SOIL COLUMN LEACHING STUDY FOR PFOA

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1.0 STUDY PURPOSE & PRINCIPLE

A soil column leaching study for perfluorooctanoic acid (PFOA) was designed by DuPont to determine the vertical mobility or leaching of air deposited ammonium perfluorooctanoate (APFO)/rainwater mobilized PFOA through clayey silt and silty clay soil. This leaching study will begin in 3Q04. Unpublished studies conducted by DuPont have indicated that APFO in air emissions is deposited as a particulate material on the ground surface. These particulates are dissolved in rain water and carried through the soil column as PFOA.

The principle of this testing is to subject natural soil columns, approximately six cm diameter by thirty five cm in length, to defined periods of artificial rain. APFO will be dissolved in a small volume of distilled/deionized water and applied to the top of the soil column. At regular time intervals, artificial rain will be applied to the top of the column and the leachate draining from the column will be collected and analyzed to determine PFOA concentration. In addition, after the leaching process is complete, soil samples from the column will be sampled from various depths within the column and analyzed for PFOA.

The test method used for this soil leaching column study is derived from *Pesticide Assessment Guidelines Subdivision N, Chemistry: Environmental Fate, Series 163: Mobility Studies* (EPA-540/9-82-021; Appendix A) prepared by the Environmental Fate Branch, Hazard Evaluation Division of the Office of Pesticide Programs in 1982.

1.1 Study Objectives

There are two main objectives of this study. The first objective is to evaluate the leaching behavior of air deposited APFO/rainwater mobilized PFOA in silty clay or clayey silt. The second objective is to provide data for estimating the leaching potential of PFOA, including determining and verifying the following parameters:

- retardation factor
- percent adsorbed/desorbed
- mass balance

1.2 Materials and Methods

The protocol for this soil leaching column study is described in *Research Methods in Weed Science* (second Edition, 1977), Truelove, B. (eds.) in a paper by Weber, J. B. and Peeper, T. F. (see Appendix B). The paper by Weber and Peeper (1977) is a recommended reference in EPA-540-9-82-021. A 1986 edition of *Research Methods in Weed Science* includes a revision of the 1977 paper by Weber and Peeper. The same soil leaching column protocol is presented in the 1986 paper by Weber et al. along with very clear figures showing details of the setup that were not included in the 1977 paper. The Weber et al. (1986) paper is included as

Appendix C and the figures referred to below are from this paper. In the following sections, the soil core acquisition and soil leaching study procedures are summarized.

1.2.1 Soil Core Acquisition

There are two major types of soil columns used to investigate leaching behavior in soils, natural soil columns and hand-packed soil columns (Weber et al., 1986). For this study, natural soil cores will be used. The natural soil columns will be obtained from the Holocene floodplain at the Washington Works Site. Ideally, a location that has minimal PFOA impact to soil will be selected. Analytical data from the site and the results from air modeling conducted at and near the site will be used to determine potential coring locations. The exact sampling location will be determined following a field visit and the sampling location will be marked with flagging and surveyed. Soil column collection will be documented with notes and photographs, if permission from the site is obtained. The core acquisition procedure, as described by Weber and Peeper (1977) and Weber et al. (1986), will be utilized. However, the procedures may be modified as necessary based on actual field conditions. Any modifications to the soil core acquisition procedure in Weber and Peeper (1977) and Weber et al. (1986) will be documented in the report issued following the completion of this study.

It is anticipated that nine soil cores will be collected from the sampling location, six for laboratory testing and the soil column leaching experiments and three for future use, if required. At the coring location, the surface conditions will be photographed and described in a field log. For soil core acquisition, nine sample tubes of pre-cleaned, schedule 5 stainless steel sample tubes (approximately six cm diameter by 35 cm long) will be used. The bottom edge will be sharpened for ease of soil penetration. The stainless steel sample tubes will be driven 30 cm into the soil using either a driving block and a sledgehammer or the weight of a backhoe bucket. All nine sample tubes will be driven into the soil immediately adjacent to each other. The soil surrounding the sample tubes will be exposed and described to a depth of 30 cm. Soil surrounding the sample tubes will be sampled on five cm intervals (0-5 cm, 5-10 cm, etc) to a depth of 30 cm. Each of these samples will be homogenized in the field and each sample will be submitted for moisture content, total organic carbon (TOC), pH, clay content and texture analysis. Each sample tube will be removed with the soil core intact, taking care not to disturb the soil core in the bottom of the pipe when removing the pipe from the ground. The top and bottoms of the sample tubes will be marked on the outsides of the sample tubes. The ends of the sample tubes will be packed with glass wool, capped and sealed with tape to prevent disturbing the soil cores during shipment to the laboratory. The sample tubes will then be sealed in individual plastic bags and shipped to the laboratory in an upright position.

