(2)
Effects of pesticides on microbes	.....	-8(f)(3)
Activated sludge metabolism	.....	-8(g)
MOBILITY STUDIES		
General	.....	163.62-9(a)
Leaching studies	163-1	-9(b)
Laboratory volatility studies	-2	-9(c)
Field volatility studies	-3	-9(c)
Adsorption/desorption	-1	-9(d)
Water dispersal	164-2	-9(e)
DISSIPATION STUDIES		
General	.....	163.62-10(a)
Field dissipation studies for terrestrial uses	164-1	-10(b)
Field dissipation studies for aquatic uses and aquatic impact uses	-2(b)(1)	-10(c)(1),(2)
Specialized aquatic uses	-2(b)(1),(2)	-10(c) 3)
Dissipation studies for forestry uses	-3	-10(d)
Aquatic impact uses	.....	-10(e)
Direct discharge	161-1,-2 162-3,-4 163-1 164-2 165-4,-5	-10(e)(1)
Indirect discharge	161-1	-10(e)(2)
Wastewater treatment	.....	-10(e)(3)
Dissipation studies for combination products and tank mix uses	164-4	-10(f)
Long-term soil dissipation studies	-5	-10(g)
ACCUMULATION STUDIES		
General	.....	163.62-11(a)

Table 1, (continued)

Lab/greenhouse/small plot accumulation studies for rotational crops	165-1	-11(b)
Field accumulation studies on rotational crops	-2	-11(b)
Accumulation studies on irrigated crops	-3	-11(c)
Lab studies of pesticide accumulation in fish	-4	-11(d)
Field accumulation studies in aquatic nontarget organisms	-5	-11(e)
REENTRY	(Subdivision K)	163.62-12
DISPOSAL AND STORAGE	(Subdivision P)	163.62-13

II. RESPONSE TO PUBLIC COMMENT

The Agency received comments from 63 commenters regarding the 1978 proposed environmental chemistry guidelines. In many cases, the commenters provided amended test protocols for consideration by the Agency and provided references or background material. In response to the public comments, the Agency has modified or clarified many sections of the guidelines. For purposes of this discussion, only the more significant and controversial issues reflected by public comments are discussed. Many minor recommendations which do not warrant discussion here were adopted by the Agency.

A. General Information and Requirements.

1. Data requirements for manufacturing-use products. In the Preamble to the 1978 proposed Guidelines, EPA asked for public comment on the question whether the data requirements of this subdivision should be extended to manufacturing-use products. After serious consideration of this issue, the Agency has concluded that extending the data requirements to such pesticides is appropriate. The Agency was influenced by the views of commenters on this issue who generally favored a data submission requirement which makes the basic manufacturer of an active ingredient responsible for providing most of the environmental fate data.

Therefore, a section of 40 CFR Part 158, entitled "Formulators' Exemption" (§ 158.50), requires a registrant of a manufacturing-use product to submit (or cite) any data pertaining to the safety of an active ingredient in its product if the same data are required to support the registration of an end-use product that could legally be produced from the registrant's manufacturing-use products. (An end-use product is a pesticide product bearing label directions for immediate end-use as a pesticide). Section 158.50 also provides that such data must be submitted by an applicant for registration of the end-use product, except that the producer of the end-use product will generally not have to submit or cite data pertaining to registered products which the end-use producer purchases and uses to formulate the end-use product. This decision reflects the Agency's expectation that manufacturing-use product registrants will be the major source of registration data, and that end-use product formulators will, in most cases, need to supply much less data. This decision is consistent with the provisions of, and Congressional intent behind, sec. 3(c)(2)(D) of FIFRA, which provides that:

> No applicant for registration of a pesticide who proposes to purchase a registered pesticide from another producer

in order to formulate such purchased pesticide into an end-use product shall be required to--

(i) submit or cite data pertaining to the safety of such purchased product; or

(ii) offer to pay reasonable compensation otherwise required by [§ 3(c)(1)(D) of FIFRA] for use of any such data.

Implicit in sec. 3(c)(2)(D) is Congress' expectation that it would be the registrant of the manufacturing-use product who would provide significant amounts of data pertaining to the safety of its product. (See, e.g., Sen. Rep. No. 334, 95th Cong., 1st Sess., pp. 8-9.)

Moreover, if data requirements were imposed solely on registrants of end-use products, sec. 3(c)(2)(D) might be read to prevent the Agency from obtaining data on the grounds that the data pertain to the safety of a purchased product.

2. Clarification of Data and Test Substance Requirements

Many public comments revealed that the proposed guidelines created confusion as to which registrants have an obligation to submit data (the "data requirements") and what test substances must be used to generate required data (the "test substance requirements"). For example, several people commented that it was unreasonable to require an aerobic soil metabolism study to be performed with all formulated products. Instead, they argued that EPA should require testing only with the active ingredients in pesticide products. In fact, the proposed environmental fate guidelines did require use of the active ingredient, not the formulated product, as the test substance in aerobic soil metabolism studies. [See proposed § 163.62-8(b) and § 162.8-4(c)(1)(i) of the FIFRA sec. 3 regulations.] Thus, the Agency concluded from this comment and many like it that there was a need to clarify the data requirements and test substance requirements in the environmental fate guidelines.

EPA has taken a number of steps to make these requirements clearer. First, the Agency has included many new definitions and additional explanatory material to clarify which products are covered by a particular use pattern. (See §§ 160-2 and 160-3.) Specifically, EPA has issued a definition for each of the use patterns which serve as the basis for the environmental fate data requirements. In addition, EPA has provided explanatory material in § 160-3 which gives numerous examples of specific uses which are covered by the use pattern definitions.

Second, the Agency has added a section titled "Application status and submittal times" to § 158.30 of 40 CFR § 158 which specifies when data must be submitted for both full registration and conditional registration [FIFRA sec.3(c)(5) and 3(c)(7), respectively].

Third, as discussed above, the Agency has addressed each different study in a separate section of the guidelines. Each of these sections now contains both a "When required" paragraph that states which products must be supported by a particular kind of data and who must submit such data, as well as a "Test substance" paragraph that identifies the substance which must be used in performing the study. Generally, the "When required" paragraphs state that a particular test will be required for all end-use products having a specific use pattern category, and for all manufacturing-use products which may legally be formulated into such end-use products.

Finally, EPA has revised the Table of Use Patterns and Data Requirements that appeared in the proposal. This table, which originally appeared in § 163.62-3, has been divided into two tables that are located in § 160-1 of the current guidelines. The first table covers terrestrial uses and forestry uses, and the second table covers aquatic uses and aquatic impact uses. It must be noted that these tables are intended for quick reference and do not include all data requirements and exemptions from data requirements found in the "When required" paragraphs of the individual sections. For example, Table 1 indicates that a photodegradation study on soil is required to support the registration of end-use products with certain terrestrial uses. The table does not include the provision in the "When required" paragraph for that study which excludes products injected into the soil or incorporated into soil during application. Most of the requirements which are not covered by the tables are listed in an accompanying footnote.

3. Testing a representative end-use product. The Agency seeks to avoid imposing a burden of duplicative testing on applicants for registration. Therefore, where 40 CFR §158 specifies that the test substance shall be a typical end-use product, testing may be performed on a representative formulation. It is not necessary to repeat the test using other similar products. A typical end-use product is defined in §160-2(b)(23) as:

> A pesticide product that is representative of a major formulation category (e.g., emulsifiable concentrate, granular product, wettable powder) and contains the active ingredient of the applicant's product.

The use of a typical end-use product in environmental fate testing is needed for tests which determine the extent of overall pesticide dissipation under actual use conditions. In Subdivision N, all

tests in §164 (dissipation studies) and some in §165 (accumulation studies) are in this category. Moreover, since manufacturing-use products may be formulated into end-use products belonging to several different formulation categories, testing is required with a typical end-use product from each formulation category. Accordingly, the test substance section of these tests now contains a provision which states:

> If the applicant's product is a manufacturing-use product intended for [forestry use], the test substance shall be a product representative of the major formulation category for that general use pattern. (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 category.

4. Definitions. In the 1978 proposed guidelines, only one definition -- "material balance" -- was included for the data requirements pertaining to environmental fate studies. In the course of clarifying and revising the subdivision, it became apparent that major terms used throughout the environmental fate sections needed definition. In particular, definitions were needed relating to pesticide use patterns. The four major use categories now employed in the subdivision (terrestrial, forestry, aquatic, and aquatic impact) are now defined, and all of the subcategories (e.g, orchard, aquatic noncrop, etc.) are also defined. See § 160-2. Examples of uses within these categories are provided in § 160-3 (Use Patterns).

5. Personnel requirements. A number of commenters raised objections to proposed § 163.62-4(a), which provided that:

> All testing and evaluation must be done under the direction of personnel who have the education, training and experience to perform the testing and evaluation in accordance with sound scientific experimental procedures.

That section also provided that the Agency may request a resume of the qualifications of personnel performing, supervising, reviewing or evaluating testing. Most commenters objected particularly to the reference to a resume, and stated that if the Agency were to have the opportunity to request resumes, the applicant should have an opportunity to request a resume of the Agency reviewer to determine if the reviewer is qualified to review the data furnished. It was also pointed out by one commenter that the proposed provision was overly broad in that testing is not always performed under the direction of managers and supervisors who have the education, training and experience to perform actual testing.

In response to public comments, the Agency has withdrawn this test standard.

6. Data requirements for small-package, low-toxicity pesticides. Several commenters objected to the imposition of environmental fate data requirements for small-package, low-toxicity pesticide products. They considered the environmental impact of such products to be minimal, and contended that such products should be exempt from these data submission requirements because of the "Agency's obligation to take into account the differences in concept and usage between various classes of pesticides."

The Agency recognizes the position of such commenters, but does not agree. Exclusion of the broad category "small-package, low-toxicity pesticide products" is too general and may preclude the Agency from obtaining information necessary for an assessment of environmental hazards resulting from pesticide products intended for domestic-use applications. For some products, great quantities (on an aggregate use basis) of small-package low-toxicity products used in domestic-use applications can result in adverse environmental effects, even though a single application of such a product would not cause any specific adverse effect beyond intended injury to the target pests. The Agency recognizes that many small-package, lowtoxicity, low-volume products do not pose an environmental hazard even when viewed from an aggregate-use standpoint, and for these, recommends that registration applicants consider submitting requests for waivers of certain data requirements, in accordance with § 158.45 of 40 CFR § 158 [referred to at § 160-1(g) of this subdivision (N)].

However, it should be noted that a single set of acceptable data for each chemical is all that is needed by the Agency. Thus, it is unlikely that individual small package producers will actually be required to conduct such studies, since these studies will ordinarily be conducted and resultant data furnished by a producer of the active ingredient.

B. BENCHMARK CONCEPT.

One commenter expressed the view that the Agency should use benchmark techniques in hazard assessment, and that the data requirements of the guidelines should be drafted with this in mind. The benchmark concept involves using presently available information about chemicals for which data have been generated to predict the behavior of chemicals whose behavior patterns are unknown. The Agency recognizes the advantages of benchmark techniques as a means of hazard assessment, and does not rule out their future use. However, it does not believe that such techniques have been developed to the point where the Agency can rely on such data to predict environmental fate as a substitute for requiring actual data about the chemical for which registration is sought.

C. DEGRADATION STUDIES

1. Hydrolysis. Many commenters suggested revisions in proposed § 163.62-7(b), which set forth proposed requirements for hydrolysis testing. The commenters believe that their proposed revisions to the data requirements would reduce the time and expense involved in performing hydrolysis testing but would still permit the Agency to obtain the data necessary for hazard evaluation.

The proposed version of the guidelines required laboratory hydrolysis studies at two concentrations, two temperatures, and three pH values. Many commenters recommended that the Agency permit hydrolysis testing to be conducted at one concentration and at one temperature. Some of these commenters stated that additional testing at different concentrations or temperatures would be appropriate in the event that initial testing results identified hydrolysis as a major route of degradation of the pesticide.

The Agency agrees with the commenters that testing at one temperature and concentration will yield satisfactory data for hazard analysis. Therefore, the Agency has revised its provisions regarding the test procedure for hydrolysis testing. The guidelines now require "one or more concentrations of the test substance" to be tested, with an upper limit on the permissible concentration of 250 parts per million. The guidelines also permit testing at one temperature, and provide that the temperature of the hydrolysis reaction shall be maintained at 25 $\pm$ 1°C. However, the Agency has retained the requirement that the study be run at pH 5, 7, and 9 because, in its judgment, the three pH's are necessary to span normally-encountered environmental conditions.

2. Soil Photodegradation. Studies of the photodegradation or photolysis of a pesticide on soil surfaces were required by proposed § 163.62-7(c). Numerous commenters objected to the requirement and suggested either deleting or modifying the section. EPA has retained the requirement but has adopted a number of suggestions for its modification. See § 161-3 of this subdivision.

One commenter recommended restricting the requirement for soil photolysis data to those products for which photodegradation is likely to be a significant mechanism of decomposition. The proposed guidelines required soil photolysis data to support the registration of any end-use product with a terrestrial non-crop use, a fruit/nut tree (orchard) crop use, a fieldvegetable crop use, an aquatic use, a forestry use, or direct discharge aquatic impact use.

The Agency agrees with the commenters that this data requirement in the proposed guidelines was overly broad and has added a "When required" paragraph to § 161-3 of the current guidelines which states that soil photolysis data are required to support the registration of only those end-use products with terrestrial crop

uses or forestry uses. The section expressly excludes from the data requirement products with uses which will not result in pesticide residue on the soil surface, i.e., "uses involving injection of the product into the soil or incorporation of the product into the soil upon application . . ."

Most of the comments focused on the test methodology. Some commenters suggested deleting the requirement because of the difficulty and cost of the study or because of the difficulty in interpreting the data. Others argued for its deletion on the grounds that comparable information could be obtained from a "sensitized" water photolysis study. Finally, some commenters proposed specific changes in the test methodology. The change most frequently suggested was that the study be performed on an inert surface rather than on soil.

EPA recognizes that a soil photolysis study requires expensive and sophisticated testing techniques. Nonetheless, the Agency believes that it is appropriate to require the study for products which are likely to leave pesticide residues on the soil surface since soil surface photolysis can be an important factor in the degradation of many pesticides not incorporated into the soil. The Agency has expanded the list of references to include more information on the performance of these studies which should aid those who find the study difficult to perform.

The Agency has considered but does not agree with the suggestion of one commenter that aqueous photolysis studies using water with and without photosensitizers would provide the same information that would be generated by a soil photolysis study. A photosensitizer is a substance which alters the rate or the path of decomposition of a chemical. The commenter's suggestion is apparently based on the assumption that the photodegradation process on soil differs from that in water only in that photosensitizers are present in the former. EPA agrees with the commenter that photolysis in water and soil may differ because of the presence of photosensitizers and that soil is more likely to have such compounds. However, this is not the only way in which soil and water may differ. The Agency anticipates that the amounts and kinds of photoproducts and second order degradation products may differ for studies done in soil and water. For example, a photoproduct formed in water is likely to be hydrolyzed, but the same photoproduct formed in soil could also react with soil organic matter or be metabolized by soil microbes. Consequently, the Agency rejects the suggestion to rely on aqueous photolysis studies.

A number of commenters critized the proposed soil photolysis data requirement because of their belief that EPA would not be able to interpret the data. In particular, EPA would be unable to distinguish between degradation resulting from exposure to sunlight and degradation caused by chemical reactions with the water or organic matter in the soil or by microbial populations in the soil.

The Agency agrees that the study required by the proposed guidelines would not have produced data that could enable it to distinguish among these various degradation mechanisms. In order to do so, the Agency has added a test standard requiring a "dark control," i.e., a requirement that the study be performed both in light and in darkness. [See § 161-3(c)(2)(v).] The differences obtained under the two conditions will indicate to what extent decomposition is attributable to photolysis.

Commenters also suggested that the results of a soil photolysis study are of limited usefulness because the test is performed on only one type of soil. Various types of soils will produce different results due to differences in organic matter content, microbial populations, and photosensitizers. EPA agrees that the differences between soil types will significantly limit the Agency's ability to make quantitative extrapolations of photolysis data from a test soil to another soil type. The Agency, however, does not intend to perform quantitative extrapolations based on these data; rather the Agency's purpose is to obtain an understanding of the importance of photolysis of soil surface pesticide residues and to identify major metabolites formed by this mechanism. The Agency concludes that the test is capable of generating data which satisfy this purpose, and therefore has retained the requirement.

Finally, EPA has considered the frequently-offered suggestion to permit the use of an inert surface such as glass or Teflon instead of soil in this study. Although these studies would be somewhat less expensive, the data generated would not permit the Agency to evaluate the effects of degradation from the combined factors associated with both sunlight and soil, a more natural and more common situation. Therefore, the Agency has rejected the proposed revision.

3. Air photolysis. Most of the public comments on proposed § 163.62-7(c) recommended deleting the requirement for air photolysis studies. While the Agency has not accepted this recommendation, the Agency has revised the proposed provision to provide that the data will be required only on a case-by-case basis and to establish standards for the performance of the test. Several comments noted that the results of an air photolysis study are not needed for non-volatile compounds and compounds that do not vaporize readily. Other comments suggested that the data are needed only to evaluate possible hazards to workers reentering a treated area. EPA agrees with both comments and has added "When required" paragraphs which provide, in § 161-4(b):

> Data from a laboratory photodegradation study in the vapor phase will be required by the Agency on a case-by-case basis to support the

registration of an end-use product with orchard or field-vegetable crop uses that involve potentially significant exposure to workers. Data from such a study will also be required to support the registration of a manufacturing-use product which legally could be used to make such an end-use product. The Agency will make an assessment of what constitutes a significant exposure to workers based on the information required by § 163-2(b)(2).

and in § 163-2(b)(2):

Data from a laboratory volatility study will be required on a case-by-case basis by the Agency to support the registration of each end-use product intended for commercial greenhouse, orchard, or field/vegetable crop uses that involve signficant inhalation exposure to workers. Such studies will also be required to support the registration of each manufacturing-use product which legally could be used to make any end-use product for which laboratory volatility data are required.

(2) The Agency will evaluate the following information provided by the registration applicant to make an assessment of what constitutes a significant inhalation exposure to workers:

(i) Vapor pressure at 25°C and water solubility of the pesticide active ingredient (§§ 64-9 and 64-8 of Subdivision D);

(ii) Soil adsorption coefficient (K_d) of the test substance using the soil from a typical intended application site;

(iii) Soil characteristics, including moisture content, at the intended site of application;

(iv) Method, rate, and intervals of pesticide application;

(v) Temperature, humidity, and air flow rates at the site of application;

(vi) Ventilation sequences or practices for commercial greenhouse applications; and

(vii) Inhalation toxicity of the pesticide (§§ 81-3 and 82-4 of subdivision F).

In accordance with these paragraphs, the Agency will consider both the volatility of the pesticide and the possibility of worker exposure in determining which products will be required to provide air photolysis data.

Other comments stated that requirement for air photolysis data should be deleted because the study is costly and complicated and the results are difficult to interpret. The Agency acknowledges that the test procedures are expensive and difficult to perform and that data are rarely easy to analyze. Nonetheless, the test procedures are reliable, and useful data have been generated from such studies. [See the references in § 161-4(e).] Therefore, when these data are needed to evaluate potentially hazardous exposures, the Agency will require the data.

D. METABOLISM STUDIES

1. Aerobic Soil Metabolism Studies. While most commenters recognized the Agency's need for data from an aerobic soil metabolism study, they had many comments on how such a study should be performed. [See proposed § 163.62-8(b).] The three data requirements in this study which received the most comment were:

- The requirement to use three different types of soil;
- The requirement to continue the study until "ninety percent loss of the pesticide occurs"; and
- The requirement to identify every residue which constitutes more than ten percent of the initial application or 0.01 ppm, whichever is greater.

After reviewing the comments on the requirement to perform the aerobic soil metabolism study on three different soil types, the Agency agrees with the reasons advanced in support of reducing the requirement to one soil type. A number of commenters stated that the variation in results from soil to soil was comparatively small and that there were rarely qualitative differences in the degradation products formed in different types of soil. Thus, the kind of soil seemed to influence only the rate of degradation. They stated, moreover, that rate calculations determined in a laboratory test such as the aerobic soil metabolism study are not highly reliable for predicting degradation rates under field conditions. Accordingly, they concluded that the results of an aerobic soil

metabolism study performed on more than one type of soil would be only marginally useful for the Agency. Many commenters also pointed out that by reducing the number of soil types required from three to one, the Agency could lower the cost of the study. The Agency has been persuaded by these reasons, and has reduced the requirement to only one soil type. See § 162-1 (c)(2)(i) of the current guidelines.

The Agency has also revised the requirements concerning the duration of an aerobic soil metabolism study. The proposed guidelines stated that if the data were used to support the registration of a product with a forestry use, a terrestrial crop use, or a terrestrial non-crop use, the study should last one year or until 90 percent of the active ingredient had degraded and the pattern of formation and decline of metabolites had been established, whichever was shorter. Several commenters stated that the 90 percent loss criterion was inappropriate.

The Agency agrees with the comments. In some cases it will be possible to establish degradation rates for the active ingredient and rates of formation and decline of the degradation products before the active ingredient has degraded 90 percent. In other cases, the active ingredients may degrade very rapidly, so that there will not have been enough time to evaluate the pattern of formation and decline of degradation products by the time that 90 percent of the active ingredient has degraded. In short, the 90 percent degradation figure often may not be relevant to the evaluation of patterns of formation and decline of degradates, one of the Agency's primary concerns in determining the duration of an aerobic soil metabolism study. In order to reflect this reasoning, the Agency has prepared § 162-1 (c)(2)(viii) to read:

> Data must be collected until patterns of decline of the parent compound and patterns of formation and decline of degradation products are established in soil, or for one year, whichever comes first . . .

Finally, the Agency has modified the provisions concerning the level of sensitivity required for the analytical methods used to identify the residues of degradation products remaining in soil. The proposal, § 163.62-8(b), required the identification of residues which constitute ten percent of the initial application level or 0.01 ppm, whichever was greater, and further provided that the experimental dose rate must approximate the field application rate. Public comments identified two problems with this requirement. First, the ten percent criterion was too broad for pesticides applied at high rates (e.g., greater than 5 ppm). If a pesticide is normally applied at 20 ppm (as is the case for some soil fumigants), an applicant would, for example, only have to

identify residues in excess of 2 ppm, 200 times higher than the requirement imposed for other pesticides. Thus, a ten percent criterion would not only deny the Agency access to residue data necessary to make a hazard assessment, but could also indirectly encourage the use of higher application rates. Second, detection of residues which constituted only 0.01 ppm might be difficult.

