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Fate, Transport and Transformation Test Guidelines

OPPTS 835.2240 Photodegradation in Water



INTRODUCTION

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

OPPTS developed this guideline through a process of harmonization of the testing guidance and requirements that existed for the Office of Pollution Prevention and Toxics (OPPT) in Title 40, Chapter I, Subchapter R of the Code of Federal Regulations (CFR), the Office of Pesticide Programs (OPP) in publications of the National Technical Information Service (NTIS) and in the guidelines published by the Organization for Economic Cooperation and Development (OECD).

For additional information about OPPTS harmonized guidelines and to access this and other guidelines, please go to http://www.epa.gov/oppts and select "Test Methods & Guidelines" on the left side menu.

OPPTS 835.2240 Photodegradation in water

(a) **Scope**—(1) **Applicability.** This guideline is intended for use in meeting testing requirements of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (7 U.S.C.136, *et seq.*). It describes procedures that, if followed, would result in data that would generally be of scientific merit for the purposes described in paragraph (b) of this guideline.

(2) **Background**. The source materials used in developing this OPPTS guideline are OPP 161-2 Photodegradation studies in water, OPP 160-4 General test standards, OPP 160-5 Reporting and evaluation of data (Pesticide Assessment Guidelines, Subdivision N - Chemistry: Environmental Fate, EPA report 540/9-82-021, October 1982) and OPP Addendum 4 on Data Reporting to Pesticide Assessment Guidelines, Subdivision N: Chemistry: Environmental Fate, Photolysis Studies, January 1988.

(b) **Purpose**. Pesticides introduced into aqueous systems in the environment can undergo photolytic transformation by sunlight. Data on rates of photolysis and half-lives are used to establish the importance of this transformation process and the persistence characteristics of photoproducts formed. Information from these studies enables the Agency to determine the stability of the pesticide when exposed to sunlight and to predict the likelihood of the pesticide persisting in the environment, the photoproducts that are likely to be produced, and their stability when exposed to sunlight.

(c) **General considerations**. Data from photo degradation studies in water support end-use products intended for terrestrial use, aquatic use, forestry use, or for any aquatic impact uses involving direct discharges of treated water into outdoor aquatic sites unless the electronic absorption spectra, measured at pHs 5, 7, and 9, of the chemical and its hydrolytic products, if any, show no absorption or tailing between 290 and 800 nm. Data from such studies also support manufacturing-use products which may legally be used to formulate such an end-use product.

(d) **Test method.**—(1) **Test substance**. Studies should be conducted with the technical or purer grade of each active ingredient in the product, or where radioisotopic analytical techniques are used (they are preferred), studies should be conducted with the analytical grade of each active ingredient in the product. Where non-radioisotopic analytical techniques are used, studies should be conducted with the technical or purer grade of each active ingredient in the product.

(2) **Test procedure**.—(i) **Methodology.** Procedures for experiments on the transformation of various pesticides in water have been set forth by Wolfe et al and are available in paragraph (f)(1). Newsom and Woods (paragraph (f)(2)) and Su and Zabik, (paragraph (f)(3)) emphasize laboratory studies of pesticide photolysis in natural water. Nakagawa et al (paragraph (f)(4)) provide procedures for pesticide photolysis in water under either artificial or natural sunlight. Niles and Zabik in paragraph (f)(5) discuss procedures for photolysis in aqueous solution, on soil and as a thin film.

(ii) **Temperature**. Studies should be conducted at $25 \pm 1^{\circ}$ C.

(iii) **Concentrations**. 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 co-solvent should not act as a photosensitizer in the rate study.

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

(v) **pH**. Photolysis rate determination and photo product identification experiments should be carried out at a pH that minimizes hydrolysis breakdown. 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) should be carried out at pHs of 5, 7 and 9.

(vi) **Light sources**. 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 paragraph (f)(4) of this guideline), data should be provided relating the intensity of the radiation used to that of natural sunlight.

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

(viii) **Duration and sampling interval**. 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.

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

(e) **Reporting and evaluation of data**. Reporting units should be in the metric system.

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

(2) **Test substance**. (i) The report should identify the test substance, and should include chemical name of the active ingredient, molecular structure of the active ingredient, and qualitative and quantitative description of the chemical composition.

(ii) If radiolabeled material is used, the chemical and radiochemical purity of the material, its activity in Curies/mole and disintegrations per minute per gram (dpm/g) or other standard unit, the site of radiolabeling, the isotope used, and the source when appropriate.

(iii) Manufacturer, and lot and sample numbers of the test substances.

(iv) Properties of the test substance, including physical state, pH, and stability.

(3) **Light source**. 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. If artificial light is used as the light source, the nature of the source, intensity, wavelength distribution, and time of exposure, as well as the relationship of the light intensity employed to that of natural sunlight should be reported..

(4) **Photoproducts**. Identification of each photo 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.

(5) **Water**. The source and quality of the water used as the solvent, and the identity and concentration of any co-solvent or other material added to the water (e.g., for buffering purposes).

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

(i) The identity of the instrumentation, equipment, reagents used, and the operating conditions of the instrumentation.

(ii) A description of the equipment used to measure the wavelength range and intensity of the incident light.

(7) **Analytical method**. A full description of each method used in this study, the method validation data, recovery and method detection limit data, quality control procedures and results, sample chromatograms, sample calculations, and a material balance. A detailed description of the procedures used in preparation and handling of the sample throughout the method.

(8) **Results/discussion**. This section should contain the scientific results of the study. Each report should contain the principal mathematical equations used in generating and analyzing data, as well as representative calculations using these equations. Data regarding rates of formation and decline of parent compounds or their degradates should be expressed as amounts, concentrations, and corresponding percentages. Rate constants should be reported in conjunction with rate data. Tabular data, as well as graphs for decline curves should be submitted.

(f) **References**. The following references should be consulted for additional background information on this guideline:

(1) 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. EPA report 600/3-76-067. 141 pp.

(2) Newsom, H.C., and W.G. Woods. 1973. Photolysis of the herbicide dinitramine $(N^3, N^3$ -diethy1-2, 4-dinitro-6-trifluoromethy1-<u>m</u>-phenylenediamine). J. Agr. Food Chem. 21:598-601.

(3) 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.

(4) Nakagawa, M., and D.G. Crosby. 1974. Photodecomposition of nitrofen. J. Agr. Food Chem. 22:849-853.

(5) Niles, G.P., and M.J. Zabik. 1975. Photochemistry of bioactive compounds. Multiphase photo degradation and mass spectral analysis of basagran. J. Agr. Food Chem. 23:410-415.