In the laboratory, five of the nine soil cores will be prepared for use in the column study. Three soil cores will be stored in a cold room for future use, if necessary. The remaining soil core will be used to obtain soil samples that will be analyzed for background PFOA concentrations. Soil samples from this core will be

collected from five-cm intervals the length of the column (0-5 cm, 5-10 cm, etc). Each five-cm interval sample will be homogenized and sampled for PFOA analysis.

1.2.2 Test System

The soil leaching procedure described by Weber and Peeper (1977) and Weber et al. (1986) will be utilized for this study. However, this procedure may be modified if needed. Any modifications of the procedure in Weber and Peeper (1977) and Weber et al. (1986) will be documented in the report issued following the completion of the study.

The five soil columns will be preconditioned by wetting the columns thoroughly and allowing them to drain overnight to field capacity. The wetting solution used will be a 60 uM $CaCl_2$ solution made from deionized water. Figure 1 (in Appendix C) from Weber et al., 1986, shows a cross section of a natural soil core leaching system using a continuous saturated flow. This study will use the same setup but with saturated/unsaturated flow. Three different volumes of APFO, equivalent to application rates of 0.05, 0.1, and 0.2 kg/hectare, will be dissolved in a small volume of distilled or deionized water and applied to the surface of three of the soil columns. The fourth column will be used as a duplicate for the soil column in which the mid-concentration of APFO was applied. The applied APFO in solution will be allowed to equilibrate with the soil prior to beginning the leaching process. In the fifth column, no APFO will be applied to the surface of the column. A nonsorbing and nondegradable polar reference substance, such as sodium bromide, will also be applied to the tops of the five soil columns to determine breakthrough point.

Prior to initiation of the leaching study, glass wool will be placed on the top surface of the columns. Artificial rain (the 60 uM $CaCl_2$ solution made from deionized water) will be applied to each of the five columns, using an application rate of approximately 1.6 cm/column/day of artificial rain. This application rate is slightly higher than the recommended rate of 1.2 cm/column/day of artificial rain but is the volume required to generate approximately 50 ml of leachate per application, the minimum volume required for PFOA and tracer analysis. Leachate will be collected daily, 24 hours after the application of the artificial rain and prior to the subsequent application. Leachate will be submitted to the laboratory once a week and analyzed on a batch basis. The column study will be considered complete when the concentration of PFOA in the leachate has returned to a non-detectable amount or has leveled off to a constant concentration. After the final leachate sample has been collected from each column, the leaching apparatus will be disassembled and the soil columns will be removed from the column and divided into five-cm intervals (0-5 cm, 5-10 cm, etc.). The soil from each 5-cm interval will be homogenized and analyzed for PFOA.

1.3 Analytical Methods

PFOA concentrations will be determined in the following media:

- solution used for preconditioning the five columns
- solutions containing various amounts of PFOA used to spike the four columns
- artificial rain applied to the five columns
- leachate from the control column that was not spiked with PFOA
- leachate from the four columns that were spiked with varying concentrations of PFOA
- soil samples (0-5 cm, 5-10 cm, etc.) from the five columns used in the leachate study after taking the last leachate sample from each column
- soil samples from one column (0-5 cm, 5-10 cm, etc.) not utilized in the column study

In aqueous solutions, PFOA is extracted from water using C_{18} solid phase extraction (SPE) cartridges. Analysis is performed by liquid chromatography-tandem mass spectrometry (LC/MS/MS) using selected reaction monitoring (SRM). Quantitation is accomplished via external standard calibration.

For soil samples, the samples are mixed with methanol, sonicated, centrifuged and filtered. The methanol extracts are analyzed by LC/MS/MS. A known quantity of the labeled compound PFOA-di-13C is added to every sample and to the batch quality control samples prior to extraction. Because the isotopically labeled compound is chemically identical to the compound of concern, it is affected by any interfering substances in the sample to the same extent, as is the compound of concern.