As a result of the many comments received on this issue, the Agency has revised the criteria for identification of soil residues. The criterion based on 10% of the original application level has been deleted, and the requirement for identification of residues at the 0.01 ppm level is to be taken as a suggested goal to be met or surpassed. See § 162-1(c)(2)(vi). The Agency believes that 0.01 ppm is a valid target level in light of the data received from many registrants and the current literature where this level is either met or surpassed. It is recognized, however, that this level of analysis cannot be achieved for all pesticide chemicals and their degradation products. Therefore, registration applicants will not be penalized for not being able to meet the 0.01 ppm goal due to limitations of the analytical method.

2. Studies of microbial effects. In the 1978 proposed guidelines, the Agency proposed the following sets of data requirements pertaining to microbial effects in relation to pesticides:

§ 163.62-8(f)(2) Effects of microbes on pesticides;

§ 163.62-8(f)(3) Effects of pesticides on microbes; and

§ 163.62-8(g) Activated sludge metabolism.

Subsequent to the proposal, public comments, Agency internal discussion, and the recommendation of the FIFRA Scientific Advisory Panel all focused on the need for the Agency to obtain more definitive information on test procedures and better assessment of the value of test results before promulgating final rules on this subject. The Agency agrees with these arguments, and has not included these data requirements in Subdivision N.

This decision should not be interpreted to suggest that the Agency is no longer interested in microbial effects, nor that their importance in environmental fate of pesticides is not important. It merely reflects agreement among scientists both within and outside the Agency that until useful conclusions can be drawn from properly designed studies, no studies should be required. In this regard, the Agency invites submittal of more suitable and useful test protocols and examples of test results and evaluations that support the protocols.

The microbial effects studies provided in the 1978 guidelines, and the microbial studies in the Subpart J proposal (45 FR 72948)

do not encompass the full scope of microbial effects studies that should be examined if a serious examination of environmental effects involving microorganisms is to be undertaken. When suitable studies can be designed to produce useful, cogent data regarding microbial effects, the Agency is likely to include all such studies within a single, separate subdivision.

E. PESTICIDE RESIDUE MOBILITY STUDIES

1. Soil column leaching studies. Proposed § 163.62-9(b) established data requirements intended to provide the Agency with information about the propensity of a pesticide to leach through soil. The leaching study required was a soil column laboratory study using a minimum of four soils, one of which must be used to study leaching of pesticide residues after the pesticide had been aged in soil under aerobic conditions.

A number of commenters recommended deletion of the requirement for column leaching studies. The consensus of the commenters was that such studies are wasteful of time and resources, because the Agency can obtain sufficient information about the leaching properties of a pesticide from data obtained from adsorption/desorption studies. One commenter gave as an additional reason for deleting the requirement that the Agency had itself recognized a number of problems associated with soil column leaching studies. Another commenter took the opposite view, and recommended that adsorption/desorption data requirements be deleted and the soil column laboratory study requirements be retained.

In response to public comments, the Agency has combined its data requirements pertaining to adsorption/desorption and leaching. The guidelines now provide that a laboratory study is required to provide a quantitative estimate of mobility in soil, but that, with some limitations, the investigator may select which technique to use. A brief discussion of the three techniques follows. Thin-layer chromatography is one laboratory technique which permits the investigator to determine the movement of pesticides in soil coated on glass. A soil column study is another laboratory procedure which provides data on the movement of pesticides in soil. However, the soil used for the study is placed in a vertical column (cylinder), and movement of the pesticide from the top to the bottom is measured. A batch equilibrium study, on the other hand, involves the collection of data on the partitioning of a pesticide between soil and water; in this study, the pesticide is first added to water which is thereafter mixed with soil. The Agency believes that it can give applicants the choice of which techniques to use to measure leachability and still obtain adequate data for the assessment of pesticide mobility.

Therefore, the guidelines now permit data relating to products intended for terrestrial and forest uses to be obtained using soil thin-layer chromatography, a soil column study, or a batch equilibrum (adsorption/desorption) study. A batch equilibrium study must be performed, however, for pesticides intended for aquatic or aquatic impact uses.

2. Effects of Pesticides on Groundwater. Several commenters recommended that the guidelines take into account the potential effects of pesticides on ground water. The Agency agrees and believes that the requirements of Subdivision N will provide the Agency with data that will enable it to ascertain and assess possible ground water contamination by pesticides.

Ground water includes both the aquifers which store water below the earth's surface and other subsurface water sources. It is a valuable resource which has been increasingly used both as a primary and supplementary source of water in many regions throughout the United States. However, since it is a hidden resource, its proper management has often been difficult to achieve. The pollution of ground water is difficult to detect because it usually takes place very slowly. Moreover, once the water is contaminated, the loss of usefulness of the water and the effort to restore the water to a useful state may extend over a long period of time.

The Agency considers that it is probably more cost efficient to prevent the contamination of ground water than to remove pollutants from it. Therefore, as part of the assessment of environmental fate of a pesticide, the Agency will evaluate its potential for ground water contamination. The characteristics of the pesticide that are most pertinent to this inquiry are:

- Leachability;
- Adsorption/desorption characteristics;
- Resistance to chemical, photochemical, and biological degradation;
- Solubility in water; and
- Volatility.

The tests described in Subdivision N provide the Agency with data from which it can assess these characteristics of a pesticide.

It should be noted that, while the data requirements for leaching studies have now been modified, this change is not considered likely to reduce the Agency's ability to assess the risk that a pesticide will contaminate ground water. In the 1978 proposed guidelines, the Agency required that an applicant conduct

both soil thin-layer chromatography testing and a soil column leaching study to measure leachability. As a result of public comment, however, the Agency has been convinced that it can obtain satisfactory data from either of these studies, or from an adsorption/desorption study. Therefore, the guidelines now provide that an applicant submit data from any one of these three studies.

F. DISSIPATION STUDIES: COMBINATION PRODUCTS AND TANK MIXES

A few commenters recommended deleting proposed § 163.62(10(f), which prescribes data requirements for pesticides applied in a combination or tank mix. The commenters questioned whether the Agency has evidence of any adverse effects associated with such combinations, or evidence that a pesticide will behave differently when added to soil at the same time as another pesticide than if it had been applied alone. The Agency has data that indicate that the persistence of a pesticide in soil may increase as a result of its application with another pesticide serially or in a mixture. Based on such information, the Agency believes that the data required by proposed § 163.62-10(f) is useful in hazard evaluation and has retained the data requirement, but only on a case-by-case basis. Refer to PR Notice 82-1, entitled "Revised Policy on Label Claims for Tank Mixing" (January 12, 1982) for a further discussion.

At the suggestion of several commenters, the Agency has amended the provision to require incorporation of the test substance in soil only for those use patterns that require soil incorporation as recommended by label instructions.

G. ACCUMULATION STUDIES

1. Rotational crop studies. Commenters have suggested a number of revisions in proposed § 163.62-11(b), which establishes data requirements for studies of pesticide accumulation in rotational crops. The Agency has substantially revised the requirements for these studies, now in §§ 165-1 and -2, to take their comments into account. The main suggestions and Agency responses are as follows:

(a) Several commenters objected to the requirement for a laboratory or greenhouse study and proposed an amendment to permit a small plot outdoor study. The commenters stated that an outdoor study would more closely approximate growing conditions than would a laboratory study. The Agency has now revised the requirements in

response to these comments to permit the applicant to furnish data from a "confined" (as contrasted to "field") study which can be a laboratory, greenhouse, or outdoor small-plot study.

(b) Several commenters recommended that the guidelines establish a trigger that would determine when field studies would be required. The suggested trigger level of 0.1 ppm of unincorporated extractable residue was proposed by two commenters. A third commenter proposed that a field study should not be required unless there is a single extractable component greater than 0.02 ppm, expressed as parent pesticide compound, present in the raw agricultural commodity. The guidelines, at § 165-2(b)(1) now provide that a field study is required "when significant C^{14} pesticide residues of concern to the Agency are detected in the crops analyzed in the confined accumulation study, § 165-1." Significant residues are defined in § 165-1(d)(1) as "parent compound, closely-related degradates, metabolites and/or their conjugates in the crop, but shall exclude C^{14} activity in the crop associated with that being incorporated into the carbon pool and ultimately into natural plant constituents."

(c) Several commenters suggested that the Agency establish tolerances for residues in rotational crops. The Agency now has a procedure for establishing such tolerances. On January 13, 1981, the Agency issued a policy statement entitled "Tolerance for Pesticides Residues in Rotational and Follow-Up Crops, Meat, Milk, Poultry and Eggs, and for Other Indirect or Inadvertent Residues." Federal Register, Vol. 46 No. 8, p. 3016, Jan. 13, 1981. In that statement, the Agency announced that it will follow the general policy of responding to requests by setting tolerances for pesticides residues resulting from crop rotation or crop replacement practices.

2. Fish accumulation studies. The Agency received numerous comments concerning the proposed data requirements for fish accumulation studies. These commenters addressed four main concerns:

- Commenters proposed that the Agency establish a tier approach to data requirements pertaining to pesticide accumulation in fish.

- Commenters questioned the need for and procedures specified for the static (catfish) accumulation test.

- Commenters expressed concern whether the fish accumulation data requirements in the environmental fate subpart are redundant of or compatible with the fish accumulation data requirements of proposed § 163.72-6 in Subpart E (now § 72-6 of Subdivision E).

- Commenters recommended changes in prescribed test procedures for performing the studies.

The Agency has responded favorably to many of the proposed revisions of this section, and as a result, the fish accumulation test requirements have changed considerably from those previously proposed.

Several commenters proposed that the requirement for a flow-through study should be contingent on whether the parent and/or significant environmental degradation product has octanol/water partition coefficients greater than 1000 and half-lives in water greater than 4 days. The Agency agrees generally with these commenters that a flow-through study need not be performed in every instance, and that there is a high correlation between octanol/water partition coefficient and pesticide accumulation in fish. Nevertheless, the Agency does not believe that testing procedures have been developed that would permit the Agency to use data on octanol/water partition coefficient on a routine basis to determine whether further testing is required. Therefore, the guidelines now provide that the flow-through test requirement may be waived if the applicant can provide evidence that the probability for accumulation is low, based on the physical properties of the pesticide and any other characteristics that bear on its environmental fate. In this way, the Agency has retained the flexibility to require the study for products for which the physical property correlations have been established or for which the use patterns, application rates or environmental fate and transport increase the possibility for accumulation.

A number of comments were received questioning the need for the proposed static "catfish" accumulation study. Commenters expressed concern that no established standard procedures exist for performing the study; that there is a likelihood that the test fish will suffer adverse health effects; that the conditions for the study bear little resemblance to actual environmental conditions; and that several chemical factors decrease the value of the test in assessing accumulation potential. The Agency has carefully studied these comments and has concluded that the major benefit that the study offers, the ability to judge the accumulation potential of pesticide degradation products, is outweighed by the collective shortcomings of the study as currently proposed. More importantly, though, some of these kinds of studies have neither been validated nor verified, and suitable design criteria related to standardization of the techniques are yet to be developed. The Agency has decided, therefore, to delete the static test from the guidelines. The Agency encourages further research in this area, with hope that suitable low-cost reproducible studies that yield the needed information can be developed.

Commenters also suggested changes in test procedures for fish accumulation studies, many of which have been incorporated into the guidelines. Most significantly, the Agency now requires identification of chemical residues only from the two samples with the highest residue levels. Residues below a specified level need not be identified.

Lastly, commenters expressed concern about the relationship between proposed Subparts D and E, both of which required data on accumulation of pesticides in fish.

Subdivision N now requires the following laboratory and field accumulation studies on fish:

(a) Section 165-4 provides that a laboratory flow-through exposure study is required to support the registration of end-use products intended for outdoor uses (except domestic outdoor and greenhouse uses), enduse products intended for aquatic impact uses resulting in direct discharges into the environment, and manufacturing-use products that could legally be used to make such end-use products. However, such data will not normally be required where the applicant can provide evidence that the pesticide and/or its principal degradates will not reach water, will not persist in water, or are unlikely to accumulate in fish.

(b) Section 165-5 provides for a field accumulation study to measure pesticide residues in edible portions of fish under more limited circumstances: if the end-use product is intended for forestry use, aquatic non-crop use, or aquatic impact use that results in direct discharge; if a laboratory accumulation test shows evidence of accumulation, <u>and</u> if no tolerance or action level for fish has been granted.

Subdivision E provides for both laboratory and field accumulation studies (§§ 72-6 and 72-7, respectively), both on a case-by-case basis.

Although Subdivisions E and N both contain data requirements pertaining to the accumulation of pesticides, the Agency believes that it is necessary to retain the requirements in both subdivisions. First, the data requirements in the two subdivisions serve different purposes. Subdivision N contains data requirements designed to obtain information about the hazard from accumulation of pesticides in fish used as edible food sources for humans, and incidentally, other animals that feed on fish or fish products. Subdivision E, on the other hand, contains data requirements intended to provide information on adverse effects of pesticides on fish as nontarget organisms in the environment.

Second, the applicant will not be required to perform duplicate tests to furnish redundant data to satisfy the requirements of both subdivisions. Where one study will satisfy the requirements of both subdivisions, data furnished in response to the requirements of one subdivision may be crossreferenced in the registrant's submission under the other.

The Agency emphasizes that the Subdivision E guidelines require accumulation testing on fish only on a case-by-case basis, with the decision whether to test and what procedure to follow being made after consultation between the registrant and the Agency. Laboratory accumulation testing under § 72-6 of Subdivision E will be required if the active ingredient or its principal degradation products are likely to persist in the aquatic environment, or if they accumulate in the organs and tissues of mammals or avian species. Simulated or actual field testing under § 72-7 will be required if there is evidence that the pesticide is likely to cause adverse effects on fish.

3. Microecosystems studies. The issue was raised that microecosystem testing is not required in the environmental fate guidelines for accumulation studies. The model ecosystem approach, once perfected, could give valuable data as to pesticide mobility, transport, toxicity, distribution, accumulation, and fate. It may be useful, therefore, for the study of current problem areas and pesticides that are currently registered for use. But more importantly, it may eventually be very helpful in providing useful data in future registrations of certain new pesticides as the state of the science of this technique improves.

Scientists are aware, however, that microecosystems are very complex, and data generated by these systems on transformation, transport, and accumulation of pesticide residues are often difficult to interpret. To be useful, several different systems would have to be used. This could result in substantial cost to prospective registrants. More importantly, though, most such systems have neither been validated nor verified, and suitable design criteria related to standardization of the techniques are yet to be developed. The Agency encourages further research in this area, with the hope that suitable low-cost reproducible systems that yield the needed information can be developed.

H. SECTIONS OF 1978 PROPOSAL TO BE ISSUED AS SEPARATE SUBDIVISIONS

1. Reentry. A commenter suggested that the Agency should not defer the issuance of re-entry guidelines but should impose data requirements relating to re-entry at the same time that these and other data requirements are imposed. The commenter expressed concern

that an applicant or registrant might be burdened with duplicative testing requirements if these studies could not be conducted simultaneously. The commenter suggested that reentry data include a determination of hazards due to chronic effects, allergic reactions, and diminished health.

Guidelines have been written by the Agency to establish data requirements to support the establishment of re-entry intervals for pesticides. These requirements are in Subdivision K "Pesticide Assessment Guidelines: Re-entry Protection."

2. Disposal. The 1978 proposal asked for suggestions as to what data should be required relating to pesticide disposal. In response to that request, one commenter suggested that the Agency could require data on incineration parameters and chemical degradation. All comments received in connection with the proposal will be addressed in the development of Subdivision P, "Data to Support Disposal Instructions." This subdivision will take into account the disposal statements in Subdivision H, "Labeling Guidelines for Pesticides and Devices," the proposed guidelines on disposal developed under the Resource Conservation and Recovery Act, and the fact that disposal of pesticide containers must be addressed as well as pesticides.

3. Pesticide Residue Data for Tolerances and Tobacco. Sections in proposed Subpart D dealing with tolerance clearance and with pesticides in tobacco, §§ 163.63-1 and 163.64-1, respectively, will be addressed in a separate subpart entitled Subdivision O, "Pesticide Assessment Guidelines: Residue Chemistry."

I. APPENDIX TO 1978 PROPOSAL

Several commenters pointed out that the Appendix to the 1978 proposed guidelines stated that acceptable test procedures were not available for Items No. 10 (Volatility), 12 (Water Dispersal), 13 (Field Dissipation), 14 (Aquatic Food Crop), 15 (Aquatic NonCrop), 17 (Combination and Tank Mixes), 18 (Long Term Study), and 19 (Accumulation). They consequently recommended that the comparable guidelines sections include only testing for which established protocols are available. Other commenters have indicated to the Agency that many Appendix references were either inaccurate, irrelevant to the subject matter addressed, or out of date and not reflective of the current state of the art in environmental fate studies.

In response to these concerns, the Agency has thoroughly reviewed the references. Those which were judged to be no longer useful for their intended purpose were deleted and replaced by

references to suitable information. In an attempt to make the references more instructive and useful, the Agency has included explanations as to extent of usefulness of each reference.

All references are now located at the ends of the appropriate sections to which they properly correspond, rather than in a single large appendix section.

SUBDIVISION N - CHEMISTRY REQUIREMENTS: ENVIRONMENTAL FATE

Series 160: GENERAL INFORMATION AND REQUIREMENTS

§ 160-1 General information.

(a) Purpose and scope. Pesticides interact with the environment with possible adverse consequences for man and other nontarget species. The purpose of this subdivision is to describe in more detail the Agency's requirements for data concerning the environmental fate of pesticides, which are set forth at 40 CFR § 158.130. These data must be submitted to support the registration of most manufacturing-use products. The Agency will use these data in the identification and assessment of the potential hazards associated with each of the anticipated uses of a pesticide in the different environments in which they are used.

(b) Application of requirements. (1) Application status and compliance. The requirements imposed by 40 CFR § 158.130 and described in this subdivision apply to products already registered as well as those being proposed for registration. The Agency will notify registrants of products already registered, either (occasionally) through the data call-in program, or (routinely) upon development of a registration standard, as to when they must satisfy the data requirements of this subdivision. Refer to § 158.30 of 40 CFR §158 for details of application status and submittal times.

(2) "When required" and "Test substance" requirements. The registration applicant should be careful to distinguish between the "When required" and the "Test substance" paragraph requirements of each section of this subdivision:

(i) The "When required" paragraphs pertain to the circumstances under which data shall be required, and specify the categories of products for which data must be generated to support registration applications. The test data are ordinarily required to support the registration of each end-use product with the prescribed use pattern and each manufacturing-use product used to make such an end-use product.

(ii) The "Test substance" paragraphs relate to the test procedure required to produce acceptable data, and state whether the test substance for a particular study may be the technical chemical, a typical end-use product, or a radioactively-labeled analytical grade chemical.

(3) Testing to meet requirements. Since studies described in this subdivision would ordinarily be conducted by the basic manufacturer, pesticide formulators would not often be expected to conduct such tests themselves to develop data to support the registration of their individual products. They may do so if they wish, but they may also rely on the basic pesticide manufacturer's data already developed. See § 158.50 of 40 CFR § 158 for details of the data submittal exemption for pesticide formulators.

(c) Approach of subpart. (1) This subdivision describes the Agency's requirements for data pertaining to environmental fate of pesticide chemicals. The data requirements are divided into five categories of tests (degradation, metabolism, mobility, field dissipation, and accumulation).

(2) The need for data pertaining to some or all of these tests depends primarily on the pesticidal use pattern. For purposes of this subdivision, pesticides which are used oudoors are categorized by one or more of the following use patterns: terrestrial, aquatic, forestry, and aquatic impact. Applicants should consult the use pattern index (Appendix A of 40 CPR § 158) to determine which use pattern category includes their specific use patterns.

(d) Summary tables. (1) Tables 1 and 2 summarize many of the data requirements set forth in 40 CFR Part 158 and described in this subdivision. Table 1 lists data requirements for terrestrial and forestry use patterns, and Table 2 lists data requirements for aquatic and aquatic impact use patterns. Terms used in these tables have been defined in § 160-2 and described in more detail with examples in § 160-3.

(2) The data requirements for long-term soil dissipation studies are not included in the tables. Also, the following specialized use patterns are not included in the tables: specialized aquatic uses (e.g., antifouling paints on ships and related protective or preservative uses), field volatility, and combination and tank mixes. These uses are covered in the text under the appropriate specific data requirements.

(3) As an aid to identification of testing requirements which may support more than one use pattern, Tables 1 and 2 are presented in a modified bar graph format. Any two or more identified use patterns which are connected by a line on the table have identical environmental fate testing requirements and therefore the data derived from any one test will satisfy the data requirements for all designated use patterns. Where a line does not connect use

patterns on the table, the stringency of the testing requirements differs sufficiently among the identified use patterns so that the data derived from any one test will not satisfy the data requirements for all other designated use patterns. In the case of soil field dissipation data requirements for terrestrial and forest use patterns, however, some degree of substitution of data requirements among identified use patterns is possible. For example, data derived from studies for use patterns (e.g., orchard crop) conducted under more rigorous testing requirements may substitute for or be used to satisfy the data requirements for use patterns (e.g., terrestrial non-crop) that require less rigorous testing requirements, but the reverse is not permissible.

(e) Organization and content of sections. (1) Section 160-2 contains definitions applicable to this subdivision.

(2) Section 160-3 describes the use patterns of pesticides which form the basis for the requirements of this subdivision.

(3) Section 160-4 describes general standards for tests to be performed pursuant to this subdivision.

(4) Section 160-5 contains general requirements for the reporting and evaluation of data.

(5) Section series 161 through 165 provide the specific test standards and reporting requirements for each major data requirement category:

(i) Section series 161 deals with degradation studies;
(ii) Section series 162 deals with metabolism studies;
(iii) Section series 163 deals with mobility studies;
(iv) Section series 164 deals with dissipation studies; and
(v) Section series 165 deals with accumulation studies.