1.4 Data Analysis and Reporting

After all of the results of the analysis of PFOA in leachate and soil have been obtained, the data will be analyzed. Following data analysis, the testing procedures, test results and data interpretation will be documented in a report.

APPENDIX A

PESTICIDE ASSESSMENT GUIDELINES
SUBDIVISION N
CHEMISTRY:
ENVIRONMENTAL FATE
(EPA-540/9-82-021)

EPA-540/9-82-021
October 1982

Pesticide Assessment Guidelines
Subdivision N

Chemistry:
Environmental Fate

Prepared by Staff of

Environmental Fate Branch
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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 nonorop 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 nonorop 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 M 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. 23:159-162. [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, M.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. 20:1224-1226. [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 or 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 catagories, 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 measurment 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]

APPENDIX B

HERBICIDE MOBILITY IN SOILS (WEBER AND PEEPER, 1977)

CHAPTER 7

HERBICIDE MOBILITY IN SOILS

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INTRODUCTION

The relative ease with which a herbicide moves vertically in soil is important in determining its efficacy, suitability for use as a placement selective herbicide, and potential for contaminating ground water or drainage effluent. Movement of a herbicide in soil is dependent on several factors, including intensity and frequency of rainfall (19), soil properties (2,3,8,12,13,15,16,20), and herbicide properties (1,9,18,22). As researchers have continued to investigate the leaching of specific herbicides under conditions relating to specific soil or cropping situations, a proliferation of variations in equipment and procedures has occurred. These variations have made it somewhat difficult to interpret the movement of herbicides through soil (22). Several investigators have quantitatively described the movement of herbicides through soils using computer and conceptual models (4,7,14), and the mass-balance approach (2). Several methods for measuring relative herbicide mobility in soils have become generally accepted as standard state-of-the-art methods. They include the use of soil columns (4,5,8,9,13,18,19), soil thin-layer plates (10,11,12,22), and soil thick-layer trays (6,22).

The soil thin-layer plate technique utilizes a soil matrix applied to a glass plate as the supporting medium. Herbicides are spotted onto the plate in a manner similar to that shown in Figure 1. One end of the plate is immersed in a small amount of water at the bottom of a closed glass chamber. The herbicides move up the plate and are separated according to the principles of ascending chromatography (see Chapter 10). The technique is relatively rapid and the results are comparable with those obtained in adsorption studies, although of an inverse natuare; *i.e.*, immobile herbicides are strongly adsorbed and do not ascend the plate, while highly mobile herbicides, which leach readily, are not adsorbed and move freely (12). The thin-layer plate technique also offers the advantage of allowing one to compare several herbicides at the same time under identical conditions.

The thick-layer chromatography technique utilizes a shallow tray filled with soil and placed in a horizontal position (6). Herbicide is applied to the soil at one end of the tray and one end of a cloth wick is placed on the herbicide-treated soil, the other end of the wick is placed into a dish of water. Water ascends the wick and diffuses into the soil carrying the herbicide along. This technique has one distinct advantage over the thin-layer plate technique in that the soil is deep enough to allow for a plant bioassay after the herbicide leaching has been completed, as shown in Figure 2.

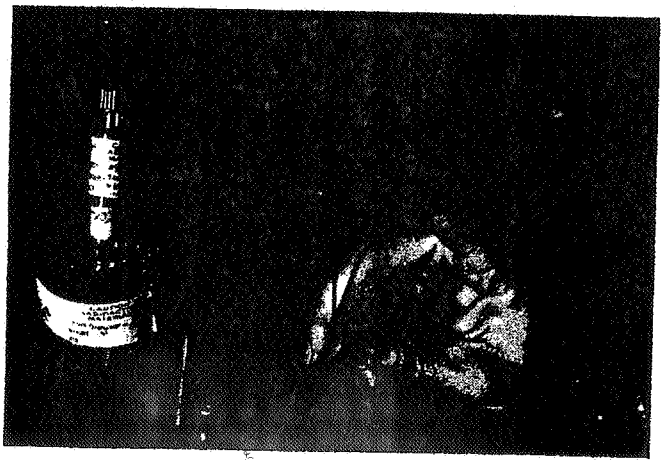


Figure 1. Application of herbicides to soil thin-layer chromatography plates (courtesy of Dr. C. S. Helling, U.S. Department of Agriculture, Beltsville, MD).