(f) References. (i) At the end of each section are referenced examples of published literature containing acceptable procedures and supplemental background or ancillary material which may be consulted in developing test protocols. To aid the registration applicant in finding appropriate information within the list of publications, the Agency has added a brief annotation following each reference. The annotations point out the usefulness of each publication for development of protocols.

(ii) The Agency recognizes that more than one referenced study may be used in developing a protocol in a given area. In all cases, if the referenced procedure(s) used to develop an alternate protocol contain(s) other information that is inconsistent with

Table I. Summary of Environmental Fate Data Requirements for Terrestrial and Forestry Use Patterns.

Data Requirements*	Terrestrial Uses: Domestic Outdoor	Green-House	Non-Crop	Orchard Crop	Field and Veg. Crop	Fores-try	Test Identical for Aquatic & Aquatic Impact Use Patterns
Degradation							
Hydrolysis	X	X	X	X	X	X	Yes
Photodegradation							
-water			X	X	X	X	Yes
-soil				X	X	X	
Metabolism							
Aerobic Soil	X	X	X	X	X	X	No
Anaerobic Soil**					X		
Anaerobic Aquatic						X	No
Mobility							
Leaching***	X	X	X	X	X	X	No
Field Dissipation							
Soil****	X		X	X	X		No
Water							
Forest						X	
Accumulation							
Rotational Crop					X		Yes
Irrigated Crop							
Fish			X	X	X	X	Yes
Aquatic Nontarget						X	Yes

* Data requirements cited in § 161-4 (Photodegradation studies in air), § 163-2 (Laboratory volatility studies), § 163-3 (Field volatility studies), § 164-4 (Dissipation studies for combination products and tank mix uses), and § 164-5 (Long-term soil dissipation studies) are not included in this table.

** The anaerobic aquatic metabolism data may be substituted for the anaerobic soil metabolism data but the reverse is not permissible.

*** For domestic outdoor and greenhouse uses a batch equilibrium (adsorption/desorption) study must be conducted.

**** Data derived from studies for use patterns (e.g., field and vegetable crop) conducted under more rigorous testing requirements may substitute for or be used to satisfy the data requirements for use patterns (e.g., orchard crop) that require less rigorous testing requirements, but the reverse is not permissible.

Table 2. Summary of Environmental Fate Data Requirements for Aquatic and Aquatic Impact Use Patterns.

Data Requirements*	Aquatic Uses: Food Crop	Aquatic Uses: Non-Crop	Aquatic Impact Uses: Direct Discharge	Aquatic Impact Uses: Indirect Discharge	Test Identical for Terrestrial and Forestry Use Patterns
Degradation					
Hydrolysis	X==========	X=========	X=========	X	Yes
Photodegradation					
-water	X==========	X=========	X		Yes
-soil					
Metabolism					
Aerobic Aquatic	X==========	X=========	X		No
Anaerobic Aquatic**	X==========	X=========	X		
Mobility					
Leaching***	X==========	X=========	X		No
Field Dissipation					
Soil (sediment)	X	X			No
Water	X	X=========	X		
Forest					
Accumulation					
Rotational Crop	X				Yes
Irrigated Crop	X==========	X			
Fish	X==========	X=========	X		Yes
Aquatic Nontarget		X=========	X		Yes

* Data requirements cited in § 161-4 (Photodegradation studies in air), § 163-2 (Laboratory volatility studies), § 163-3 (Field volatility studies), § 164-4 (Dissipation studies for combination products and tank mix uses), and § 164-5 (Long-term soil dissipation studies) are not included in this table.

** The anaerobic aquatic metabolism data may be substituted for the anaerobic soil metabolism data, but the reverse is not permissible.

*** Mobility studies for aquatic and aquatic impact uses are not applicable for leaching, but are for interpretation of surface runoff mobility and dispersion in an aquatic habitat. Therefore, a batch equilibrium (adsorption/desorption) study must be conducted.

test standards and requirements as specified in the guidelines, then the alternate protocol must be modified to conform with the test requirements in the guidelines.

(iii) In 40 FR 26802 (June 25, 1975, pages 26878-26896), the Agency provided a detailed discussion of many of the tests described in §§ 161-1 through 165-4. This information may be of help to the registrant.

(g) Waivers. Refer to 158.50 of 40 CFR § 158 for details on the policy for waiver of data requirements.

§ 160-2 Definitions.

(a) Terms used in this subdivision shall have the meanings set forth in FIFRA in § 162.3 of the FIFRA Sec. 3 regulations, and in § 60-2 of Subdivision D.

(b) In addition, for the purposes of this subdivision:

(1) The term "agricultural use" means the use of a pesticide product in the production of animals and plants for food, feed, fiber, lumber, flowers, ornamental value, pets, condiments, beverages, chemicals, fuels, smoking and chewing products, and related commodities and purposes.

(2) The term "aquatic crop" means a planting of vegetation and the produce thereof for which all or part of the life cycle involves immersion or suspension of above-ground plant parts in water.

(3) The term "aquatic food crop use" means the use of a pesticide product at any aquatic site for the purpose of controlling pests or providing protection from pests in any aquatic crop grown for the production of human food or domestic animal feed, or for plant regulating purposes in such crops.

(4) The term "aquatic impact use" means use of a pesticide product on water in an enclosed facility or aquatic site that is not accessible to wildlife, birds, fish, or aquatic organisms but from which treated water may subsequently be discharged into natural or outdoor bodies of water accessible to wildlife, birds, fish, or other aquatic organisms.

(5) The term "aquatic noncrop use" means the use of a pesticide product for the purpose of controlling pests or providing protection

from pests in or adjacent to any aquatic site other than that used for production of human food or domestic animal feed, or for plant regulating purposes on such plants.

(6) The term "aquatic use" means use of a pesticide in or adjacent to any outdoor aquatic site readily accessible to wildlife or to aquatic and semiaquatic animals and plants.

(7) The term "direct discharge" of a pesticide means the release, treatment, or application of a pesticide product directly to water at sites within or directly connected to bodies of water to which wild animals, birds, fish, and similar organisms have free access.

(8) The term "domestic outdoor use" means the domestic (non-commercial) application of a pesticide product around (but not in) the home.

(9) The term "field and vegetable crop use" means use of a pesticide product for the purposes of controlling pests or providing protection from pests in any field crop and/or vegetable crop, or for plant regulating purposes in such crops.

(10) The term "forestry use" means use of a pesticide product for the purpose of controlling pests or providing protection from pests in forests, forest tree nurseries, or reforestation sites, or for plant regulating purposes on plants at such sites.

(11) The term "greenhouse use" means use of a pesticide product for the purpose of controlling pests or providing protection from pests in crops grown in commercial greenhouses, or for plant regulating purposes on such plants.

(12) The term "indirect discharge" of a pesticide means release, treatment, or application of a pesticide product to water at sites not directly connected to bodies of water to which wild animals, birds, fish, and similar organisms have free access.

(13) The term "material balance" means an accounting of the quantities of a chemical and its degradates in a defined system based on total radioactivity and/or other recognized analytical methodology.

(14) The term "nonagricultural use" means the use of a pesticide product for all purposes other than those included under the term "agricultural uses."

(15) The term "orchard crop use" means use of a pesticide product for the purpose of controlling pests or providing protection from pests in trees, vines, and shrubs grown or maintained for

production of fruits and nuts, or for plant regulating purposes on such plants.

(16) The term "outdoor use" is generally synonymous with "outdoor application." See sec. 162.3 (cc) of the FIFRA sec. 3 regulations. For the purposes of this subdivision, uses of pesticides in greenhouses, for pulp and paper mill water treatments, and for industrial cooling water treatments are considered outdoor uses.

(17) The term "plant regulatory purposes" means those purposes indicated in sec. 162.3 (ff)(14) of the FIFRA sec. 3 regulations.

(18) The term "serial application" refers to the label-recommended use of a pesticide on a site before or after application of another pesticide to that site, such that the presence of one of the pesticides may affect (usually enhance or complement) the effectiveness and usefulness of the other.

(19) The term "tank mix" refers to the mixture of two or more different pesticide products in a spray tank or other application equipment for the purpose of subsequent application of all products simultaneously.

(20) The term "terrestrial crop" means a planting of vegetation and the produce thereof for which the entire life cycle of the plants involves germination, growth, and maturation in association with anchorage in soil above the water table.

(21) The term "terrestrial noncrop use" means the use of a pesticide product for the purpose of controlling pests or providing protection from pests in any terrestrial vegetation other than that used for production of human food or domestic animal feed, or for plant regulatory purposes on such plants.

(22) The term "terrestrial use" means use of a pesticide in greenhouses or in any or all outdoor land sites except forests and forestry use sites.

(23) The term "typical end-use product" means a pesticide product that is representative of a major formulation category (e.g., emulsifiable concentrate, granular product, wettable powder) and contains the active ingredient of the registration applicant's product.

§ 160-3. Use Patterns.

(a) General. Environmental fate data are required for pesticides intended for outdoor uses. Outdoor uses include most agricultural uses of pesticides and many non-agricultural uses, mostly in

the terrestrial and aquatic non-crop categories. To help specify data requirements to which a pesticide is subject, the Agency has grouped pesticides into the following categories: terrestrial, aquatic, aquatic impact, and forestry uses.

(b) Terrestrial uses. Terrestrial uses include, but are not limited to:

(1) Domestic outdoor uses such as lawn, garden, patio, home swimming pool, and non-commercial greenhouse pesticide uses;

(2) Greenhouse uses, such as for pest control on edible crop plants and on flowering, tropical, and ornamental plants grown in commercial greenhouses. Commercial greenhouse pesticide applications are considered "outdoor uses" since commodities produced in these sites, being of high economic value and requiring intensive pesticide applications for pest control and intensive use of agricultural labor, represent a farm environment with similar - but not identical - pesticide fate characteristics as for many "typical" outdoor uses."

(3) Non-crop uses, such as for vegetation control along utility and highway rights-of-way, at utility substations, in industrial outdoor storage areas, on golf course sandtraps, and at outdoor parking lots.

(4) Orchard crop uses; and

(5) Field and vegetable crop uses.

(c) Aquatic uses. Aquatic uses include, but are not limited to: limited to:

(1) Aquatic food crop uses. These uses include the application of pesticides to areas intended for the production of aquatic or semiaquatic crops such as rice, cranberry, and taro, or for the commercial production of crayfish and catfish; and

(2) Aquatic non-crop uses. These uses generally involve the intentional application of pesticides directly to water to control water pests in areas where food crops are not produced. Uses include applications of products such as larvicides, piscicides, algicides, aquatic weed herbicides, antifouling paints, and molluscicides. Products intended for application to ditchbanks and shorelines are also included in this use pattern category.

(d) Aquatic impact uses. Uses in this category generally involve pesticide applications to water in or within man-made structures (e.g., municipal and industrial wastewater treatments, pulp and paper mill treatments and industrial cooling tower treatments) but which have the potential for adverse consequences which

extend beyond the man-made structures. These consequences may have an impact on organisms in such environments as holding ponds, wastewater treatment facilities, and natural or open aquatic environments. Aquatic impact uses are divided into two categories: direct discharges, and indirect discharges and wastewater treatment.

(1) Direct discharge. This category includes the practice of discharging end-use products directly into the natural aquatic environment in association with their use or the typical method of disposal of pesticide-treated water. Also included are pesticides that are discharged into any man-made aquatic facility where the water is not intercepted by the facility and thus flows directly into natural or open aquatic environments. Since cooling tower water is commonly discharged into lakes, streams, and rivers, most pesticides used to control bacteria or other pests in cooling towers are considered to have direct discharge uses.

(2) Indirect discharges and wastewater treatments. This category includes the practice of applying or supplying pesticides to wastewater treatment facilities where the water is captive, such as for filter fly control. Water in such facilities is generally released only occasionally into natural or open aquatic environments.

(e) Forestry uses. Forestry uses involve pesticide applications to areas that include both terrestrial and aquatic environments (e.g., woods, marshes, streams) consisting principally of forest and reforestation sites.

§ 160-4 General test standards.

(a) Overview. The standards contained in this section apply to all studies in this subdivision unless another section of this subdivision contains a specific standard on the same subject. In such a case, the specific standards in the other section apply to the conduct of that particular study.

(b) Test substance. (1) Data submitted in support of an application for registration shall be derived from tests conducted with the technical (or purer) grade of the active ingredient, a radioactively-labeled analytical grade of the active ingredient, or a typical end-use product, as specified in the test procedure for the particular test.

(2) Although the guidelines permit use of either radiolabeled or non-radiolabeled material as the test substance for some studies, the applicant should be aware that, under almost all circumstances, use of the radiolabeled test substance would generally be the

logical choice for developing satisfactory data. This is particularly true for studies that require a material balance.

(3) The composition of the test substance should be determined, including the names and quantities of known contaminants and impurities, as far as is technically feasible.

(4) The applicant should assign and record lot and sample number of the test substance.

(5) In addition to or in lieu of testing otherwise required by this subdivision, the Administrator may require testing to be conducted with:

(i) An analytically pure grade of an active ingredient;

(ii) The technical grade of an active ingredient;

(iii) An intentionally added inert ingredient of a pesticide formulation;

(iv) A contaminant or impurity of an active or inert ingredient;

(v) A plant or animal metabolite or degradation product of an active or inert ingredient;

(vi) A pesticide formulation; or

(vii) Any additional substance which could act as a synergist to the product for which registration is sought.

(c) Field studies. (1) Location. Field studies should be conducted in areas considered representative of major areas where the pesticide is intended to be used.

(2) Endangered species. Field studies should not be conducted in critical habitats or areas containing or suspected to contain endangered or threatened plants or animals which may be threatened by the test to be conducted.

(d) Inter-relationship among studies with respect to soil type. The same soil type should be used for the accumulation study on rotational crops (§ 165-1), the study of photodegratation on soil surfaces (§ 161-3), the aerobic soil metabolism study (§ 162-1), the anaerobic soil metabolism study (§ 162-2), the leaching study (§ 163-1), and the terrestrial field dissipation study (§ 164-1). The Agency will consider requests for exceptions to this requirement on a case-by-case basis.

§ 160-5 Reporting and evaluation of data.

(a) Overview. This section describes general reporting and evaluation requirements which apply to studies in the subdivision. Each test report submitted under this subdivision should satisfy the reporting requirements of this section, unless a specific section elsewhere in this subdivision directs otherwise.

(b) Submission. Data submitted in response to 40 CFR Part 158 should be provided in a single report to the extent possible. Any data that have been furnished in response to the requirements of another subdivision and that are also required by this subdivision either should be referenced to specific pages in other volumes or should be duplicated and submitted in the volumes containing environmental fate data.

(c) Content. The test report should include a complete and accurate description of test procedures and evaluation of the test results. It should also contain a summary of the data, an analysis of the data, sufficient data for the Agency to verify calculated statistical values, and a statement of conclusions to be drawn from the analysis. The summary should contain sufficient detail to permit the reader to understand the conclusions of the author. In addition to the specific information required by §§ 161-1 through 165-5 of this subdivision, the test report should include the following information:

(1) General information. Each report should contain:

(i) Dates on which study began and ended;

(ii) Name and address of laboratory or institution performing the test;

(iii) Location where the test was performed;

(iv) Names of principal investigators;

(v) Signatures of each of the senior scientific personnel responsible for the study; and

(vi) Certification by the applicant that the report is a complete and unaltered copy of the report provided by the testing facility.

(2) Test method. Each report should contain a statement regarding the test method used, including a full description of the experimental design and procedures.

(3) Test substance. (i) The report should identify the test substance, and should include chemical name and percentage of active ingredient, molecular structure of the active ingredient, and qualitative and quantitative description of the chemical composition, including the results of the analysis conducted in accordance with § 160-4(d)(3), when applicable;

(ii) Manufacturer and lot and sample numbers of the test substances; and

(iii) Properties of the test substance, including physical state, pH, and stability, when not reported for Subdivision D.

(4) Control Values. Due to the wide diversity of pesticide properties, use patterns, and organisms likely to be exposed in the field environment, specific reporting requirements for control values (as to source, sampling regime, and total number submitted) will depend upon the complexity and variability of the environment in which the test is to be conducted.

(5) Test equipment. The report should include a description of the test equipment used, and photographs or detailed descriptions of nonstandard equipment.

(6) Units of measurement. Reporting units should be in the metric system, but the English system may be used, in addition. In no instance should the systems be mixed (e.g., kilograms/acre).

(7) Calculations and tabular, graphic information. Each report should contain the principal mathematical equations used in generating and analyzing data, as well as representative calculations using these equations. When rates of formation and decline of parent compounds or their degradates are reported in any test, data should be expressed as amounts, concentrations, and corresponding percentages. Rate constants, when required, should be reported in conjunction with rate data. Tabular data, as well as graphs for decline curves and soil sorption, should be submitted.

(8) Analysis for and identification of degradation products. Analysis and identification of pesticide residues in field studies is required only for those degradation products that were found to form in the lab studies. This position is taken because the purpose of the lab studies is to identify degradation products and derive kinetics while the purpose of field studies is to derive levels of degradation products as a result of pesticide use under field conditions. Results from the field studies are used in the regulatory process.

(9) Media characteristics. (i) Soils. Characterization of soils utilized in laboratory soil photodegradation, metabolism, and mobility studies, and soils sampled at all field use sites

must be reported, including texture (percent sand, silt, and clay), percent organic matter, moisture content, pH, cation exchange capacity, and bulk density (under field conditions). Soil from foreign sources may be used in those lab studies requiring soil, providing the foreign soil will have the same characteristics as soil in the United States common to the proposed use area. Characteristics to be matched are:

- soil class
- % organic matter
- pH soil
- ratio of soil bacteria to soil fungi to soil actinomycetes

Field studies are to be conducted in the United States.

(ii) Water. In cases of aquatic field tests, characteristics of water obtained from a use site must be reported (e.g., pH, temperature, oxygen content, flow rate, and percent suspended solids).

(10) Data evaluation. Data submitted from studies described in this subdivision will be evaluated by the Agency for relevance to the proposed use, technical adequacy, completeness and overall scientific value, and will be used in assessing the potential occurrence of the following environmental hazards:

Direct hazards to humans;
Direct hazards to fish and wildlife;
Potential for contaminating groundwater;
Potential for magnification in the food chain; and
Potential for uptake by rotational crops.

Series 161: DEGRADATION STUDIES

§ 161-1 Hydrolysis studies.

(a) Purpose. Hydrolysis studies are used to establish the significance of chemical hydrolysis as a route for degradation of a pesticide and to identify, if possible, the hydrolytic products formed which may adversely affect nontarget organisms and may contaminate their food.

(b) When required. Hydrolysis data are required by 40 CFR §158 to support the registration of an end-use product intended for outdoor or aquatic impact use, and to support each application for registration of a manufacturing-use product which may legally be used to formulate such an end-use product. See, specifically, 40 CFR §158.50 and §158.130 to determine whether these data must be submitted. Section II-A of this Subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(c) Test standards. Hydrolysis data submitted in response to 40 CFR § 158.130 should be derived from tests which comply with the general test standards of §160-4 of this subdivisions and all of the following specific test standards:

(1) Test substance. (i) These studies shall be conducted with each active ingredient in the product.

(ii) Where radioisotopic analytical techniques are used (they are preferred), studies shall be conducted with the analytical grade of each active ingredient in the product.

(iii) Where non-radioisotopic analytical techniques are used, studies shall be conducted with the technical or purer grade of each active ingredient in the product.

(2) Test procedures. (i) Laboratory hydrolysis studies should be conducted in darkness.

(ii) One or more concentrations of the test substance should be used for this study. The concentration(s) selected should be within the aqueous solubility range of the pesticide and at a level high enough to define the kinetics of the reaction and also permit isolation and identification of hydrolysis products formed. However, the maximum concentration(s) selected should not exceed 250 ppm. For pesticides of low water solubility (less than 10 ppm), an appropriate solubilizing cosolvent may be added to increase water solubility. However, use of such agents should be avoided whenever possible, and, if used, the concentration of

cosolvent in the final solution should not exceed 1 percent by volume.

(iii) The water used for this study should be free of all live bacteria, and the glassware should be sterilized to minimize the possibility of microbial degradation of the test substance.

(iv) Precautions should be taken during the test to minimize loss of test substance through volatilization.

(v) The temperature of the hydrolysis reaction should be maintained at 25 ± 1°C.

(vi) Hydrolysis experiments should be carried out in solutions buffered at pH's of 5, 7, and 9.

(vii) Results of hydrolysis experiments using high concentrations of buffer should be carefully evaluated to determine whether buffer catalysis effects have occurred.

(viii) Aliquots should be taken at zero time and at sufficient sampling time intervals to define decline of the pesticide and appearance of degradates. The duration of the test need not exceed 30 days.

(d) Reporting and evaluation of data. In addition to data meeting the applicable reporting requirements specified in § 160-5, the test report should contain the following specific information:

(i) The method of adjusting pH.

(ii) Identification of each hydrolysis product produced in greater than 10 percent yield at any point during the course of the study, and material balance and half-life estimates for the parent substance.

(e) References. (1) The following references contain experimental procedures for conducting hydrolysis studies:

(i) Krzeminski, S.F., C.K. Brackett, and J.D. Fisher. 1975. Fate of microbicidal 3-isothiazolone compounds in the environment: modes and rates of dissipation. J. Agr. Food Chem. 23:1060-1068. [The effects of temperature and solution pH on hydrolysis rates are illustrated in this paper.]

(ii) Gomaa, H.M., I.H. Suffet, and S.D. Faust. 1969. Kinetics of hydrolysis of diazinon and diazoxon. Residue Rev. 29:171-190. [This article contains excellent and concise discussions of the kinetics and mechanisms of acid/base catalyzed hydrolysis of an organophosphorus pesticide and its products. It also discusses the effect of temperature on hydrolysis rate, and

illustrates calculation of energies of activation for the hydrolysis reactions. This article is recommended for information on theory and development of rate constants, but the more recent and definitive gas chromatographic/mass spectrographic (GC-MS) technique is recommended for identification of hydrolysis products rather than the methods used here.]

(iii) Under the Toxic Substances Control Act, the Agency has proposed test standards for public review regarding hydrolysis (and certain other studies). These may be found in 44 FR 16240, (March 16, 1979), entitled "Toxic Substances Control: Discussion of Premanufacturing Testing Policy and Technical Issues; Request for Comment."

(iv) [Reserved for: OECD Guidelines for Testing Chemicals. Section 1, Number 111. Hydrolysis as a Function of pH.]

(v) [Reserved]

(2) Information on GC-MS for identification of pesticides and products can be found in:

(i) Ryan, J.F. 1977. Residue Analysis Applications of Mass Spectrometry. Pp. 1-49 in Analytical Methods for Pesticides and Plant Growth Regulators. IX. Spectroscopic Methods of Analysis. G. Zweig and J. Sherma (eds). Academic Press, Inc. N. Y.

(ii) Wolfe, N.L., R.G. Zepp, G.L. Baughman, R.C. Fincher, and J.A. Gordon. 1976. Chemical and Photochemical Transformation of Selected Pesticides in Aquatic Systems. Ecological Research Series. USEPA 600/3-76-067. 141 pp. [This publication contains reviews and experiments on the photolysis of various pesticides in water. Extensive information is presented that may be useful for the design of experiments and evaluation of data.]

§ 161-2 Photodegradation studies in water.

(a) Purpose. Pesticides introduced into aqueous systems in the environment can undergo photolytic transformation by sunlight. Data on rates of photolysis and half-lives are needed to establish the importance of this transformation process and the persistence characteristics of photoproducts formed.

(b) When required. Data from a photodegradation study in water are required by 40 CFR §158 to support the registration of an end-use product intended for any terrestrial use (except greenhouse and domestic outdoor use), aquatic use, or forestry use, or for any aquatic impact uses involving direct discharges of treated

water into outdoor aquatic sites. Data from such a study are also required to support each application for registration of a manufacturing-use product which may legally be used to formulate such an end-use product. See, specifically, 40 CFR § 158.50 and §158.130 to determine whether these data must be submitted. Section II-A of this subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(c) Test standards. Photodegradation data submitted in response to CFR §158.130 should be derived from tests which comply with the general test standards of §160-4 of this Subdivision and all of the following specific test standards.

(1) Test substance. These studies shall be conducted with each active ingredient in the product.

(i) Where radioisotopic analytical techniques are used (they are preferred), studies shall be conducted with the analytical grade of each active ingredient in the product.

(ii) Where non-radioisotopic analytical techniques are used, studies shall be conducted with the technical or purer grade of each active ingredient in the product.

(2) Test procedures. (i) Studies should be conducted at 25± 1°C.

(ii) One or more concentrations of the test substance should be used for this study at levels which will define the kinetics of the reaction and permit isolation and identification of photoproducts formed. For pesticides of low water solubility, an appropriate solubilizing co-solvent may be added to increase water solubility. However, use of such agents should be avoided whenever possible, and, if used, the concentration of co-solvent in the final solution should not exceed 1 percent by volume. The cosolvent should not act as a photosensitizer in the rate study.

(iii) Precautions should be taken during the test to minimize loss of test substance through volatilization.

(iv) Photolysis rate determination and photoproduct identification experiments should be carried out at a pH that minimizes hydrolytic breakdown as determined in § 161-1. The pH selected should be maintained by the use of an appropriate buffer. The buffer solution should be prepared in distilled or deionized water free of all live bacteria, and the glassware should be sterilized to minimize the possibility of microbial degradation of the test substance. For compounds that reversibly ionize or protonate within the pH range of environmental concern, aqueous photolysis

rate determination studies (only) shall be carried out at pH's of 5, 7, and 9.

(v) Samples should be exposed to either natural or simulated (including UV greater than 290 nm wavelength) sunlight conditions. If high intensity radiation studies are conducted to allow shorter testing periods (e.g., use of Crosby reactor, as described in reference (i) of paragraph (e) of this section), data should be provided relating the intensity of the radiation used to that of natural sunlight.

(vi) Non-irradiated samples of one or more concentrations of test substance in water held in darkness should be used as experimental controls.

(vii) Aliquots for analysis should be taken at four or more sampling time intervals, with at least one observation made after one-half of the test substance is degraded or after the equivalent of 30 days natural sunlight (12 hours of light per day), whichever comes first.

(viii) A supplemental rate and photoproduct identification study may also be carried out in the presence of a photosensitizer.

(d) Reporting and evaluation of data. In addition to the applicable information specified in § 160-5, the test report should contain the following specific information:

(1) If sunlight is used as the light source, a record of the intensity of incident sunlight, time of exposure, latitude, time of year, atmospheric cover, and other major variables which affect incident light.

(2) If artificial light is used as the light source, the nature of the source, intensity, wave length distribution, and time of exposure, as well as the relationship of the light intensity employed to that of natural sunlight.

(3) Identification of each photoproduct produced in greater than 10 percent yield at any point during the course of the study, and material balance and half-life estimates for the parent substance.

(e) References. The following references contain experimental procedures for conducting water photolysis studies:

(i) Nakagawa, M., and D.G. Crosby. 1974. Photodecomposition of nitrofen. J. Agr. Food Chem. 22:849-853. [This detailed study provides procedures for photolysis of a pesticide in water under either artificial or natural sunlight.]

(ii) Newsom, H.C., and W.G. Woods. 1973. Photolysis of the herbicide dinitramine (N^3,N^3-diethyl-2,4-dinitro-6-trifluoromethyl-m-phenylenediamine). J. Agr. Food Chem. 21:598-601. [This article contains procedures for study of pesticide photolysis in natural water.]

(iii) Niles, G.P., and M.J. Zabik. 1975. Photochemistry of bioactive compounds. Multiphase photodegradation and mass spectral analysis of basagran. J. Agr. Food Chem. 23:410-415. [Procedures for photolysis in aqueous solution, on soil, and as a thin film are discussed in this article.]

(iv) Su, G.C.C., and M.J. Zabik. 1972. Photochemistry of bioactive compounds. Photolysis of arylamidine derivatives in water. J. Agr. Food Chem. 20:320-323. [Procedures here are well defined and useful for a laboratory study of pesticide photolysis in natural water.]

(v) (Reserved)

(2) Supplemental information for developing a protocol to conduct a water photolysis study for reentry assessment is given in the following references:

(i) Wolfe, N.L., R.G. Zepp, G.L. Baughman, R.C. Fincher, and J.A. Gordon. 1976. Chemical and Photochemical Transformation of Selected Pesticides in Aquatic Systems. Ecological Research Series. USEPA 600/3-76-067. 141 pp. [This publication contains reviews and experiments on the transformation of various pesticides in water. Extensive information is presented that may be useful for the design of experiments and evaluation of data.]

(ii) Under the Toxic Substances Control Act, the Agency has proposed test standards for public review regarding photolysis (and certain other studies). These may be found in 44 FR 16240 (March 16, 1979), entitled "Toxic Substances Control: Discussion of Premanufacturing Testing Policy and Technical Issues; Request for Comment."

§ 161-3 Photodegradation studies on soil.

(a) Purpose. Pesticides are applied to the surface of soil and/or on the exposed surfaces of plants, and are then subject to photodegradation. This study will provide data on photolytic pesticide dissipation and on the nature and persistence of photoproducts formed by soil surface catalyzed photolysis.

(b) When required. Data from a photodegradation study on soil surfaces are required by 40 CFR § 158 to support the registration of an end-use product intended for orchard crop use, field and vegetable crop use, or forestry use. Data from such a study are also required to support each application for registration of a manufacturing-use product which may legally be used to formulate such an end-use product. However, such data are not required to support the registration of end-use products with uses involving application to soils solely by injection of the product into the soil or by incorporation of the product into the soil upon application. See, specifically 40 CFR §158.50 and §158.130 to determine whether these data must be submitted. Section II-A of this Subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(c) Test standards. Soil photodegradation data submitted in response to 40 CFR § 158.130 should be derived from tests which comply with the general test standards of § 160-4 of this Subdivision and all of the following specific test standards:

(1) Test substance. These studies shall be conducted with each active ingredient in the product.

(i) Where radioisotopic analytical techniques are used (they are preferred), studies shall be conducted with the analytical grade of each active ingredient of the product.

(ii) Where non-radioisotopic analytical techniques are used, studies shall be conducted with the technical or purer grade of each active ingredient in the product.

(2) Test procedures. (i) One or more concentrations of the test substance should be used for this study at levels that will permit isolation and identification of photoproducts formed.

(ii) One of the soils (e.g., sandy loam, silt loam, or other soil appropriate to the application site) specified in § 162-1 (Aerobic soil metabolism study) should be used, if data from that study are also submitted.

(iii) Samples of soil should be exposed to either natural or simulated sunlight conditions.

(iv) Samples of soil treated with the pesticide at the same application rate as irradiated soil samples and maintained in darkness should be used as experimental controls.

(v) Soil samples should be taken for analysis at four or more sampling time intervals, with at least one observation made after

one-half of the test substance has degraded or 30 days, whichever comes first. The maximum duration of the study need not exceed 30 days.

(d) Reporting and evaluation of data. In addition to the applicable information specified in § 160-5, the test report should contain the following specific information:

(1) If sunlight is used as the light source, a record of the intensity of incident sunlight, time of exposure, latitude, time of year, atmospheric cover, and other major variables which affect incident light.

(2) If artificial light is used as the light source, the nature of the source, intensity, wave length, distribution, and time of exposure.

(3) Identification of each photoproduct produced in greater than 10 percent yield at any point during the course of the study, and material balance and half-life estimates for the parent substance.

(e) References. (1) The following references contain experimental procedures for conducting soil photolysis studies:

(i) Koshy, K.T., A.R. Friedman, A.L. van der Slik, and D.R. Graber. 1975. Photolysis of benzoic acid 2-(2,4,6-trichlorophenyl)-hydrazide. J. Agr. Food Chem. 23:1084-1088. [A procedure for photolysis of a thin film of pesticide by artificial light is described in this paper.]

(ii) Niles, G.P., and M.J. Zabik. 1975. Photochemistry of bioactive compounds. Multiphase photodegradation and mass spectral analysis of basagran. J. Agr. Food Chem. 23:410-415. [Procedures for photolysis in aqueous solution, on soil, and as a thin film are discussed in this article.]

(2) Under the Toxic Substances Control Act, the Agency has proposed test standards for public review regarding photolysis (and certain other studies). These may be found in 44 FR 16240, (March 16, 1979), entitled "Toxic Substances Control: Discussion of Premanufacturing Testing Policy and Technical Issues; Request for Comment." This discussion can provide supplemental information for developing a protocol to conduct a soil photolysis study.

§ 161-4 Data requirements for photodegradation studies in air.

(a) Purpose. When pesticides are used, humans and other non-target organisms could be exposed to relatively high concentrations of pesticide photoproducts in air. This study will provide data on photolytic pesticide dissipation and on the nature and persistence of photoproducts formed from pesticides in the vapor phase.

(b) When required. Data from a laboratory photodegradation study in the vapor phase are required by 40 CFR § 158 on a case-by-case basis to support the registration of an end-use product intended for orchard or field vegetable crop uses that involve potentially significant exposure to workers. Data from such a study are also required to support each application for registration of a manufacturing-use product which legally could be used to formulate such an end-use product. The Agency will make an assessment of what constitutes a significant inhalation exposure of workers based on the information required by § 163-2(b)(2) of this Subdivision. See, specifically, 40 CFR 158.50 and 158.130 to determine whether these data must be submitted. Section II-A of this Subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(c) Test standards. Air photodegradation data submitted in response to 40 CPR § 158.130 should be derived from tests which comply with the general test standards in § 160-4 and all of the following specific test standards:

(1) Test substance. These studies shall be conducted with one of the following test substances:

(i) Where radioisotopic analytical techniques are used (they are preferred), studies shall be conducted with the analytical grade of each active ingredient in the product; or

(ii) Where non-radioisotopic analytical techniques are used, studies shall be conducted with the technical or purer grade of each active ingredient in the product.

(2) Test procedures. (i) One or more concentrations of the test substance should be used for this study and at levels that will permit isolation and identification of photoproducts formed.

(ii) Air samples should be exposed to a spectrum of light providing or simulating expected use conditions. Temperature should be held relatively constant at 30°C.

(iii) Samples of air treated with the pesticide at the same application rates for irradiated samples and maintained in darkness should be used as experimental controls.

(iv) Air samples should be analyzed at four or more sampling time intervals with at least one observation made after one-half of the test substance has degraded or 30 days, whichever comes first. The maximum duration of the study need not exceed 30 days.

(d) Reporting and evaluation of data. In addition to the applicable information specified in § 160-5, the test report should contain the following specific information:

(1) If sunlight is used as the light source, a record of the intensity of incident sunlight, time of exposure, and other major variables which affect incident light such as latitude, time of year, and atmospheric cover.

(2) If artificial light is used as the light source, the nature of the source, intensity, wave length distribution, and time of exposure.

(3) Identification of each photoproduct produced in greater than 10 percent yield at any point during the course of the study, and material balance amd half-life estimates for the parent substance.

(e) References. The following references contain information for developing a protocol to conduct an air photolysis study:

(1) Crosby, D.G., and K.W. Moilanen. 1974. Vapor-phase photodecomposition of aldrin and dieldrin. Arch. Environ. Contam. Toxicol. 2:62-74. [The reaction vessel described here allows the investigation of vapor phase photolysis while minimizing the effect of reactions on vessel walls.]

(2) Under the Toxic Substances Control Act, the Agency has proposed test standards for public review regarding photolysis (and certain other studies). These may be found in 44 FR 16240, (March 16, 1979), entitled "Toxic Substances Control: Discussion of Premanufacturing Testing Policy and Technical Issues; Request for Comment."

Series 162: METABOLISM STUDIES

§ 162-1 Aerobic soil metabolism studies.

(a) Purpose. Pesticides which come into contact with soil can be metabolically transformed. The purpose of soil metabolism studies is to determine the nature and extent of formation of pesticide degradation products to which rotational crops and nontarget organisms will be exposed, and to facilitate assessment of potential disposal problems.

(b) When required. Data from an aerobic laboratory soil metabolism study are required by 40 CFR § 158 to support the registration of an end-use product intended for terrestrial use or forestry use, and to support each application for registration of a manufacturing-use product which may legally be used to formulate such an end-use product. See, specifically, 40 CFR § 158.50 and § 158.130 to determine whether these data must be submitted. Section II-A of this subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general use.

(c) Test standards. Aerobic Soil metabolism data submitted in response to 40 CFR § 158.130 should be derived from tests which comply with the general tests standards in § 160-4 and all of the following test standards:

(1) Test substance. The study shall be conducted using each active ingredient in the product.

(i) If radioisotopic analytical techniques are used, (they are preferred), the study shall be conducted with the analytical grade of each active ingredient in the product.

(ii) If non-radioisotopic analytical techniques are used, the study shall be conducted with the technical or purer grade of each active ingredient in the product.

(2) Test procedures. (i) Rate, type, and degree of metabolism of the pesticide and its major degradates should be determined in a sandy loam, silt loam, or other soil representative of the soil at the intended application sites.

(ii) One or more concentrations of the test substance should be added to soil at levels sufficient to permit measurement of the disappearance of parent compound and identification of major degradates formed.

(iii) Treated soil should be maintained at any constant temperature between 18 and 30°C with a recommended soil moisture content at 75 percent of 0.33 bar moisture.

(iv) Preferred soil sampling times are at pre-treatment, at 1, 3, 7, and 14 days, and 1, 2, 3, 4, 6, 9 and 12 months post-treatment.

(v) Sufficient soil samples should be taken at each sampling interval to ensure interpretable results.

(vi) Residues occurring at a level of 0.01 ppm or greater at normal field application rates under the label treatment schedule should be identified when feasible. The Agency realizes that searching for and identifying unknown compounds at the 0.01 ppm level in environmental substrates is possible for some but not all compounds. Therefore, the 0.01 ppm level is to be taken as a suggested 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.

(vii) Data should be collected until patterns of decline of the test substance and patterns of formation and decline of degradation products are established in soil, or for one year, whichever comes first, when terrestrial crop, noncrop, and forestry uses are involved. An aerobic soil metabolism study extending to two half-lives of the test substance or to six months duration, whichever comes first, is required for pesticides intended only for greenhouse uses and/or domestic outdoor uses.

(d) Reporting and evaluation of data. In addition to the applicable reporting requirements specified in § 160-5, the test report should contain the following specific information:

(1) Representative residue data for soil samples analyzed in accordance with paragraph (c)(2) of this section;

(2) Soil temperature;

(3) Description of soil source and characteristics;

(4) Material balance;

(5) Half-life estimates;

(6) Identity of residues occurring at levels of 0.01 ppm or greater; and

(7) Residue decline curves.

(e) References. (1) The following references contain experimental procedures for conducting aerobic soil metabolism studies:

(i) Bartha, R., and D. Pramer. 1965. Features of a flask and method for measuring the persistence and biological effects of pesticides in soil. Soil Sci. 100:68-70. [The apparatus described in this paper provides a simple, rapid method for demonstrating microbial degradation, persistence, and relative toxicity of a xenobiotic in soil under laboratory conditions.]

(ii) Betts, P.M., C.W. Giddings, and J.R. Fleeker. 1976. Degradation of 4-aminopyridine in soil. J. Agr. Food Chem. 24:571-574. [This paper contains procedures for study of radio-labeled pesticide in soils and in cultures of soil microorganisms.]

(iii) Ferris, Ian G., and E. Paul Lichtenstein, 1980. Interactions between agricultural chemicals and soil microflora and their effects on the degradation of [14C]-parathion in a cranberry soil. J. Agric. Food Chem. 28:1011-1019. [This paper illustrates the importance of interactions of soil microorganisms and agricultural chemicals in the degradation of other pesticides and contains procedures for necessary investigations The procedures include methods for treatments and incubation of soil, for trapping of volatile products, for extraction of materials from soil, and for analyses.]

(iv) Fleeker, J.R., H.M. Lacy, I.R. Schultz, and E.C. Houkom. 1974. Persistence and metabolism of thiophanate-methyl in soil. J. Agr. Food Chem. 22:592-595. [The soil metabolic procedures in this paper are recommended for development of a protocol.]

(v) Parr, J.F., and S. Smith. 1969. A multipurpose manifold assembly: Use in evaluating microbiological effects of pesticides. Soil Sci.107:271-276. [The procedure here is useful for soil respiration studies, and the style and directions are clear.]

(vi) Parr, J.F. and S. Smith. 1973. Degradation of trifluralin under laboratory conditions and soil anaerobiosis. Soil Sci. 115:55-63. [This paper contains a procedure for the investigation of metabolism of a pesticide in soil using the apparatus discussed in Parr and Smith (1969). The procedures contained in this paper are reported to allow separation of effects of volatilization, photolysis, and nonbiological degradation from microbiological metabolism with respect to dissipation of a pesticide from soil.]

(vii) Schooley, D.A., K.M. Creswell, L.E. Staiger, and G.B. Quistad. 1975. Environmental degradation of the insect growth regulator isopropyl (2E,4E)-11-methoxy-3,7,11-trimethyl2,4-dodecadienoate (methoprene). IV. Soil Metabolism. J. Agr. Food Chem. 23:369-373. [This is an excellent study, and contains procedures for investigation of metabolism of a pesticide in soil.]

(viii) Smith, R.A., W.S. Belles, K.W. Shen, and W.G. Woods. 1973. The degradation of dinitramine (N^3,N^3-diethyl 2,4-dinitro-6-trifluoromethylm-phenylenediamine) in soil. Pest. Biochem. Physiol.

3:278-288. [The procedures reported in this study were well planned and executed, and they describe the required tests.]

(ix) Starr, R.I., and D.J. Cunningham. 1975. Leaching and degradation of 4-aminopyridine-^{14}C in several soil types. Arch. Environ. Contam. Toxicol. 3:72-83. [This paper provides a procedure for a soil metabolism study with a radio-labeled pesticide using soils varying in pH, organic matter content, and sand-silt-clay content.]

(2) Supplemental information for developing a protocol for the determination of non-extractable residues is given in the following references: (i) Kazano, H., P.C. Kearney, and D.D. Kaufman. 1972. Metabolism of methylcarbamate insecticides in soils. J. Agr. Food Chem. 20:975-979. [Among the points of special consideration in this study are the reporting of soil characteristics, the flow sheet and detail of experimental work, and the reporting of recoveries of parent compound and metabolite from soil.]

(ii) Stevenson, F.J. 1965. Gross Chemical Fractionation of Organic Matter. Pp. 1409-1421 in Methods of Soil Analysis. C.A. Black, D.D. Evans, J.L. White, L.E. Ensminger, and F.E. Clark (eds.). Amer. Soc. Agron. Publ. No. 9. Madison, Wisconsin. [The procedures outlined in this publication may be useful for isolation of and accounting for pesticide added to soil. However, care must be exercised when interpreting metabolism from extracts done with acid or alkali, since artifacts can arise with such drastic extraction procedures.]

§ 162-2 Anaerobic soil metabolism studies.

(a) Purpose. The purpose of an anaerobic soil metabolism study is to determine the rate and pattern of pesticide metabolism under anaerobic conditions. This information is used to ascertain effects of flooding or waterlogging on a well-aerated soil, a condition which can have an effect on many oxidation-reduction systems that, in turn, may indirectly affect pesticide metabolism and fate.

(b) When required. (1) Data from an anaerobic soil metabolism study are required by 40 CFR § 158 to support the registration of an end-use product intended for field-vegetable crop use, and to support each application for registration of a manufacturing-use product which any legally be used to make such an end-use product. See, specifically, 40 CFR § 158.50 and §158.130 to determine whether these data must be submitted. Section II-A of this Subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(2) Data from an anaerobic soil metabolism study need not be submitted if data from the anaerobic aquatic metabolism study described in § 162.3 of this subdivision have been submitted.

(c) Test standards. Anaerobic soil metabolism data submitted in response to 40 CFR § 158.130 should be derived from tests which comply with the general test standards in § 160-4 and all of the following specific their test standards:

(1) Test substance. This study shall be conducted using each active ingredient in the product.

(i) If radioisotopic analytical techniques are used (they are preferred), studies shall be conducted with the analytical grade of each active ingredient in the product.

(ii) If non-radioisotopic analytical techniques are used, studies shall be conducted with the technical or purer grade of each active ingredient in the product.