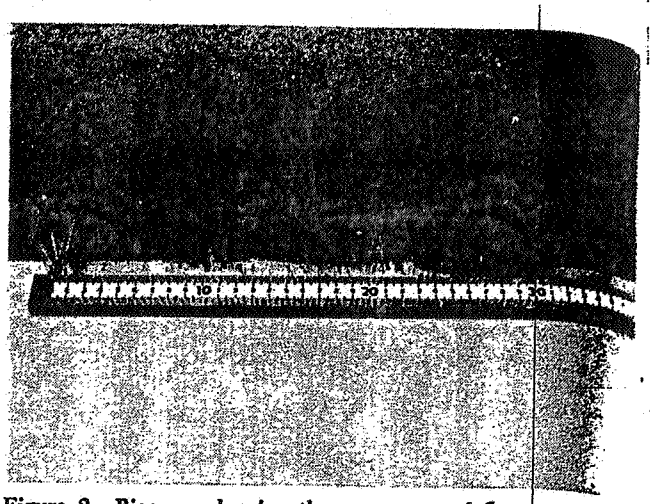


Figure 2. Bioassay showing the movement of fluometuron in sandy soil thick-layer chromatographic tray [Wu and Santelman (21)].

The soil column technique is somewhat slower than the thin-layer and thick-layer techniques but it does have several features not present in the others: (a) soil columns may be used with field moist soils or soils at specific moisture levels which is preferable to using dried soils; (b) natural soil cores may be obtained or surface soil and subsoil may be placed in columns simulating soils in their natural state; (c) herbicide leaching under saturated or unsaturated flow conditions may be studied; (d) soil columns may be readily disassembled to permit the taking of serial samples for chemical and radio chemical analyses and plant bioassay; and (e) herbicides may be applied to soils in soil columns and allowed to decompose under near natural conditions before they are leached, thus providing data on both parent herbicides and metabolites (21). This chapter describes methods for measuring the relative mobilities of herbicides in soils using soil columns.

DESCRIPTION OF METHODS

Basically, there are two major types of columns used to investigate the leaching behavior of herbicides in soils: (a) natural soil columns, and (b) hand-packed soil columns. Three types of hand-packed soil columns are used, depending upon the kind of soil assays to be performed after the leaching is completed. They include: (a) solid columns (in some cases holes or slots are cut into the columns to aid in removing the soil or to allow for bioassays to be carried out when leaching is completed), (b) stacked-cylinder columns, and (c) split columns. Figure 3 illustrates these various kinds of soil columns.