(2) Test procedures. (i) The study should be conducted on the same soil selected for testing in the aerobic soil metabolism study, § 162-1, if data from that study are also submitted.

(ii) A sample of the soil treated with one or more concentrations of the test substance and incubated for 30 days or one half-life (whichever is shorter) should be converted from aerobic to anaerobic conditions by either water-logging or purging the soil with inert gases. Where organic content of the soil is deficient, organic amendments should be supplied to the treated soil within 30 days to ensure a substrate for anaerobic metabolism.

(iii) Treated soil should be maintained at a constant temperature between 18 and 30°C after anaerobic conditions have been established. (The temperature chosen should be the same as that selected in the aerobic soil metabolism study § 162-1, if that study is also required.)

(iv) Preferred sampling intervals are 30 and 60 days after anaerobic conditions have been established.

(v) The length of the study need not extend beyond 60 days.

(vi) Residues occurring at a level of 0.01 ppm or greater at normal field application rates under the label treatment schedule should be identified, when feasible [refer to § 162-1(c)(2)(vi)].

(d) Reporting and evaluation of data. In addition to the applicable reporting requirements specified in § 160-5, the test report should contain the following specific information:

(1) Representative residue data for soil samples analyzed in accordance with paragraph (c)(2) of this section.

(2) Selected soil temperature;

(3) Description of soil source and characteristics;

(4) Material balance;

(5) Half-life estimates;

(6) Identity of residues occurring at levels of 0.01 ppm or greater;

(7) Residue decline curves.

(e) References. (1) The following reference contains experimental procedures for conducting anaerobic soil metabolism studies:

Gowda, T.K.S., and N. Sethunathan. 1976. Persistence of endrin in Indian rice soils under flooded conditions. J. Agr. Food Chem. 24:750-753. [Procedures are reported in this publication for the study of relative persistence of a pesticide in several flooded soils. This paper also provides information of the effects of pH, organic matter content, and microorganism metabolism on persistence of the compound.]

(2) Refer to § 162-1(e) for further references on methods to conduct soil metabolism studies.

§ 162-3 Anaerobic aquatic metabolism studies.

(a) Purpose. The purpose of an anaerobic aquatic metabolism study is to assess the nature and extent of formation of pesticide residues in water and in hydrosoil, since these residues may then be taken up by irrigated crops and passed on to other parts of the aquatic food web. Anaerobic conditions are more likely to prevail where pesticides are found in aquatic environments than in strictly terrestrial environments.

(b) When required. Data from an anaerobic aquatic metabolism study are required by 40 CFR § 158 to support the registration of an end-use product intended for aquatic use, forestry use, or for any aquatic impact uses involving direct discharges of treated

water into outdoor aquatic sites. Data from such a study are also required to support each application for registration of a manufacturing-use product which may legally be used to make such an end-use product. See, specifically, 40 CFR § 158.50 and § 158.130 to determine whether these data must be submitted. The anaerobic soil metabolism study in § 16-22 of this Subdivision may not be substituted for this study. Section II-A of this subdivision contains an additional discussion of the "Formulators' Exemption" and who must submt the required data as a general rule.

(c) Test standards. Anaerobic aquatic-metabolism data submitted in response to 40 CFR § 158.130 should be derived from tests which comply with the general test standards in § 160-4 and all of the following test standards:

(1) Test substance. This study shall be conducted using each active ingredient in the product.

(i) If anaerobic analytical techniques are used (they are preferred), studies shall be conducted with the analytical grade of each active ingredient in the product.

(ii) If non-radioisotopic analytical techniques are used, studies shall be conducted with the technical or purer grade of each active ingredient in the product.

(2) Test procedures. (i) Rate, type, and degree of metabolism of the pesticide should be determined in the laboratory in water plus sediment obtained from and representative of that found at an intended use site. The preferred substrate for this laboratory study is sediment covered with water, but the use of a flooded soil may be adequate.

(ii) If the test is performed using flooded soil, oxygen depletion should be established by flooding for 30 days prior to adding the test substance. The test substance should be applied at a rate sufficient to permit measuring the disappearance of the parent compound and identification of major degradates. Where organic content of the soil is deficient, organic amendments should be supplied within 30 days of application of test substance to ensure a substrate for anaerobic metabolism.

(iii) Treated soil/sediment should be maintained at any constant temperature between 18 and 30°C.

(iv) Data should be collected until patterns of decline of the test substance and patterns of formation and decline of degradation products are established in water and sediment, or for one year, whichever comes first.

(v) Residues occurring at a level of 0.01 ppm or greater at normal field application rates under the label treatment schedule should be identified, when feasible. [Refer to § 161-1(c)(2)(vi)]

(d) Reporting and evaluation of data. In addition to the applicable reporting requirements specified in § 160-5, the test report should contain the following specific information:

(1) Representative residue data for water and sediment samples analyzed in accordance with paragraph (c)(2) of this section.

(2) Soil/sediment temperature, and

(3) Description of soil/sediment/water source and characteristics;

(4) Material balance;

(5) Half-life estimates;

(6) Identity of residues occurring at levels of 0.01 ppm or greater; and

(7) Residue decline curves.

(e) References. The following references contain experimental procedures for conducting anaerobic aquatic metabolism studies:

(i) Gowda, T.K.S., and N. Sethunathan. 1976. Persistence of endrin in Indian rice soils under flooded conditions. J. Agr. Food Chem. 24:750753. [Although the procedure used in this study can provide useful information, it is not necessary to measure the redox potential to establish anaerobiosis if the 30-day flooding requirement is met.]

(ii) Hance, R.J., and G. Chesters. 1969. The fate of hydroxyatrazine in a soil and a lake sediment. Soil Biol. Biochem. 1:309-315. [Although this is a study of a metabolite rather than a pesticide, it is a useful model to illustrate use of a sediment and a soil, establishment of anerobiasis by use of streams of nitrogen or air, comparison of aerobic and anaerobic aquatic metabolism, and use of sterile and inoculated media for study of metabolism with a radio-labeled compound.]

(iii) Miyazaki, S., H.C. Sikka, and R.S. Lynch. 1975. Metabolism of dichlobenil by microorganisms in the aquatic environment. J. Agr. Food Chem. 23:365-368. [This report provides a good model on which to base experimental protocols.]

§ 162-4 Aerobic aquatic metabolism studies.

(a) Purpose. The purpose of aerobic aquatic metabolism studies is to determine the effects on a pesticide of exposure to aerobic conditions in water or sediment during the period of dispersal of the pesticide throughout the aquatic environment, and to compare rates and formation of metabolites with those observed under conditions of anaerobic aquatic metabolism.

(b) When required. Data from an aerobic aquatic metabolism study are required by 40 CFR §158 to support the registration of an end-use product intended for aquatic use or for any aquatic impact uses involving direct discharges of treated water into outdoor aquatic sites, and to support each application for registration of a manufacturing-use product which may legally be used to formulate such an end-use product. See, specifically, 40 CFR § 158.50 and § 158.130 to determine whether these data must be submitted. Section II-A of this Subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(c) Test standards. Aerobic aquatic metabolism data submitted in response to 40 CFR § 158.130 should be derived from tests which comply with the general test standards in § 160-4 and all of the following specific test standards:

(1) Test substance. This study shall be conducted using each active ingredient in the product.

(i) If radioisotopic analytical techniques are used (they are preferred), studies shall be conducted with the analytical grade of each active ingredient in the product.

(ii) If non-radioisotopic analytical techniques are used, studies shall be conducted with the technical or purer grade of each active ingredient in the product.

(2) Test procedures. (i) Pesticide metabolism should be determined in the laboratory in water plus sediment obtained from and representative of that found at an intended use site. The test substance should be added to water at a rate sufficient to permit measuring the disappearance of the parent compound in water and identification of major degradates in water and sediment.

(ii) The treated water/sediment should be maintained at a constant temperature between 18 and 30 °C. (The temperature chosen should be the same as that selected in the anaerobic aquatic metabolism study, § 162-3, if that study is also being conducted.)

(iii) Data should be collected until patterns of decline of the test substance and patterns of formation and decline of degradation products are established in water and sediment or for 30 days, whichever comes first.

(iv) Residues occurring at a level of 0.01 ppm or greater at normal field application rates under the label treatment schedule should be identified, when feasible [Refer to § 162-1(c)(2)(vi)].

(v) For additional procedures and supplementary information on aerobic aquatic metabolism studies, see § 162-4(e).

(d) Reporting and evaluation of data. In addition to data submitted in response to the applicable reporting requirements specified in § 16-05, the test report should contain the following specific information:

(1) The results of analysis of each water and sediment sample required in paragraph (c)(2) of this section;

(2) Soil/sediment temperature;

(3) Description of soil/sediment/water source and characteristics;

(4) Material balance;

(5) Half-life estimates;

(6) Identification of residues occurring at levels of 0.01 ppm or greater; and

(7) Residue decline curves.

(e) References. The following references contain experimental procedures for conducting aerobic aquatic metabolism studies:

(1) Krzeminski, S.F., C.K. Brackett, and J.D. Fisher. 1975. Fate of microbial 3-isothiazolone compounds in the environment: Modes and rates of dissipation. J. Agr. Food Chem. 23:1060-1068.

(2) Krzeminski, S.F., C.K. Brackett, J.D. Fisher, and J.F. Spinnler. 1975. Fate of micccrobicidal 3-isothazolone compounds in the environment: Products of degradation. J. Agr. Food Chem. 23:1068-1075.

[These two papers in combination constitute an excellent model for an aerobic metabolic study. The papers compare degradation and accumulation in several systems and contain an extensive compilation of well-identified metabolites. Of special interest is the inhibition and induction in metabolism reported here.]

(3) Schaefer, C.H., and E.F. Dupras, Jr. 1976. Factors affecting the stability of dimilin in water and the persistence of dimilin in field waters. J. Agr. Food Chem. 24:733-739.

Series 163: MOBILITY STUDIES

§ 163-1 Leaching and adsorption/desorption studies.

(a) Purpose. The movement of pesticide residues by means of leaching through the soil profile or transport to and dispersion in the aquatic environment may cause contamination of food, result in loss of usable land and water resources to man due to contamination of groundwater supplies, or cause habitat loss to wildlife. Therefore, laboratory studies are required to predict:

(1) The leaching potential or pesticides and their degradates through the soil profile at terrestrial sites; and

(2) The movement of pesticides and their degradates to and dispersion in aquatic sites.

(b) When required. Leaching or absorption/desorption data are required by 40 CFR § 158 to support the registration of an end-use product intended for domestic outdoor use, greenhouse use, terrestrial noncrop use, orchard crop use, field-vegetable crop use, forestry use, aquatic use, and aquatic impact uses involving direct discharges of treated water into outdoor aquatic sites. Such data are also required to support each application for registration of a manufacturing-use product which may legally be used to make such an end-use product. See, specifically, 40 CFR § 158.50 and § 158.130 to determine whether these data must be submitted. Section II-A of this Subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(c) Test standards. Leaching or absorption/desorption data submitted in response to 40 CFR § 158.130 should be derived from tests which comply with the general test standards in § 160-4 and all of the following specific test standards:

(1) Test substance. Studies shall be conducted using each active ingredient in the product.

(i) If radioisotopic analytical techniques are used (they are preferred), studies shall be conducted with the analytical grade of each active ingredient in the product;

(ii) If non-radioisotopic analytical techniques are used, studies shall be conducted with the technical or purer grade of each active ingredient in the product.

(2) Test procedure. (i) Analytical technique selection. A laboratory study should be conducted to provide a quantitative estimate of pesticide mobility in soil or absorption/desorption on sediments.

(ii) Amount of test substance. An amount of test substance equal to the highest recommended rate for a single application of the pesticidal active ingredient should be added to the soils/sediment utilized in these studies.

(iii) Soil selection. Each study should include, at a minimum, four soils, such as sand (agricultural), sandy loam, silt loam, clay, or clay-loam, each having a pH within the range of 4-8. However, if the pesticide is to be limited to use with one specific soil type, then the soils selected should include that specific soil type. In addition, if the pesticide is intended for an aquatic use or for an aquatic impact use involving direct discharges of treated water into outdoor aquatic sites, batch equilibrium (adsorption/desorption) studies on one aquatic sediment obtained from or representative of the proposed use area should be provided.

(A) At least one of the soils selected should have an organic matter content less than or equal to one percent (sand or sandy loam preferred).

(B) One of the soils should be the soil used for § 162-1 (aerobic soil metabolism study). This soil preferably should be a sandy-loam soil. This soil shall be used to study leaching of pesticide degradates.

(iv) Preparation of soil for study of pesticide degradates. The test substance should be aged under aerobic conditions for 30 days or one half-life (whichever is shorter) in the soil selected in paragraph (c)(2)(iii)(B) of this section. The treated soil should be maintained at a constant temperature between 18 and 30°C. The temperature chosen shall be the same as that selected in the aerobic soil metabolism study § 162-1) if that study is also required. The treated soil should be maintained at a soil moisture content of 75 percent of 0.33 bar moisture content during the aging period. At the end of the aging period, either a portion of the aged soil containing the pesticide and its degradates or extracts obtained from the aged soil should be tested by one of the methods set forth below:

(A) The extract may be tested on soil thin layer chromatographic (TLC) plates as required by paragraph (c)(2)(v)(A) of this section; or

(B) The portion of aged soil may be added to the prepared soil columns as required by paragraph (c)(2)(v)(B) of this section; or

(C) Alternatively, the mobility of individual degradates which have been demonstratee independently to occur in soil after the aging period specified in paragraph (c)(2)(v) of this section.

(v) Analysis methods. For terrestrial noncrop uses, orchard crop uses, field-vegetable crop uses, and forestry uses, the mobility of the test substance and its degradates in soil should be assessed either by soil thin layer chromatography, soil column, or batch equilibrium (adsorption/desorption) procedures described below in paragraphs (A), (B), and (C), respectively. For domestic outdoor uses, greenhouse uses, aquatic uses, and aquatic impact uses, the mobility of the test substance and its degradates in soil shall be assessed only by the batch equilibrium (adsorption/desorption) procedure. Whatever procedure is selected must be followed for all soils studied.

(A) Soil thin-layer chromatography (TLC) study. Soil TLC studies to predict the leaching potential of pesticides and their degradates in soil should be performed as follows: TLC plates should be prepared using the soils described in paragraph (c)(2)(iii) of this section, to which both the test substance (parent pesticide and degradates) are applied. Application of reference pesticide standards on each TLC plate in addition to the test substance is required, to assess the relative mobility of the test substance to that of other pesticides whose laboratory and field leaching behavior is already known. For experimental procedures on soil and plate preparation, pesticide application, plate development, pesticide visualization, and Rf calculations, see reference (1)(ii) of paragraph (e) of this section.

(B) Soil column study. Soil column studies to define the vertical distribution of the test substance and its degradates in the soil profile should be performed as follows: The column(s) should be from 30 to 300 cm in height, consisting of soils described in § 1631(c)(2)(iii), and should be eluted with a volume of water equal to [groundwater recharge values of] 20 inches (50.8 cm) times the cross sectional area of the column. A distribution curve of the test substance in the column shall be determined by quantification of the test substance and its degradates in 6 cm segments and in the eluate. For experimental procedures on conducting a soil column study, see references (1)(i), (iii), (iv) and (v) of paragraph (e) of this section.

(C) Batch equilibrium (adsorption/desorption) study. Adsorption/desorption coefficients calculated from a batch equilibrium study are used along with solubility data to predict the extent or depth of pesticide leaching in the different soil types tested, and also the extent of pesticide adsorption/desorption on sediments when aquatic or aquatic impact uses are proposed. The study should be conducted using the soils described in paragraph (c)(2)(iii) of this section, plus one representative aquatic sediment (if an

aquatic or aquatic impact use involving direct discharge is proposed). The test substance including its degradates identified in and extracted from the aerobic soil metabolism study (§ 162-1) should be equilibrated with the soils and aquatic sediment selected for this study at four concentrations in a 0.01 N or M Ca ion solution. If necessary, a small amount of acetone or other solvent may be used to achieve solution of poorly soluble pesticides or degradates. For experimental procedures on conducting batch equilibrium (adsorption/desorption) studies, including calculation of Kd values, see references (3)(i) through (xii) and (4)(i) and (ii) of paragraph (e) of this section.

(d) Reporting and evaluation of data. In addition to the applicable reporting requirements specified in § 160-5, the test report should contain the following specific information:

(1) Soil thin layer chromatography (TLC). The mobility of pesticides and their degradates should be reported as mobility class 1 to 5, corresponding to Rf values of 0.0 to 0.09 [immobile (class 1)], 0.10 to 0.34 [low (class 2)], 0.35 to 0.64 [intermediate (class 3)], 0.65 to 0.89 [mobile (class 4)], and 0.90 to 1.0 [very mobile (class 5)], respectively. Values of soil/water relationships (K_d) should be reported using appropriate R_f to K_{oc}/K_d equations. Examples of calculations used in determining K_d values should be provided.

(2) Soil column study. Values of soil/water relationships (K_d) should be reported for the test substance and its degradates using appropriate equations. Examples of calculations used in determining K_d values should be provided.

(3) Batch equilibrium (adsorption/desorption) study. Adsorption/desorption data to be reported should include concentrations of the test substance, including its degradates, partitioned between soil and water and calculated as K_d values from the concentrations using appropriate equations for calculating such values. If the Freundlich equation is used, examples of calculations for 1/n and K values should be provided.

(e) References. (1) The following references contain experimental procedures for conducting mobility (leaching) studies:

(i) Grover, R. 1972. Mobility of dicamba, picloram and 2,4-D in soil columns. Weed Sci. 25:159-162. [This paper compares leaching rates using soil columns and adsorption parameters for several soil-pesticide combinations. It illustrates that theories relating adsorption and movement can be verified with soil columns and the resulting data can be related to field movements.]

(ii) Helling, C.S. 1971. Pesticide mobility in soils. I. Parameters of thin-layer chromatography. Soil Sci. Soc. Amer. Proc. 35: 732-737. [This paper discusses the usefulness of soil thin-layer chromatography and details experimental parameters.]

(iii) Krzeminski, S.F., C.K. Brackett, and J.D. Fisher. 1975. Fate of microbicidal 3-isothiazolone compounds in the environment: modes and rates of dissipation. J. Agr. Food Chem. 23:1060-1068. [This paper contains a procedure for a column leaching study.]

(iv) Lichtenstein, E.P., K.R. Schulz, and T.W. Fuhremann. 1972. Movement and fate of dyfonate in soils under leaching and nonleaching conditions. J. Agr. Food Chem. 20:831-838. [Both GLC and radio-tracer analyses were used in this study with radio-labeling in two positions to allow illustration of different types of degradation products and their movement in soils.]

(v) Weber, J.B., and T.F. Peeper. 1977. Herbicide Mobility in Soils. Pp. 73-78 in Research Methods in Weed Science. B. Truelove (ed.). S. Weed Sci. Soc. Second Edition. Auburn Printing, Inc. Auburn, Alabama. [This paper provides a brief but descriptive analysis of procedures for the study of herbicide leaching in soil, and it discusses the two major types of columns used for these studies.

(2) The following references contain supplemental information pertaining to mobility studies:

(i) Bailey, G.W., and J.L. White. 1970. Factor influencing the adsorption and movement of pesticides in soils. Residue Rev. 32:29-92. [This is a good general review discussing pitfalls to be aware of in planning or interpretation of leaching experiments.]

(ii) Hamaker, J.W., and J.M. Thompson. 1972. Adsorption. Pp. 49-143 in Organic Chemicals in the Soil Environment. Vol. I. C.A.I. Goring and J.W. Hamaker (eds.). Marcel Dekker, Inc., New York. [This is a basic review of the theoretical foundation of pesticide adsorption on soils and an excellent source for equations and the derived constants characterizing pesticidesoil adsorption. The tables of data may aid in initial range-finding.]

(iii) Leistra, M., and W.A. Dekkers. 1976. Computed effects of adsorption kinetics on pesticide movement in soils. J. Soil Sci. 28:340-350. [This is a theoretical paper that may be useful for interpretation of leaching studies, since it illustrates the importance of rainfall pattern with respect to pesticide leaching.]

(iv) Leistra, M., J.J. Smelt, and R. Zanvoort. 1975. Persistence and mobility of bromacil in orchard soils. Weed Res. 15:177-181. [This article is recommended for those planning and interpreting pesticide leaching experiments. It reports that the leaching of a pesticide in field experiments was substantially lower than predicted by calculation from results of soil-TLC experiments.]

(v) Lindstrom, F.T., L. Boersma, and P. Stockard. 1971. A theory on on the mass transport of previously distributed chemicals in a water saturated sorting porous medium: Isothermal cases. Soil Sci. 112:291-300. [This paper presents a theoretical model for predicting pesticide movement from adsorption data and flow rates.]

(vi) Oddson, J.K., J. Letey, and L.V. Weeks. 1970. Predicted distribution of organic chemical in solution and adsorbed as a function of position and time for various chemical and soil properties. Soil Sci. Soc. Amer. 34:412-417. [This paper presents a theoretical model for the movement of pesticides in soils.]

(vii) Van Genuchten, H.T., P.J. Wierenga, and G.A. O'Connor. 1977. Mass transfer studies in sorbing media: III. Experimental evaluation with 2,4,5-T. Soil Sci. Soc. Amer. 41:278-285. [This paper presents comparisons of model calculations and experimental data, and it may be useful for planning or interpretation of leaching experiments.]

(3) The following references contain experimental procedures for conducting adsorption/desorption studies:

(i) Aharonson, N., and U. Kafkafi. 1975. Adsorption, mobility and persistence of thiabendazole and methyl 2-benzimidazolecarbamate in soils. J. Agr. Food Chem. 23:720-724. [The techniques and methods used in this study are useful for both adsorption/desorption and leaching studies.]

(ii) Farmer, W.F., and Y. Aochi. 1974. Picloram sorption by soils. Soil Sci. Soc. Amer. Proc. 38:418-423. [Methods of adsorption and desorption can be found in this study.]

(iii) Grover, R., and R.J. Hance. 1970. Effect of ratio of soil to water on adsorption of linuron and atrazine. Soil Sci. 109:136-138. [This paper presents information on the soil-water ratio to be used in laboratory studies of pesticide adsorption to soils.]

(iv) Hamaker, J.W., C.A.I. Goring, and C.R. Youngson. 1966. Sorption and leaching of 4-amino-3,5,6-trichloropicolinic acid in soils. Advances in Chemistry Series 60:23-37. [The techniques and methods used in this study are standard except for the time allowed for equilibration. The data presented demonstrates the

effect of pH on adsorption of an ionized species and the inverse relationship between partition coefficient and adsorption.]

(v) Hance, R.J. 1967. The speed of attainment of sorption equilibria in some systems involving herbicides. Weed Res. 7:29-36. [This study illustrates the use of range finding experiments to find an equilibration time for meaningful adsorption experiments. Techniques for adsorption and desorption experiments and use of Freundlich isotherms are presented in this paper.]

(vi) Harvey, R.G. 1974. Soil adsorption and volatility of dinitroanilineherbicides. Weed Sci. 22:120-124. [Use of absorption isotherms for the calculation of latent heat of adsorption and the effect of adsorption on volatility of pesticides are illustrated in this paper.]

(vii) Leistra, M., and W.A. Dekkers. 1976. Computed effects of adsorption kinetics on pesticide movement in soils. J. Soil Sci. 28:340-350. [This is a simulation of pesticide behavior on soils in the field by computer.]

(viii) Leistra, M., and W.A. Dekkers. 1977. Some models for the adsorption kinetics of pesticides in soil. J. Environ. Sci. Health B12(2):85-103. [This continuation of the 1976 paper (above) discusses the multimechanism, multirate phenomena responsible for the differences observed in rates of adsorption and rates of desorption.]

(ix) Murray, D.S., P.W. Santelmann, and J.M. Davidson. 1975. Comparative adsorption, desorption, and mobility of dipropetryn and prometryn in soil. J. Agr. Food Chem. 23:578-582. [The correlation between adsorption, cation exchange capacity, organic matter, and clay content is illustrated in this paper, and adsorption/desorption is compared with soil TLC experiments.]

(x) Saltzman, S., L. Kliger, and B. Yaron. 1972. Adsorption/desorption of parathion as affected by soil organic matter. J. Agri. Food Chem. 20:12241226. [The importance of organic matter in absorption of pesticides by soil is discussed in this report.]

(xi) Savage, K.E., and R.D. Wauchope. 1974. Fluometuron adsorption/desorption equilibria in soil. Weeds 22:106-110. [This paper discusses equations used for computation of adsorption isotherms and provides information for equation selection for quantitative depiction of adsorption and desorption.]

(xii) Wu, C.H., N. Buehring, J.M. Davidson, and P.W. Santelmann. 1975. Napropamide adsorption, desorption, and movement in soils. Weed Sci. 23:454457. [Column leaching and soil TLC experiments conducted and reported here are correlated with adsorption/desorption experiments.]

(xiii) (Reserved for: OECD Guidelines for Testing Chemicals. Section 1, Number 106. Adsorption/Desorption.)

(4) The following references contain supplemental information for developing a protocol for adsorption/desorption studies:

(i) Bailey, G.W., and J.L. White. 1970. Factors influencing the adsorption, desorption, and movement of pesticides in soils. Residue Rev. 32: 29-92. [This review provides background information on the principles underlying the processes of adsorption and mobility of pesticides in soil.]

(ii) Weber, J.B. 1977. Soil Properties, Herbicide Sorption, and Model Soil Systems. Pp. 59-72 in Research Methods in Weed Science. 2nd Ed. S. Weed Sci. Soc. B. Truelove (ed). Auburn Printing, Inc. Auburn, Ala. [This is a general review of experimental methods for determination of soil properties, herbicide adsorption, and construction of simple model soil systems.]

§ 163-2 Laboratory volatility studies.

(a) Purpose. Volatilization can be a major mode for the movement of pesticides from treated areas. The vapors resulting from volatilization of some pesticides can cause adverse effects to man via inhalation exposure at sites of application or biological effects in nontarget organisms at some distance from the treated site. The Agency is particularly concerned about commercial greenhouse applications involving intensive use of volatile pesticides, use patterns which are characteristically involved with commodities having high economic value and high labor requirements; such uses can result in significant inhalation exposure to workers and applicators.

(b) When required. (1) Data from a laboratory volatility study are required by 40 CFR § 158 on a case-by-case basis to support the registration of each end-use product intended for commercial greenhouse, orchard, or field-vegetable crop uses that involve significant inhalation exposure to workers. Data from such a study are also required to support each application for registration of a manufacturing-use product which may legally be used to formulate such an end-use product. See, specifically, 40 CFR § 158.50, § 158.130, and the following discussion in § 163.3-2 (b)(2) to determine whether these data must be submitted. Section II-A of this subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(2) The Agency will evaluate the following information provided by the registration applicant to make an assessment of what constitutes a significant inhalation exposure to workers:

(i) Vapor pressure at 25°C and water solubility of the pesticide active ingredient (§§ 63-9 and 63-8 of Subdivision D);

(ii) Soil adsorption coefficient (K_d) of the test substance using the soil from a typical intended application site (§ 163-1 of this Subdivision);

(iii) Soil characteristics, including moisture content, at the intended site of application;

(iv) Method, rate, and intervals of pesticide application;

(v) Temperature, humidity, and air flow rates at the site of application;

(vi) Ventilation sequences or practices for commercial greenhouse applications; and

(vii) Inhalation toxicity of the pesticide (§§ 81-3 and 82-4 of Subdivision F).

(3) The data requirements of this section may also be satisfied by data produced from a study that meets the test standards contained in § 163-3 (field volatility studies).

(c) Test standards. Laboratory volatility data submitted in response to 40 CFR § 158.26 should be derived from tests which comply with the general test standards in § 160-4 and all of the following specific test standards:

(1) Test substance. The test substance shall be a typical end-use product.

(i) If the applicant's product is an end-use product, the test substance shall be a product whose formulation is typical of the formulation category (e.g., wettable powder, emulsifiable concentrate, wettable powder) to which the product belongs.

(ii) If the applicant's product is a manufacturing-use product which legally could be used to make an end-use product for which volatility data are required, the test substance shall 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.)

(2) Test procedure. A laboratory study should be conducted to determine the actual rate or extent of pesticide volatilization from soil under controlled conditions only for those pesticides with uses the Agency considers pose a potentially significant

inhalation exposure to workers. Applicants may omit the laboratory studies and perform a greenhouse and/or field study instead. (See § 163-3.)

(i) Laboratory experimental conditions should represent, to the extent possible, an environment where the pesticide is intended for use.

(ii) The rate of test-substance application to soil should approximate the intended rate of field usage.

(iii) The following factors should be addressed in designing a laboratory volatility study:

(A) Properties of the pesticide such as vapor pressure, and water solubility, which can influence the trapping medium and air sampling rates;

(B) Properties relating to the soil, such as adsorption to soil and soil texture, to avoid untoward reduction of the rate of volatility (e.g., sandy soil is preferred);

(C) Environmental factors, such as air temperature, humidity, and movement, to avoid untoward dehydration or flooding of the soil, and to assure efficiency of sampling.

(iv) Air samples should be collected and analyzed for residues in the laboratory experimental equipment used. Monitoring should be conducted continuously or at intervals which increase with time after the start of the experiment. Monitoring should continue until the nature of the residue decline curve has been clearly established.

(d) Reporting and evaluation of data. In addition to the basic reporting requirements specified in § 160-5, the test report should include the following specific information:

(1) Volatility data expressed as $ug/cm^2/hour$;

(2) Air concentrations expressed as ug/m^3 or mg/m^3;

(3) Vapor pressure expressed as torr (or the equivalent expressed in other conventional units);

(4) Temperature and relative humidity;

(5) A description of the soil used; and

(6) A description of the laboratory test equipment used.

(e) References. (1) The following references contain laboratory studies of pesticide volatility; information in these papers could be useful for protocol development:

(i) Kearney, P.C., and A. Kontson. 1976. A simple system to simultaneously measure volatilization and metabolism of pesticides from soils. J. Agr. Food Chem. 24:424-426. [A polyurethane foam trap and a potassium hydroxide trap were used to recover sequentially the parent compound and degradation product from air.]

(ii) Spencer, W.F. and M.M. Claith. 1974. Factors affecting vapor loss of trifluralin from soil. J. Agr. Food Chem. 22:987-991. [The laboratory methods used for determining volatilization of chemicals used in this study allow measurement of effects of several variables. The use of hexane as a trapping medium limits the gas flow rates and volumes that can be used.]

(iii) Spencer, W.F., T.D. Shoup, M.M. Cliath, W.J. Farmer, and R. Haque. 1979. Vapor pressure and relative volatility of ethyl and methyl parathion. J. Agr. Food Chem. 27:273-278. [Polyurethane foam traps and GLC detection largely specific for the compounds of interest were used here. Specific detection avoids interference that may cause falsely high vapor levels in field testing.]

(2) Volatilization studies require methods for the trapping, extraction, cleanup, and quantitation of pesticides. A review of reported methods for laboratory investigations of pesticides in air can be found in:

(i) Lewis, R.G. 1976. Sampling and Analysis of Airborne Pesticides. Pp. 51-94 in Air Pollution from Pesticides and Agricultural Processes. R.E. Lee (ed.). CRC Press, Inc. Cleveland, Ohio.

(ii) [Reserved]

§ 163-3 Field volatility studies.

(a) Purpose. Volatilization can be a major mode for the movement of pesticides from treated areas. The vapors resulting from volatilization of some pesticides can cause adverse effects to man via inhalation exposure at sites of application or biological effects in nontarget organisms at some distance from the treated site. The Agency is particularly concerned about commercial greenhouse applications involving intensive use of volatile pesticides, use patterns which are characteristically involved with commodities having high economic value and high labor requirements; such uses can result in significant inhalation exposure to workers and applicators.

(b) When required. Data from a volatility study conducted on-site in a commercial greenhouse and/or in the field will be required by 40 CFR § 158 on a case-by-case basis only for those pesticides that the Agency considers pose a potentially significant inhalation exposure to workers [see § 163-2(b)] and, based on the results of the laboratory study described in § 163-2, that also demonstrate, in the opinion of the Agency, a significant rate of volatilization from soil. See, specifically, 40 CFR § 158.50 and § 158.130 to determine whether these data must be submitted. Section II-A of this Subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(c) Test standards. Field volatility data submitted in response to 40 CFR § 158.130 should be derived from tests which comply with the general test standards in § 160-4 and all of the following specific test standards:

(1) Test substance. The test substance shall be a typical end-use product.

(i) If the applicant's product is an end-use product, the test substance shall be a product whose formulation is typical of the formulation category (e.g., wettable powder, emulsifiable concentrate, granular product) to which the product belongs.

(ii) If the applicant's product is a manufacturing-use product that legally could be used to make an end-use product for which volatility data are required, the test substance shall be a product representative of the major formulation category which includes that end-use product. (If the end-use products that could be made from the manufacturing-use product belong to two or more major formulation categories, a separate study must be performed for each such category.)

(2) Test procedures. (i) The test substance should be applied to a site which is typical of one of the sites to which the product would be applied.

(ii) The test substance should be applied to soil at the rate and by the method stated in the label directions for the pesticide.

(iii) The following factors should be addressed in designing a greenhouse or field volatility study:

(A) Properties of the pesticide such as vapor pressure and water solubility, which can influence the trapping medium and air sampling rates;

(B) Properties relating to the soil, such as adsorption to soil and soil texture, to avoid untoward reduction of the rate of volatility (e.g., sandy soil is preferred);

(C) Environmental factors, such as air temperature, humidity, and movement, to avoid untoward dehydration or flooding of the soil, and to assure efficiency of sampling.

(iv) Air samples should be monitored for residues at treated sites at intervals which increase with time after pesticide application. For example, the following schedule of sampling times might be appropriate for some situations: 0 and 12 hours, 1, 2, 4, 7, 14, and 21 days. Sampling should be continued until the nature of the dissipation curve has been clearly established.

(d) Reporting and evaluation of data. In addition to information meeting the basic reporting requirements specified in § 160-5, the test report should include the following specific information:

(1) Volatility data expressed as g/ha/day;

(2) Air concentrations expressed as ug/m^3 or ng/m^3;

(3) Vapor pressure expressed as torr (or the equivalent expressed in other conventional units); and

(4) Meterologic conditions (temperature, relative humidity, wind velocity and direction, and cloud cover) during the time of the field study.

(e) References. (1) The following references contain supplemental information for developing a protocol to conduct field volatility studies:

(i) Cliath, M.M., W.F. Spencer, W.J. Farmer, T.D. Shoup, and R. Grover. 1980. Volatilization of S-ethyl N,N-dipropylthiocarbamate from water and wet soil during and after flood irrigation of an alfalfa field. J. Agr. Food Chem. 28:610-613. [This is a well-designed and well-executed field study of volatilization with simultaneous study of other modes of dissipation of a pesticide.]

(ii) Harper, L.A., A.W. White, Jr., R.R. Bruce, A.W. Thomas, and R.A. Leonard. 1976. Soil and microclimate effects on trifluralin volatilization. J. Environ. Qual. 5:236-242. [Ethylene glycol vapor traps and non-specific GLC quantitation were used in this study. The influence of water in soil and thus rainfall during the study on volatilization of a pesticide are illustrated as are effects of wind, turbulence, and temperature.]

(iii) Parmele, L.H., E.R. Lemon, and A.W. Taylor. 1972. Micrometeorological measurement of pesticide vapor flux from bare soil and corn under field conditions. Water, Air, and Soil Pollut. 1:433-451. [This study used hexylene glycol vapor traps and sampling periods adjusted to compensate for decrease in pesticide vapor

concentration during the study. Pesticide vapor flux from soil was calculated and related to micrometeorological measurements.]

(iv) Soderquist, C.J., D.G. Crosby, K.W. Moilanen, J.N. Seiber, and J.E. Woodrow. 1975. Occurrence of trifluralin and its photoproducts in air. J. Agr. Food Chem. 23:304-309. [Although this study was concerned with photolysis of pesticides in air, there are procedures in this paper for measurement of volatilization of a pesticide from soil.]

(2) Volatilization studies require methods for the trapping, extraction, cleanup, and quantitation of pesticides. A review of reported methods for field investigations of pesticides in air can be found in:

(i) Lewis, R.G. 1976. Sampling and Analysis of Airborne Pesticides. Pp. 51-94 in Air Pollution from Pesticides and Agricultural Processes. R.E. Lee (ed.). CRC Press, Inc. Cleveland, Ohio.

(ii) [Reserved]

Series 164: DISSIPATION STUDIES

§ 164-1 Field dissipation studies for terrestrial uses.

(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 mobility, degradation, and dissipation of residues. These studies are required because pesticide dissipation may proceed at a different rate under field conditions and therefore result in the formation of levels of degradates differing from those observed in laboratory studies.

(b) When required. Data from a terrestrial field dissipation study are required by 40 CFR § 158 to support the registration of an end-use product intended for any terrestrial use (except greenhouse use), and to support each application for registration of a manufacturing-use product which may legally be used to make such an end-use product. See, specifically, 40 CFR § 158.50 and § 158.130 to determine whether these data must be submitted. Section II-A of this Subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the requiired data as a general rule.

(c) Test standards. Field dissipation data submitted in response to 40 CFR 158.130 should be derived from testing which complies with the general test standards in § 160-4 and all of the following specific test standards:

(1) Test substance. The test substance shall be a typical end-use product.

(i) If an applicant's product is an end-use product, the test substance shall be a product whose formulation is typical of the formulation category (e.g., wettable powder, emulsifiable concentrate, granular product) to which the product belongs.

(ii) 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 shall be a product representative of the major formulation category which includes that enduse 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.)

(2) Test procedures. (i) Sites. Field dissipation studies should be conducted in at least two different sites 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, terrain, or other pertinent characteristics.

(ii) Application. The test substance should be applied using the method of application stated in the directions for use specified on the product label and at the highest rate recommended on the product label.

(iii) Soil sampling. Soil from the treated area should be sampled following treatment for the purpose of ascertaining the extent of pesticide dissipation.

(A) Soil samples serving as test controls should be obtained from the intended application sites immediately prior to application of the test substance and, to the extent possible, from adjacent untreated areas at intervals during the course of the study and at the termination of the study.

(B) Sampling times should include pre-application, date of application, and immediate post-application. In the case of multiple applications, only immediate post-application samples (and not preapplication and date of application samples) should be taken in addition.

(C) Soil samples should be taken in increments, to a maximum depth of 15 cm, provided that the results of studies on pesticide leaching indicate that the test substance is not likely to leach into soil to a depth greater than than 15 cm; and

(D) If data on leaching indicate that the test substance is likely to leach into soil to a depth greater than 15 cm, or if the pesticide is incorporated into soil, then samples should be taken to a depth sufficient to define the extent of leaching.

(iv) Test duration. Residue data should be collected until patterns of decline 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:

(A) Field and vegetable crop uses: 18 months;

(B) Orchard crop and pastureland uses: 12 months;

(C) Domestic outdoor, park, ornamental, and turf uses: four months; and

(D) Rights-of-way, shelter belts, and related uses: two months.

(d) Reporting and evaluation of data. In addition to the basic reporting requirements specified in § 160-5, the test report should include the following specific information:

(1) Residue decline curves in the tested soil; and

(2) Field test data, including:

(i) Amount of rainfall and irrigation water (accumulated from first application to each sampling);

(ii) Water table;

(iii) Grade (slope);

(iv) Soil and air temperature data;

(v) Techniques and times of planting and harvesting;

(vi) Application time and method;

(vii) Sampling times and techniques;

(viii) Dates and stages of crop and pest development;

(ix) Application-to-harvest (if applicable) and application-to-sampling intervals for each treatment; and

(x) Depth, weight, or volume of each sample taken for analysis.

(e) References. (1) The following references contain information that could be useful for development of a protocol for conducting field dissipation studies:

(i) Caro, J.H., H.P. Freeman, and B.C. Turner. 1974. Persistence in soil and losses in runoff of soil-incorporated carbaryl in a small watershed. J. Agr. Food Chem. 22:860-863. [This is a wellplanned and well-executed field dissipation study.]

(ii) Miller, C.H., T.J. Monaco, and T.J. Sheets. 1976. Studies on nitralin residues in soils. Weed Sci. 24:288-291. [The experimental design and sampling procedures in this paper are well devised.]

(iii) Polzin, W.J., I.F. Brown, Jr., J.A. Manthey, and G.W. Probst. 1971. Soil persistence of fungicides - Experimental design, sampling, chemical analysis, and statistical evaluation. Pest. Monit. J. 4:209215. [The factors causing variability in field dissipation studies are considered and analyzed in this paper. However, this study is more detailed than required for pesticide registration.]

(iv) Smith, A.E., and A. Walker. 1977. A quantitative study of asulam persistence in soil. Pestic. Sci. 8:449-456. [The experimental design and statistical analyses of data in this paper are described in detail for field dissipation studies.]

(2) The following reference contains supplemental information for developing a protocol for field dissipation studies:

(i) Goring, C.A.I., D.A. Laskowski, J.W. Hamaker, and R.W. Meikle. 1979. Principles of Pesticide Degradation in Soil. Pp. 135-172 in Environmental Dynamics of Pesticides. R. Haque and V.H. Freed (eds.). Plenum Press. New York. [This is an excellent review for analyses of data and for an understanding of factors affecting persistence of pesticides in soil.]

(ii) [Reserved.]

§ 164-2 Field dissipation studies for aquatic uses and aquatic impact uses.

(a) Purpose. The purpose of aquatic field dissipation studies for pesticides for aquatic uses is to determine the extent of dissipation and mobility of pesticide residues under actual use conditions. These dissipation studies will generate on-site data for evaluating potential hazards of a pesticide under actual use conditions (e.g., mobility, formation of metabolites, and disappearance of parent compound) and provide information with respect to mechanisms of dissipation in various aquatic environments. An aquatic field dissipation study is also required because pesticide dissipation may proceed at a different rate in the aquatic environment than in laboratory aquatic studies.

(b) When required. (1) Except as provided in § 164-2(b)(2), data from an aquatic field dissipation study are required by 40 CFR § 158 to support the registration of an end-use product intended for aquatic food crop uses, for aquatic non-crop uses (which include antifouling paints and other outdoor protective uses where the pesticide-containing surface is in contact with water, and also pesticide application to ditchbanks and shorelines), and for any aquatic impact uses involving direct discharge of treated water into outdoor aquatic sites. Data from such a study are also required to support each application for registration of a manufacturing-use product which may legally be used to make such an end-use product. See, specifically, 40 CFR § 158.50 and § 158.130 to determine whether these data must be submitted. Section II-A of this Subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(2) Pesticides intended for use as antifouling paints and for similar related protective aquatic uses are exempt from the aquatic field dissipation data requirements of 40 CFR § 158.130 if the following conditions are met:

(i) The octanol/water partition coefficient of the product is approximately 1000 or less; and

(ii) The half-life of the active ingredient in water is less than four days as demonstrated by the hydrolysis studies, § 161-1.

(c) Combined testing. Testing conducted to fulfill this data requirement may be combined with the testing conducted to meet the requirements of § 165-4 (field accumulation studies in aquatic nontarget organisms), provided that the test standards for each study are met.

(d) Test standards. Aquatic field dissipation data submitted in response to 40 CFR § 158.130 should be derived from testing which complies with the general test standards in § 160-4, and all of the following test standards:

(1) Test substance. The test substance shall be a typical end-use product.

(i) If the applicant's product is an end-use product, the test substance shall be a product whose formulation is typical of the formulation category (e.g., wettable powder, emulsifiable concentrate, granular product) to which the product belongs.

(ii) If the applicant's product is a manufacturing-use product that legally could be used to make an end-use product for which aquatic field dissipation data are required, the test substance shall be a product representative of the major formulation category which includes that end-use product. [Except for antifouling paints and other related protective-use products (which fall into one formulation category), 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.]

(2) Test sites. Aquatic field dissipation studies should be conducted in at least two different sites which are representative of the areas where the pesticide is expected to be discharged or applied. For restricted use patterns where only one typical area is involved, data from two similar sites are needed. Studies in additional locations may be needed if the pesticide is intended for an aquatic food crop use, and the sites of application vary in climate, terrain, or other pertinent characteristics.