APPARATUS, CHEMICALS, AND OTHER MATERIALS

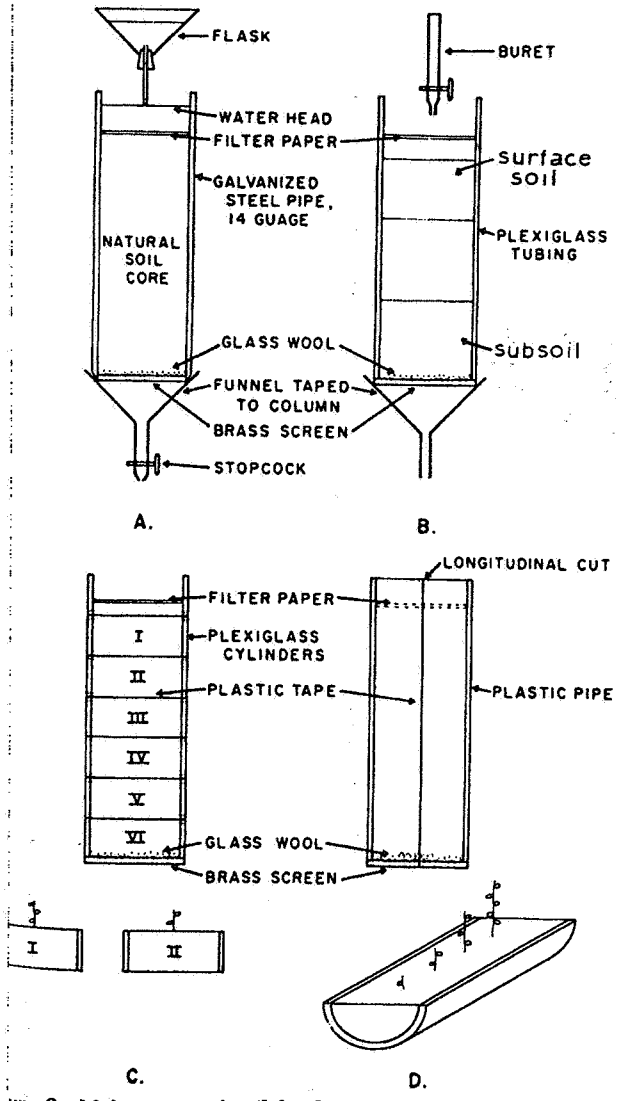
Natural Soil Column Method

(A motorized, truck-mounted, column-driving unit would be useful if available.)
Columns (7 to 30-cm diam by 30-cm long galvanized steel pipes)
Hardwood driving block
Sledge hammer
Shovel
Plastic bags
Marking pen
Cardboard box

Filter paper disks
Glass wool
Buret, 500 to 1000-ml
Erlenmeyer flask, 1-L
Funnels (same diam as columns)
Brass screen (same diam as columns)
Teflon-lined tubing
Plastic tape
Deionized water

ND-PACKED SOIL COLUMN METHOD

Columns [9.5-cm (inside diam) by 30-cm lengths of polyvinylchloride (PVC plastic) pipe, threaded and capped on one end]
Soil sieve, 2-mm



ure 3. Major types of soil leaching columns: A. Natural soil using a solid column. The scheme demonstrates the set-up d for saturated flow studies (B, C, and D are hand-packed soil umns). B. Simulated soil profile, where surface soil and subsoil added to the column in the position in which they occur in natural state. The scheme demonstrates the set-up used for aturated flow studies. C. Stacked-cylinder soil column. After ching, the cylinders may be separated and assayed independtly. D. Split soil column. After leaching, the column may be ided vertically to provide two continuous half columns, one bioassay and another for chemical or radiochemical assay.

1.2-cm drill bit
Tubing connector
Marking pen
Silicone sealer
Vortex-type mixer
Teflon-lined tubing
Buret, 500 to 1000-ml
Filter paper disks
Quartz sand
Deionized water
Spatula
Plastic tape
Glass wool
Saw

PREPARATION AND USE OF COLUMNS

NATURAL SOIL COLUMNS

Seven to 30-cm diam, 14-gauge galvanized steel pipe is cut into sections 30 cm long. A 1.5-cm steel rim is welded to the top of each column for reinforcement. The bottom is sharpened for ease of soil penetration. A brass screen is cut to fit flush with the bottom of the column (see A of Figure 3). If columns of less than 23 cm diam are employed, it would be desirable to use the divided-bottom technique of McNeal and Reeve (17). This technique provides a column within-a-column and reduces boundary-flow errors resulting from water and herbicide moving down the walls. The soil must be removed from this column and transferred to plastic bags for chemical analysis or to small pots for plant bioassay.

HAND-PACKED SOIL COLUMNS

Each of the following columns is fitted with a plastic pipe cap (see Figure 4). A 1.2-cm hole is drilled in the center of the cap and the hole fitted with the female half of a tubing connector packed with glass wool (see Figure 5).

Solid Columns

Solid columns, 30 to 40 cm long are cut from plastic pipe and threaded on one end. Since the soil must be removed from the columns for bioassay or chemical analysis, the columns should not be longer than 40 cm (see Figure 3.B.).

Stacked-Cylinder Columns

Stacked-cylinder columns are prepared from desired lengths of plastic pipe with pipe cap attached. The pipe is

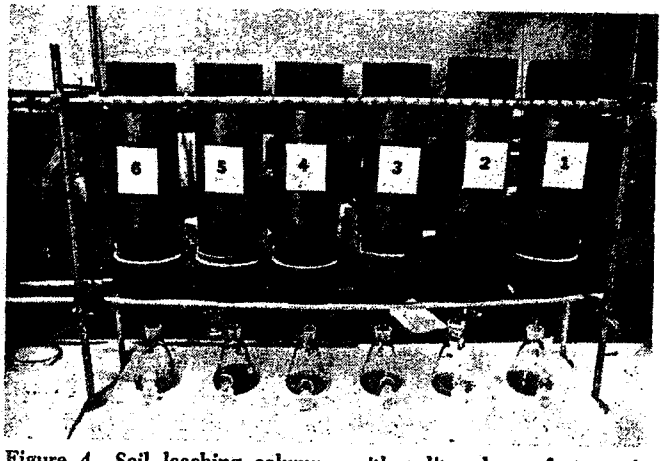


Figure 4. Soil leaching columns, with split column feature, in position for herbicide leaching. Note white silicone sealer at joints and tape used to hold column halves together.