(3) Application. The test substance should be applied using the method of application stated in the directions for use specified on the product label and at the highest rate recommended on the product label. If the products are for use in pulp and paper mills or industrial cooling towers where direct discharge of pesticide-treated water would be expected, sufficient test substance should be applied to the receiving water in the study to produce the maximum concentration expected for each discharge event.

(4) Sampling. Soil, sediment, and water samples serving as test controls should be obtained from the intended sites of application or from direct aquatic discharges immediately prior to application or discharge of the test substance, and to the extent possible from the adjacent untreated areas, at intervals during the course of the study, and at the termination of the study. Soil, sediment, and water from the treated area should be sampled following treatment for the purpose of ascertaining the extent of pesticide dissipation in accordance with the following:

(i) Sampling times should include pre-application (control), date of application, and immediate post-application for each single or multiple application of the test substance.

(ii) For aquatic food crop uses, soil and water should be sampled.

(iii) For aquatic non-crop uses, soil sediment and water should be sampled.

(iv) For aquatic impact uses resulting in direct discharges, sediment and water should be sampled.

(v) Soil should be sampled in increments to a depth of 15 cm.

(vi) Sediment should be sampled in increments to a depth of 5

(vii) Water should be sampled to a depth dependent upon the use patterns of the pesticide and the site of pesticide action in water (bottom, surface, etc.), and flow meters or comparable techniques shall be used to measure water flow.

(5) Test duration. Residue data should be collected until patterns of decline of the test substance and patterns of formation and decline of degradation products are established in the media samples, or to the maximum time specified below for all use patterns in representative areas, whichever comes first.

(i) Aquatic food crop uses: maximum test duration should be 12 months after application for soil sampling and one month after application for water sampling.

(ii) Aquatic non-crop uses (all use patterns):

(A) Maximum test duration for sediment sampling should be six months for a single application, and for multiple applications, the longer of the following: nine months after the first application, or six months after the last application.

(B) The maximum test duration for water sampling should be one month following each discharge event.

(iii) Aquatic non-crop uses (products intended for application to ditchbanks and shorelines only): the maximum test duration for soil sampling should be six months for a single application, and for multiple applications, the longer of the following: nine months after the first application or six months after the last application.

(iv) Aquatic impact uses resulting in direct discharges:

(A) The maximum test duration for sediment sampling should be six months following a single discharge event, and following multiple discharge events, the longer of the following: nine months after the first discharge or six months after the last discharge.

(B) The maximum test duration for water sampling should be one month following each discharge event.

(e) Reporting and evaluation of data. In addition to the basic reporting requirements specified in § 160-5, the test report should include the following specific information:

(1) Decline curves of residues in each major substrate analyzed; and

(2) Field test data, including:

(i) Dates of planting and harvesting of crops, if applicable;

(ii) Application time(s) and method;

(iii) Sampling times and techniques;

(iv) Dates and stages of crop and pest development, if applicable;

(v) Application-to-harvest (if applicable) and application-to-sampling intervals for each treatment;

(vi) Depth, weight, or volume of each sample, and weights and volumes of aliquots taken for analysis; and

(vii) Flow data expressed in terms of volume or linear flow.

(f) References. (1) The following references contain supplemental information for developing a protocol for conducting aquatic crop studies:

(i) Demint, R.J., J.C. Pringle, Jr., A. Hattrup, V.F. Bruns, and P.A. Frank. 1975. Residues in crops irrigated with water containing trichloroacetic acid. J. Agr. Food Chem. 23:81-84. [This paper presents a procedure for assessment of pesticide carry-over in irrigation water.]

(ii) Rice, C.P., H.C. Sikka, and R.S. Lynch. 1974. Persistence of dichlobenil in a farm pond. J. Agr. Food Chem. 22:533-534. [This paper presents procedures for assessment of fate of a pesticide in a water-sediment system.]

(iii) Schaefer, C.H., and E.F. Dupras, Jr. 1976. Factors affecting the stability of dimilin in water and the persistence of dimilin in field waters. J. Agr. Food Chem. 24:733-739. [This paper contains a small-scale technique for assessment of the fate of a pesticide in a water-sediment ecosystem.]

(2) The following references contain supplemental information for developing a protocol for conducting aquatic non-crop studies:

(i) Rice, C.P., H.C. Sikka, and R.S. Lynch. 1974. Persistence of dichlobenil in a farm pond. J. Agr. Food Chem. 22:533-534. [This paper contains a procedure for assessment of fate of a pesticide in a watersediment system. Information on background interference and pesticide recovery from soil and water are presented.]

(ii) Schaefer, C.H., and E.F. Dupras, Jr. 1976. Factors affecting the stability of dimilin in water and the persistence of dimilin in field waters. J. Agr. Food Chem. 24:733-739. [This paper contains a small-scale technique for assessment of fate of a pesticide.]

§ 164-3 Dissipation studies for forestry uses.

(a) Purpose. Data from a residue dissipation study, conducted under actual use conditions, will indicate the extent and rate of pesticide residue dissipation and mobility in both aquatic and terrestrial environments which are encompassed in forestry sites.

(b) When required. Data from a field dissipation study for forestry uses are required by 40 CFR § 158 to support the registration of an end-use product intended for forestry use, and by each applicant for registration of a manufacturing-use product which may legally be used to make such an end-use product. See, specifically,

40 CFR § 158.50 and § 158.130 to determine whether these data must be submitted. Section II-A of this subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(c) Combined testing. Testing conducted to fill this data requirement may be combined with testing conducted in accordance with § 165-5 (field accumulation studies in aquatic nontarget organisms), provided that the test standards for each study are met.

(d) Test standards. Forestry dissipation data submitted in response to 40 CFR § 158.130 should be derived from testing which complies with the general test standards in § 160-4 and all of the following specific test standards:

(1) Test substance. The test substance shall be a typical end-use product.

(i) If the applicant's product is an end-use product, the test substance shall be a product whose formulation is typical of the formulation category (e.g., wettable powder, emulsifiable concentrate, granular product) to which the product belongs.

(ii) If the applicant's product is a manufacturing-use product that legally could be used to make an end-use product intended for forestry use, the test substance shall 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.]

(2) Test procedures. (i) Sites. A dissipation study should be conducted in at least one location representative of the areas in which the pesticide product would usually be used. Studies at additional sites may be necessary if the product is intended for use in forest sites with substantially differing characteristics.

(ii) Application. The test substance should be applied using the method of application stated in the directions for use specified on the product label, and at the highest rate recommended on the label.

(iii) Environmental components. The level of pesticide residues shall be measured in the following items:

(A) Foliage (if the pesticide is foliar-applied);

(B) Leaf litter;

(C) Soil under leaf litter;

(D) Exposed soil;

(E) Standing (pond) water;

(F) Moving (stream) water; and

(G) Sediments from both ponds and streams.

(iv) Controls. Test control samples of the environmental components described in paragraph (d)(2)(iii) of this section should be obtained from the intended sites of application immediately prior to application of the test substance and, to the extent possible, from adjacent untreated areas at intervals during the course of the study and at the termination of the study.

(v) Sampling intervals. (A) For exposed soil, soil under leaf litter, and foliage, sampling times should include, at a minimum, preapplication (control), date of application, and three samplings within the first week post application for each single or multiple application of the test substance.

(B) For sediments, standing (pond) water, and moving (stream) water, sampling should include, at a minimum, pre-application (control), date of application, and immediately post-application for each single or multiple application of the test substance.

(v) Test duration. Residue data should be collected until patterns of decline of the test substance and patterns of formation and decline of degradation products are established in the media sampled or the maximum times specified below, whichever comes first: 12 months after the last application for soil and leaf litter, 6 months after the last application for sediment, and 1 month after the last application for water (pond and stream).

(vi) Dissipation curves. Decline curves shall be constructed for residues in leaf litter, soil, foliage, and standing water.

(e) Reporting and evaluation of data. In addition to the basic reporting requirements specified in § 160-5, the test report should include the following specific information:

(1) Decline curves of residues in each major substrate analyzed; and

(2) Field test data, including:

(i) Precipitation (accumulated from first application to each sampling);

(ii) Water table;

(iii) Grade (slope);

(iv) Application time;

(v) Sampling time;

(vi) Dates and stages of pest development;

(vii) Application-to-sampling intervals for each treatment;

(viii) Depth, weight, or volume of each sample, and weights and volumes of aliquots taken for analysis; and

(ix) When water flow is measured, flow data expressed in terms of volume or linear flow.

(f) References. The following references contain supplemental information for developing a protocol for conducting forest field dissipation studies:

(1) Symons, P.E.K. 1977. Dispersal and toxicology of the insecticide fenitrothion; predicting hazards of forest spraying. Residue Rev. 68:1-31. [This review provides general information and an overview of problems that have occurred in a forest environment in association with use of an insecticide for control of a forest pest. Pesticide residues in organisms and physical environment and dissipation of the residues are discussed.]

(2) Roberts, J.R., Greenhalgh, R., and Marshall, W.K., eds. 1977. Proceedings of a Symposium on Fenitrothion: The Long-term Effects of its Use in Forest Ecosystems. (Natl. Res. Council Can.: Ottawa, Canada) NRCC/CNRC No. 16073:573-614. [Individual papers within these proceedings contain protocols for the study of pesticide dissipation in a forest ecosystem.]

(3) Giles, R.H., Jr. 1970. The Ecology of a Small Forested Watershed Treated with the Insecticide Malathion-S 35. Wildlife Monographs. No. 24. The Wildlife Society. Washington, D.C. [This paper contains experimental procedures for conducting terrestrial/aquatic (forest) dissipation studies. Studies contained in the reference are more extensive than generally required.]

(4) Maguire, R.J. and E.J. Hale. 1980. Fenitrothion sprayed on a pond: kinetics of its distribution and transformation in water and sediment. J. Agr. Food Chem. 28:372-378. [This paper contains protocols for the study of dissipation of a pesticide from a pond within a forest and from segments within that environment.]

(5) Peiper, G.R. 1979. Residue analysis of carbaryl on forest foliage and in stream water using HPLC. Bull. Environ. Contam. Toxicol. 22:167-171. [This paper contains studies of residue concentrations and dissipation of those residues from plant surfaces and from forest streams after serial pesticide application.]

(6) Szeto, S.Y., H.R. MacCarthy, P.C. Oloffs and R.F. Shepherd, 1978. Residues in Douglas-fir needles and forest litter following an aerial application of acephate (Orthene). J. Environ. Sci. Health (B) 13:87-103. [This paper contains protocols for the study of distribution, transformation, and dissipation of a pesticide within a forest canopy after aerial application.]

§ 164-4 Dissipation studies for combination products and tank mix uses.

(a) Purpose. The objective of this study is to determine the dissipation characteristics of a pesticide in soil when applied as a tank mix or in combination with other pesticides, whether in a combination product or pursuant to labeling directions recommending the simultaneous or serial application of two or more products. The Agency requires these data to ascertain if overall soil persistence of pesticides is affected by the simultaneous or serial application of two or more pesticides.

(b) When required. A laboratory or field soil dissipation study is required by 40 CFR § 158 on a case-by-case basis to support the registration of an end-use product containing more than one active ingredient intended for use as a component in tank mixtures, or customarily applied serially with another pesticide product. See, specifically, 40 CFR § 158.50 and § 158.130 to determine whether these data must be submitted. Section II-A of this subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(c) Test standards. The dissipation studies described in paragraph of this section should be derived from testing which complies with the general test standards in § 160-4 and all of the following specific test standards:

(1) Test substance. (i) For studies on combination products, if the end-use product contains two or more active ingredients (combination product), the test substances shall be the end-use product and similarly formulated products containing each active ingredient singly.

(ii) For studies on tank mixtures, if the use directions state that two or more end-use products containing different active

ingredients may be applied as a tank mixture, the test substances shall be the mixture of the end-use products prepared in accordance with the label directions, and each separate end-use product.

(iii) For studies on serial applications, if the use directions state that two or more end-use products containing different active ingredients may be applied serially, the test substances shall consist of the two or more end-use products to be used in the sequence specified in the label directions.

(2) Test procedures. (i) Application. The test substance(s) should be applied at the highest rate recommended by product labeling and as follows:

(A) For combination products, apply the test substances at the label-recommended field application rates to both light- and heavy-textured soils. Incorporate the test substances into the soil if recommended by label directions.

(B) For tank-mixed pesticides, apply the test substances at the label-recommended field application rates to both light- and heavy-textured soils. Incorporate each test substance into the soil if recommended by label directions.

(C) For serially-applied pesticides, apply the test substances individually and as the sequential combination at the label-recommended field application rates to both light- and heavy-textured soils. Incorporate each test substance into the soil if recommended by label directions.

(ii) Soil sampling. Soil from the treated area or laboratory container should be sampled following treatment for the purpose of ascertaining the extent of pesticide dissipation.

(A) Soil samples obtained from the intended site(s) of application or from the laboratory containers immediately prior to application of the test substance should be used as experimental controls.

(B) Sampling times should include pre-application, date of application, and immediate post-application. In the case of multiple applications, only immediate post-application samples (and not preapplication and date of application samples) are to be taken in addition.

(C) Soil samples should be taken in increments to a depth of 15 cm, unless results of studies on pesticide mobility indicate that the test substance is likely to leach into soil deeper than 15 cm.

(D) If data on leaching indicate that the test substance is likely to leach into soil deeper than 15 cm, or if the pesticide is incorporated into soil deeper than 5 cm, samples should be taken to a depth sufficient to include most of the leached pesticide.

(iii) Test duration. Residue data should be collected until patterns of decline of the test substance and patterns of formation and decline of degradation products are established in soil, or for a maximum duration of six months, whichever occurs sooner.

(d) Reporting and evaluation of data. In addition to the basic reporting requirements specified in § 160-5, the applicable reporting requirements as specified in § 164-1(d) apply.

(e) References. The following references contain supplemental information for developing a protocol to conduct a combination or tank mix study:

(i) Kaufman, D.D., J. Blake, and D.E. Miller. 1971. Methylcarbamates affect acylanilide herbicide residues in soil. J. Agr. Food Chem. 19:204-206. [This paper provides techniques to assess a complex pesticide degradation problem.]

(ii) Kaufman, D.D., P.C. Kearney, D.W. Von Endt, and D.E. Miller. 1970. Methylcarbamate inhibition of phenylcarbamate metabolism in soil. J. Agr. Food Chem. 18:513-519. [This precursor of the 1971 paper (above) contains procedures that may be useful for the design of experimental studies required on combination and tank mixes.]

§ 164-5 Long-term soil dissipation studies.

(a) Purpose. The objective of this study is to enable the Agency to assess the fate of pesticide residues that do not readily dissipate in the soil environment. Slow pesticide dissipation in soil may increase the residue burden imposed by pesticides by increasing their residence time in the environment.

(b) When required. (1) Data from a long-term soil dissipation study are required by 40 CFR § 158 to support the registration of any end-use product:

(i) If it contains an active ingredient with residues that do not reach 50 percent dissipation in soil prior to recommended subsequent application of that same active ingredient to the same sites utilized for the field dissipation study described for field and vegetable crops in § 164-1 and for aquatic food crops in § 164-2(b)(1); or

(ii) If the aerobic soil metabolism study described in § 162-1 demonstrates that, for field and vegetable crop uses and aquatic food crop uses, the total of pesticide (excluding bound) residues in soil are greater than fifty percent of the amount of pesticide initially applied at the time when a subsequent application would occur.

(2) Data from a long-term soil dissipation study are also required to support each application for registration of a manufacturing-use product that legally could be used to make an end-use product meeting the criteria of paragraphs (b)(1)(i) or (ii) of this section. See, specifically, 40 CFR § 158.50 and § 158.130 to determine whether these data must be submitted. Section II-A of this Subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(c) Test standards. Long-term soil dissipation data submitted in response to 40 CFR § 158.130 should be derived from testing which complies with the general test standards in § 160-4 and all of the following test standards:

(1) Test substance. The test substance shall be a typical enduse product.

(i) If the applicant's product is an end-use product, the test substance shall be a product with a formulation typical of the formulation category (e.g., wettable powder, emulsifiable concentrate, granular product) to which the product belongs.

(ii) If the applicant's product is a manufacturing-use product that legally could be used to make an end-use product for which longterm soil dissipation data are required, the test substance shall 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.]

(2) Test procedures. The applicant should follow the test procedure applicable to the use pattern or patterns of the product:

(i) Field and vegetable crop uses. (A) The test substance should be applied using the method and highest rate of application stated in the directions for use specified in the product label.

(B) Soil sampling (methods and scheduling) should be performed in accordance with the standards set forth in § 164-1(c)(2)(iii).

(C) Total duration of this study need not exceed three years or extend two years beyond the length of the terrestrial field dissipation study for field and vegetable crop uses.

(ii) Aquatic food crop uses. (A) The test substance should be applied using the method and highest rate of application stated in the directions for use specified on the product label.

(B) Soil sampling (method and scheduling) shall be performed in accordance with the standards set forth in § 164-2(d)(4).

(C) Total duration of this study need not exceed three years or extend two years beyond the length of the aquatic field dissipation study for aquatic food crop uses.

(d) Reporting and evaluation of data. In addition to the applicable reporting requirements specified in § 160-5, the specific reporting requirements described in § 164-1(d) apply for studies involving field and vegetable crop uses, and those in 164-2(e) apply for studies involving aquatic food crop uses.

(e) References. The following references contain supplemental information for developing a protocol to conduct a long-term soil dissipation study:

(1) Burnside, O.C. 1974. Trifluralin dissipation in soil following repeated annual applications. Weed Sci. 22:374-377. [This paper reports a long-term pesticide dissipation study with repeated applications at different levels of treatment and with replication. Assessment of residue levels was accomplished by bioassays with several crops and by a chemical analysis of soil extracts. The use of this bioassay technique can indicate the quantity of active herbicide remaining, but the technique is limited to herbicides. A chemical pesticide residue analysis is more generally applicable.]

(2) Caro, J.H., H.P. Freeman, and B.C. Turner. 1974. Persistence in soil and losses in runoff of soil-incorporated carbaryl in a small watershed. J. Agr. Food Chem. 22:860-863. [This paper is recommended as a model for the design of a long-term study protocol. The use of a field standard applied with the subject pesticide might aid in interpretation of dissipation kinetics.]

(3) Demint, R.J., J.C. Pringle, Jr., A. Hattrup, V.F. Burns, and P.A. Frank. 1975. Residues in crops irrigated with water containing trichloroacetic acid. J. Agr. Food Chem. 23:81-84. [The methods described here may be useful in designing protocols for long-term study of pesticides applied in irrigation water.]

(4) Miller, C.H., T.J. Monaco, and T.J. Sheets. 1976. Studies on nitralin residues in soils. Weed Sci. 24:286-291. [This study evaluated the effect of residue build-up from repeated application of three levels of nitralin to soils. Both biological and chemical assays were used with a sensitive crop for the bioassay. Combination of the two assays may in some cases aid

in interpretation of data. The use of plastic for storing samples should be avoided to prevent possible interferences from desorbed plastic components or loss of residues by sorption to the plastic.]

(5) Polzin, W.J., I.F. Brown, Jr., J.A. Manthey, and G.W. Probst. 1971. Soil persistence of fungicides - Experimental design, sampling, chemical analysis and statistical evaluation. Pest. Monit.J. 4:209215. [This paper was not intended as a long-term study, but rather was a study to improve the reliability of soil persistence data. It is cited here as a guide for improving soil sampling protocols.]

(6) Rice, C.P., H.C. Sikka, and R.S. Lynch. 1974. Persistence of dichlobenil in a farm pond. J. Agr. Food Chem. 22:533-534. [This paper reports dissipation of pesticide from water and the associated sediment in a pond. The use of blanks and fortified samples to evaluate recovery of pesticide from substrates and interference to quantitation as was done in this paper are good practice.]

(7) Schaefer, C.H., and E.F. Dupras, Jr. 1976. Factors affecting the stability of dimilin in water and the persistence of dimilin in field waters. J. Agr. Food Chem. 24:733-739. [Several of the phenomena observed in this paper are worth considering. Dissolution of pesticide formulation can be the rate-limiting step in a pesticide dissipation, and the whole system must be sampled, including strata, to give an accurate material balance. The evaluation of pesticide stability in samples is recommended especially if there will be delay between sampling and analysis.]

Series 165: ACCUMULATION STUDIES

§ 165-1 Confined accumulation studies on rotational crops.

(a) Purpose. Data from confined (laboratory/greenhouse/outdoor small plot) accumulation studies on rotational crops will enable the Agency to determine the nature and amount of pesticide residue uptake in rotational crops. Such data are used to establish realistic crop rotation restrictions (time from application to a time when crops can be rotated) or to provide information for determining if tolerances are needed in rotational crops.

(b) When required. Data from a confined accumulation study on rotational crops are required by 40 CFR § 158 to support the registration of an end-use product intended for field-vegetable crop use, aquatic crop use, or use on any other site on which it is reasonably foreseeable that any food or feed crop may be produced after application of a pesticide. Such data are also required to support each application for registration of a manufacturing-use product which legally could be used to make such an end-use product. See, specifically, 40 CFR § 158.50 and § 158.130 to determine whether these data must be submitted. Section II-A of this Subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(c) Test standards. Rotational crop accumulation data submitted in response to 40 CFR § 158.130 should be derived from testing which complies with the general test standards in § 160-4 and all of the following specific test standards:

(1) Test substance. This study shall be conducted using the radioactively-labeled analytical grade of the active ingredient.

(2) Test procedures. (i) This study should be performed using a sandy loam soil which has been treated with the test substance applied at a rate equivalent to that expected under actual field use conditions. However, if the label instructions of the product limit its use to one soil type other than the sandy loam, then the study should be run with the soil type specified on the label.

(ii) Following soil treatment, the pesticide should be aged under aerobic conditions in the soil for a time approximating the anticipated agricultural practice (e.g., 1 year for crops rotated the following year, 120 days for crops rotated immediately after harvest, and 30 days for assessing circumstances of crop failure). Growing the treated crop in the soil during the aging period is not precluded.

(iii) Crops planted in the treated and aged soil should include those expected in the proposed rotational schedule and, where possible, be representative of each of the following crop groupings: root (e.g., beets, carrots); small grain (e.g., wheat, barley), and leafy vegetable (e.g., spinach, lettuce). The selected crops shall be analyzed for residues at appropriate harvest intervals. (Residue analyses should be performed on selected crops at multiple intervals if both immature and mature crops are normally harvested in the course of usual agricultural practices.)

(iv) Residues in the soil should be analyzed at the time of treatment, at the time of planting of the rotational crop, and at the time of harvest of the rotational crop. However, if this confined accumulation study is carried in the same soil and at the same time as the aerobic soil metabolism study (§162-1) or the terrestrial field dissipation study (§164-1), then the soil residue analyses from these studies will suffice. See also §160-4(e) of this Subdivision.

(d) Reporting and evaluation of data. In addition to the applicable reporting requirements specified in § 160-5, the following data should be reported:

(1) The registration applicant should characterize and, when feasible, identify and provide analytical values for significant residues in the crops tested. Significant residues include parent compound, closely-related degradates, metabolites and/or their conjugates in the crop, but do not include C^{14} activity in the crop associated with that being incorporated into the carbon pool and ultimately into natural plant constituents. In cases where identification of residues is not feasible due to insufficient sample, then pooling of samples obtained from replicate experiments conducted simultaneously should be carried out to enable residue identification to be achieved. From the results of this study, the Agency will determine whether additional studies to measure the accumulation of pesticide residues in rotated crops under actual field conditions are needed. If such field studies are needed, the registration applicant will need to determine whether to conduct the field study described in § 165-2 of this Subdivision or to carry out residue uptake studies described in Subdivision O (Residue Chemistry Data Requirements) necessary to support the establishment of a tolerance in the rotated crop. (See also FR 46(8), 3016, January 13, 1981.)

(2) Depending on the crop tested, separate analyses should be conducted on different portions of the plant. For example, both the aerial and root portions of root crops should be analyzed.

(3) Analyses, including a description of data variability, for residues of parent compound and degradates in soil for each sampling interval.

(4) A description of the growing conditions should be reported. If the study is conducted outdoors, rainfall data, temperature monitoring data, and general climatic conditions should be reported for the test period.

(e) References. The following references contain information for developing a protocol for study of the uptake of residues in rotational crops:

(1) Burnside, O.C. 1974. Trifluralin dissipation in soil following repeated annual applications. Weed Sci. 22:374-377. [The general methods used by this author could be adapted to small-scale field studies. The techniques used in this study should be considered for development of a protocol to obtain data on pesticide uptake with rotational crops.]

(2) Burnside, O.C., C.R. Fenster, and G.A. Wicks. 1971. Soil persistence of repeated annual applications of atrazine. Weed Sci. 19: 290-293. [This paper contains procedures for investigation of pesticide fate with different soils and cropping practices.]

(3) Sirons, G.J., R. Frank, and T. Sawyer. 1973. Residues of atrazine, cyanazine, and their phytotoxic metabolites in a clay loam soil. J. Agr. Food Chem. 21:1016-1020. [This is not a study of uptake of a pesticide in a rotational crop system, but the procedures used could be applicable to design such a study. The study of a phytotoxic metabolite is included in this study.]

(4) Bull, D.L., and G.W. Ivie, 1982. Fate of O-[4-[(4-chlorophenyl)thio]phenyl] O-ethyl S-propyl phosphorothioate (RH-0994) in soil. J. AGR. Food Chem 30: 150-155. [This paper is a good example of procedures for a combined soil metabolism and rotational crop uptake study. The paper differs from the requirements of § 165-1 in that the 14C residues in the rotated crops were not characterized.]

§ 165-2 Field accumulation studies on rotational crops.

(a) Purpose. Data from field accumulation studies on rotational crops will enable the Agency to determine under actual field-use conditions the nature and amount of pesticide residue uptake in rotational crops. Such data are used to establish realistic crop rotation restrictions (time from application to a time when crops can be rotated) and to provide information for determining if tolerances are needed in rotational crops.

(b) When required. Data from a field accumulation study to determine the uptake of soil residues by rotational crops are

required by 40 CFR § 158 to support the registration of an end-use product, and to support each application for for registration of a manufacturing-use product used to make such an end-use product, only under the following circumstances:

(1) When significant C^{14} pesticide residues of concern to the Agency are detected in the test crops analyzed in the confined accumulation study, § 165-1[See § 165-1(d)(1) for a discussion of significant residues]; or

(2) When a subsequent crop is treated with the same active ingredient as the initial crop.

(3) See, specifically, 40 CFR § 158.50 and § 158.130 to determine whether these data must be submitted. Section II-A of this Subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(c) Test standards. Field accumulation data submitted in response to 40 CFR § 158.130 should be derived from testing which complies with the general test standards in § 160-4 and all of the following test standards:

(1) Test substance. The test substance shall be a typical end-use product.

(i) If the applicant's product is an end-use product, the test substance shall be a product whose formulation is typical of the formulation category (e.g., wettable powder, emulsifiable concentrate, granular product) to which the product belongs.

(ii) If the applicant's product is a manufacturing-use product that legally could be used to make an end-use product for which rotational crop accumulation data are required, the test substance shall 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.)

(2) Test procedure. (i) Sites. Field accumulation studies should be conducted in at least two different sites which are representative of the areas where rotated crops are expected to be grown. The soil type at one of the test sites should be the same as that used in the confined accumulation study of § 165-1. For restricted use patterns where only one typical area is involved, data from two similar sites should be submitted. See, specifically, 40 CFR § 158.50 and § 158.130 to determine whether these data must be submitted. Section II-A of this Subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(ii) Application. (A) The soil at the test site should be treated with the test substance applied by the method stated in the directions for use specified on the product label and at the highest recommended label rate.

(B) Following soil treatment, the pesticide should be aged under aerobic conditions in the soil for a time approximating the anticipated agricultural practice (e.g., one year for crops rotated the following year, 120 days for crops rotated immediately after harvest, and 30 days for assessing circumstances of crop failure). Growing the treated crop in the soil during the aging period is not precluded.

(iii) Sampling. (A) Representative root, small grain, and leafy vegetable crops typical of the area where the product is to be applied should be planted as rotational crops.

(B) If the registration applicant is proposing a tolerance for residues in a rotated crop, then that crop should be planted, harvested, and analyzed for residues at test sites selected in accordance with the requirements of 40 CFR § 158.125, described in detail in Subdivision O (Residue Chemistry Data Requirements).

(C) The rotational crops should be analyzed for residues at appropriate harvest times. (Residue analyses should be performed on selected crops at multiple intervals if both immature and mature crops are normally harvested in the course of usual agricultural practices.)

(D) Residues in the soil should be analyzed at times of treatment, at time of planting rotational crops, and at the time of rotational crop harvest. These soil analyses may not be needed if the aerobic soil metabolism study (§ 162-1) or the terrestrial field dissipation study (§ 164-1) provide soil residue data that demonstrate essentially complete dissipation of the pesticide by the time the original crop is harvested. (In some cases, this study can be combined with the aerobic soil metabolism study and the terrestrial field dissipation study.)

(iv) Test duration. Residue data should be collected in soil and rotational crops until the time that the rotational crop is normally harvested.

(d) Reporting and evaluation of data. In addition to the applicable reporting requirements specified in § 160-5, the following data should be reported:

(1) Field test data including:

(i) Dates of planting and harvesting;

(ii) Amount of rainfall and irrigation water (accumulated from application to harvest);

(iii) Depth of water table;

(iv) Slope of test site(s);

(v) Temperature monitoring data and a description of the general climatic conditions at the test site during the study;

(vi) Techniques and times of planting, culture, and harvesting;

(vii) Application time and method;

(viii) Sampling times and techniques;

(ix) Stages of crop development at times of sampling;

(x) Application-to-harvest interval; and

(xi) Depth, weight, or volume of each sample taken for analysis.

(2) Analysis for residues of parent compound and degradates in the crops. Depending on the crop, separate analyses should be conducted on different portions of the plant. For example, analysis of both the aerial and root portions of root crops should be conducted.

(3) Analyses for residues of parent compound and degradates in soil for each sampling interval.

(4) A description of residue data variability in soil and rotational crops.

(e) References. The following references contain information for developing a protocol for study of the uptake of residues in rotational crops:

(1) Burnside, O.C. 1974. Trifluralin dissipation in soil following repeated annual applications. Weed Sci. 22:374-377. [The general methods used by this author could be adapted to small-scale field studies. The techniques used in this study should be considered for development of a protocol to obtain data on pesticide uptake with rotational crops.]

(2) Burnside, O.C., C.R. Fenster, and G.A. Wicks. 1971. Soil persistence of repeated annual applications of atrazine. Weed Sci. 19:290-293. [This paper contains procedures for investigation of pesticide fate with different soils and cropping practices.]

(3) Sirons, G.J., R. Frank, and T. Sawyer. 1973. Residues of atrazine, cyanazine, and their phytotoxic metabolites in a clay loam soil. J. Agr. Food Chem. 21:1016-1020. [This is not a study of uptake of a pesticide in a rotational crop system, but the procedures used could be applicable to design such a study. The study of a phytotoxic metabolite is included in this study.]

(4) [Reserved]

§ 165-3 Accumulation studies on irrigated crops.

(a) Purpose. The purpose of these studies is to determine residue uptake and levels in representative crops which are expected to be irrigated with water from a field treated with a pesticide (e.g., reclaimed waste water or water from a rice field used to irrigate upland crops). Such studies are needed to establish realistic label restrictions to prevent residues in irrigated crops and/or to provide information for a determination as to whether tolerances may be needed in the irrigated crop.

(b) When required. Data from a study of residue accumulation in irrigated crops under actual field use conditions are required by 40 CFR § 158 to support the registration of an end-use product intended for aquatic food crop or aquatic non-crop uses, for uses in and around holding ponds used for irrigation purposes, or for uses involving effluents or discharges to water used for crop irrigation. Data from such a study are also required to support each application for registration of a manufacturing-use product which legally could be used to make such an end-use product. See, specifically, 40 CFR § 158.50 and § 158.130 to determine whether these data must be submitted. Section II-A of this Subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(c) Test standards. Irrigated crop accumulation data submitted in response to 40 CFR § 158.130 should be derived from testing which complies with the general test standards in § 160-4 and all of the following specific test standards:

(1) Test substance. The test substance shall be a typical end-use product.

(i) If the applicant's product is an end-use product, the test substance shall be a product whose formulation is typical of the formulation category (e.g., wettable powder, emulsifiable concentrate, granular product) to which the product belongs.

(ii) If the applicant's product is a manufacturing-use product that legally could be used to make an end-use product for which irrigated crop accumulation data are required, the test substance shall be a product representative of the major formulation category which includes the 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.)

(2) Test procedures. (i) Field accumulation studies on irrigated crops should be conducted in at least two different sites which are representative of the areas where irrigated crops are expected to be grown.

(ii) Application. The irrigated crops should receive irrigation water containing the test substance at the highest expected concentration either consistent with the maximum rate recommended on the product label at the original site of application (aquatic food crop, aquatic non-crop, holding ponds) or consistent with the maximum rate calculated from direct discharges.

(iii) Irrigation. Irrigated crops should be irrigated at the maximum frequency consistent with good agricultural practices.

(iv) Sampling. (A) Foliage and/or crop produce samples should be collected from the test crops receiving irrigation water containing the test substance prior to the first irrigation treatment and at the earliest possible normal harvest interval following the last irrigation treatment.

(B) Water samples should be collected from the irrigation water at the time of each irrigation.

(C) Soil samples should be collected from the site of the irrigated crop prior to the first irrigation treatment, one day after each irrigation treatment, and at harvest of the irrigated crop.

(iv) Analysis. Residue data should be obtained for the soil, irrigation water, and irrigated crop samples collected during the course of this study.

(d) Reporting and evaluation of data. In addition to data submitted in response to the applicable reporting requirements specified in § 160-5, the test report should contain the following information:

(i) Analysis for residues of parent compound and degradates in the test crops, the irrigation water, and soil. Decline curves of the residues in soil should be included.

(ii) A description of residue data variability for the test crop, irrigation water, and soil sampled in this study.

(iii) Field test data, including:

(A) Dates of planting and harvesting;

(B) Method and frequency (times) of irrigation treatments;

(C) Sampling times and techniques;

(D) Stages of crop development at sampling times;

(E) Irrigation-to-harvest and irrigation-to-sampling intervals for each irrigation treatment;

(F) Depth, weight, or volume of each sample, and weights and volumes of aliquots taken for analysis;

(G) Flow data for irrigation water expressed in terms of volume or linear flow; and

(H) Rainfall data, temperature monitoring data, and a description of the general climatic conditions at the test sites.

(e) References. The following reference contains supplemental information for developing a protocol for conducting an accumulation study in irrigated crops:

(1) Demint, R.J., J.C. Pringle, Jr., A. Hattrup, V.F. Bruns, and P.A. Frank. 1975. Residues in crops irrigated with water containing trichloroacetic acid. J. Agr. Food Chem. 23:81-84. [This paper presents a procedure for assessment of pesticide carryover in irrigation water.]

(2) [Reserved.]

§ 165-4 Laboratory studies of pesticide accumulation in fish.

(a) Purpose. The purpose of these studies is to determine if pesticide residues accumulate in fish used as human food sources and to determine the extent of pesticide residues in edible portions of such fish. Data from pesticide accumulation studies in fish are used by the Agency to establish label restrictions (e.g., to prevent pesticide applications to certain sites so that there will be minimal residues entering edible fish or shellfish such as catfish or crayfish inhabiting rice fields). The data may also be used to

provide information for the setting of tolerances or action levels in these organisms where necessary.

(b) When required. (1) Data from a fish accumulation study are required by 40 CFR § 158 to support the registration of an end-use product intended for outdoor use (except domestic outdoor and greenhouse uses), or aquatic impact uses involving direct discharge of treated water into outdoor aquatic sites, except when any of the criteria in paragraph (b)(2) of this section are satisfied. Data from such a study are also required to support each application for registration of a manufacturing-use product that could be legally used to produce such an end-use product, except when any of the criteria in paragraph (b)(2) of this section are satisfied. See, specifically, 40 CFR § 158.50 and § 158.130 to determine whether these data must be submitted. Section II-A of this Subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(2) Fish accumulation data will not normally be required in situations where the registrant can offer evidence acceptable to the Agency showing that the active ingredient and/or its principal degradation product(s):

(i) Will not reach water, or

(ii) Will not persist in water (i.e., has a half-life of approximately four days or less), or

(iii) Has a relatively low potential for accumulation in fish as indicated by an octanol/water partition coefficient less than approximately 1000.

(c) Combined testing. Testing conducted as described in this section may be combined with testing conducted to meet the requirements of § 72-6 of Subdivision E, Hazard Evaluation: Wildlife and Aquatic Organisms, provided the test standards of each study are met.

(d) Test standards. Fish accumulation data submitted in response to 40 CFR § 158.130 should be derived from testing which complies with the general test standards in § 160-4 and all of the following specific test standards:

(1) Test substance. Accumulation studies shall be conducted using the active ingredient as the radioactively-tagged analytical grade or as the technical grade. If the study requires testing with a degradation product, the purest form that the applicant can obtain shall be used.

(2) Test procedures. (i) Residue studies should be conducted with radioisotopic (preferred) or non-radioisotopic analytical techniques.

(ii) Flow-through exposure studies are recommended. Exposure systems must maintain a constant concentration of chemical in a non-colloidal solution (use of carrier solvents to introduce the test substance to dilution water is permissible) and the concentration must not exceed 1/10 of the 96-hour LC_{50} of the test species. Within these constraints, the concentration of the test substance should be high enough to facilitate chemical identification of residues in fish. Bluegill sunfish or channel catfish are the preferred species, although other species may be appropriate. A control (non-treated) group of fish is recommended.

(iii) Exposure duration is 28 days with depuration (withdrawal) of 14 days with suggested sampling times and total residue analyses as follows:

(A) Water: days 0, 7, 14, 21, and 28 of the accumulation period;

(B) Fish: total residues in whole body, edible tissue, and viscera should be determined on days 0, 3, 7, 14, 21, and 28 of the accumulation period, and days 1, 3, 7, 10, and 14 of the depuration period.

(iv) Residues in two samples of edible tissue and two samples of viscera containing the highest residue levels during the accumulation period should be identified (if sufficient material exists). In general, extractable residues present at 0.05 ppm or greater should be identified.

(v) The Agency recognizes that special circumstances may be present (e.g., the occurrence of multiple persistent degradates, particular use patterns, or accumulation mechanisms) under which alternative experimental designs may be desirable. Therefore, the registration applicant may wish to discuss with the Agency the appropriateness of alternative experimental designs for fish accumulation studies (e.g., short-term kinetic studies or simulated field studies).

(e) Reporting and evaluation of data. In addition to the applicable reporting requirements specified in § 160-5, the following should be reported:

(1) A detailed description of the test conditions should be provided. This should include water characteristics (e.g., dissolved oxygen, pH, temperature, and dissolved salts), information on the test organisms (scientific name, source, weight, observed mortality, disease treatment, and acclimation procedures), and test methodology (detailed protocol, organism loading ratio, lighting, temperature, feeding schedule, and similar information).

(2) Total residue levels in whole body, edible tissue, and viscera, and in exposure water at all sampling times, including a description of data variability, shall be reported, as well as the identity of residues at specifed times.

(f) References. (1) The following reference is a review of accumulation of pesticides in fish:

Hamelink, J.L., and A. Spacie. 1977. Fish and chemicals: The process of accumulation. Ann. Rev. Pharmacol. Toxicol. 17:167-177. [This paper contains information on the parameters, kinetics, and processes that influence the accumulation of pesticides in fish. It could provide useful background information for design of accumulation studies.]

(2) The following references contain experimental procedures relative to design of studies of pesticide accumulation with sunfish:

(i) Branson, D.R., G.E. Blau, H.C. Alexander, and W.B. Neely. 1975. Bioconcentration of 2,2',4,4'-tetrachlorobiphenyl in rainbow trout as measured by an accelerated test. Trans. Am. Fish. Soc. 104:785792. [Accelerated accumulation tests such as those reported in this paper may be an acceptable substitute for full-length studies under certain conditions. Examples might include instances where concerns about multiple persistent degradates exist.]

(ii) Krzeminski, S.F., C.K. Brackett, and J.D. Fisher. 1975. Fate of microbicidal 3-isothiazolone compounds in the environment: Modes and rates of dissipation. J. Agr. Food Chem. 23:1060-1068. [This is an example of a flow-through study. It demonstrates high levels of steadystate accumulation under steady dosing conditions and a rapid residue decline when the dosing rate goes to zero.]

(iii) Macek, K.J., M.E. Barrows, R.F. Frasny, and B.H. Sleight, III. 1975. Bioconcentration of ^{14}C-pesticides by bluegill sunfish during continuous aqueous exposure. Pp. 119-142 in Structure Activity Correlations in Studies of Toxicity and Bioconcentration with Aquatic Organisms. G.D. Veith and D.E. Konasewich (eds). Great Lakes Advisory Board. International Joint Commission. Windsor, Ontario, Canada.

[This is a good prototype for design of a protocol for study of pesticide accumulation in fish.]

§ 165-5 Field accumulation studies of aquatic non-target organisms.

(a) Purpose. Field accumulation studies are required to determine if, following aquatic non-crop applications of pesticides, pesticide residues are accumulated in the edible tissues of fish that normally inhabit sites in or adjacent to these treated areas. The residue-bearing fish subsequently may be used as human food sources. Furthermore, these studies are needed to establish realistic label restrictions necessary to protect man and the environment and to provide information for determining if tolerances or action levels may be needed. These studies complement the laboratory data required for those uses by taking into account the contributions of pesticide degradation, partitioning, and movement under field use conditions in determining the amount and nature of the residues available to the nontarget aquatic organisms via accumulation.

(b) When required. (1) Data from a field accumulation study in aquatic nontarget organisms are required by 40 CFR § 158 to support the registration of an end-use product:

(i) Which is intended for forestry use, aquatic non-crop use, or aquatic impact use that results in direct discharges of treated water into outdoor aquatic sites;

(ii) For which data from the laboratory fish accumulation study (§165-4) show a potential for residues of the pesticide to accumulate.

(iii) For which no tolerance or action level for fish has been granted.

(2) Data from such a study are also required to support each application for registration of a manufacturing-use product which legally could be used to make an end-use product described in paragraph (b)(1) of this section. See, specifically, 40 CFR § 158.50 and § 158.130 to determine whether these data must be submitted. Section II-A of this Subdivision contains an additional discussion of the "Formulators' Exemption" and who must submit the required data as a general rule.

(c) Combined testing. Testing conducted as described in this section may be combined with testing conducted to meet the requirements of § 164-2 (field dissipation studies for aquatic uses and aquatic impact uses) or § 165-4 (laboratory studies of pesticide accumulation in fish), provided the test standards of each study are met.

(d) Test standards. Aquatic non-target field accumulation data submitted in response to 40 CFR § 158.130 should be derived from testing which complies with the general test standards in § 160-4 and all of the following specific test standards:

(1) Test substance. The test substance should be a typical end-use product representative of a major formulation category (e.g., wettable powder, emulsifiable concentrate, granular product) and containing the active ingredient of the applicant's product.

(i) If the applicant's product is an end-use product, the test substance should be a product whose formulation is typical of the formulation category to which the product belongs.

(ii) If the applicant's product is a manufacturing-use product that legally could be used to make an end-use product for which non-target organism field accumulation data are required. The test substance shall 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.)

(2) Test procedure. (i) The rate and method of test substance application should approximate the intended use pattern of the pesticide.

(ii) Fish (bottom, middle, and surface feeders, if available) including water, should be sampled in representative application areas.

(iii) Sampling times for fish and water should include pre-application, date of application, and immediate post-application for each single or multiple application of the test substance, and then at 3, 7, 14, 21, and 28 days following the last application.

(iv) Residue analyses should be performed on the whole body and edible tissue of fish and on the water samples for each sampling interval.

(e) Reporting and evaluation of data. In addition to the applicable reporting requirements specified in § 160-5, the reporting requirements specified in §§ 164-3(e) and 165-4(e) apply.

(f) References. (1) Consult the references cited in § 164-2(f) for guidance on the general conduct of aquatic non-target organism field accumulation studies.

(2) Consult the references cited in § 165-4(f) for guidance in the sampling and residue analysis of fish.

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