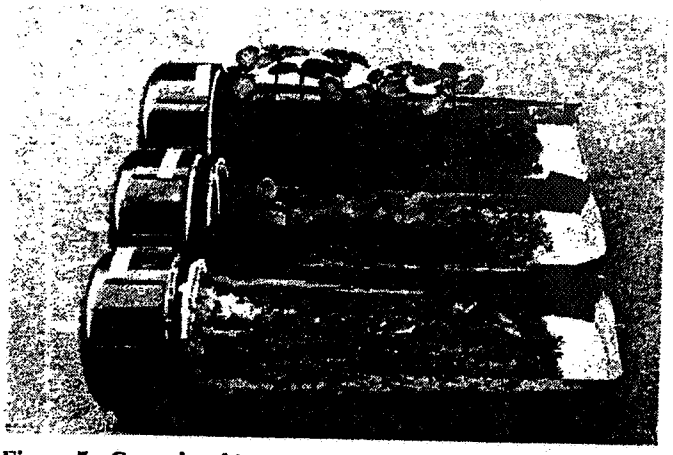


Figure 5. Cucumber bioassay of split soil leaching column. The herbicide applied to the upper column was immobile and was retained in the upper 4 cm of the soil column, thus only cucumber seedlings in the upper 4 cm were affected. The herbicide applied to the center soil column was very mobile and leached readily through the soil and out of the column. Herbicide which was retained by the soil was uniformly phytotoxic to the cucumber seedlings. The herbicide applied to the lower soil column was very mobile in the soil and leached readily, but was present at such high concentrations that it completely killed the seedlings throughout the length of the column.

then sawed into 5-cm sections and reassembled by placing the sections together with silicone sealer and tape (see Figure 3.C.).

Split Columns

Split columns are prepared from desired lengths of plastic pipe, capped on one end. The columns are cut longitudinally, reassembled using silicone sealer, and reinforced by wrapping with tape (see Figures 4 and 5).

APPLICATION OF HERBICIDE

When possible, herbicide should be applied to the soil in a manner analogous to that employed in the field. Herbicide may be mixed with water and applied to the surface or it may be incorporated into the top 2.0-cm of soil. In either case, the applied herbicide should be equilibrated with the soil for several hours before the leaching process is initiated.

When ^{14}C-tagged herbicides are employed, mix formulated, non-radioactive herbicide and ^{14}C-tagged herbicide to provide approximately 5 to 10 μCi of activity with the desired application rate per soil column.

PROCEDURE FOR NATURAL SOIL COLUMNS

Preparing the Columns

Select a representative site for obtaining the soil sample. Examine and describe surface cover conditions. Record the kind of crop and stage of growth, and any surface litter or mulch cover. Describe the surface soil conditions, freshly cultivated, cloddy, cracked, or crusted. Drive the 30-cm long steel column approximately 25 cm into the soil using the driving block and sledge hammer. Remove the soil from around the pipe to allow for easy removal of the column without disturbing the soil at the bottom of the core. At the same time, collect soil samples in plastic bags, from various depths for soil moisture determinations. Examine and describe the soil profile at this time. Determine texture and soil structure and note any conditions that might influence water intake.

Carefully remove the soil column from the earth, place it in a plastic bag, and stand it upright in a cardboard box for transport back to the laboratory. If longer columns are desired, it will generally be necessary to use a pipe with a diameter smaller than the recommended minimum of 23 cm. If columns of lesser diameter are employed, it is suggested that the divided-bottom technique of McNeal and Reeve (1) be used.

In preparing the column for leaching, remove the plastic bag and place a small mat of glass wool and a brass screen on the bottom of the column. For many studies it is desirable to establish the columns at moisture levels approximating field capacity. This may be accomplished most easily by standing the columns in deionized water and applying a small amount of suction to the top of the column (see B of Figure 6).

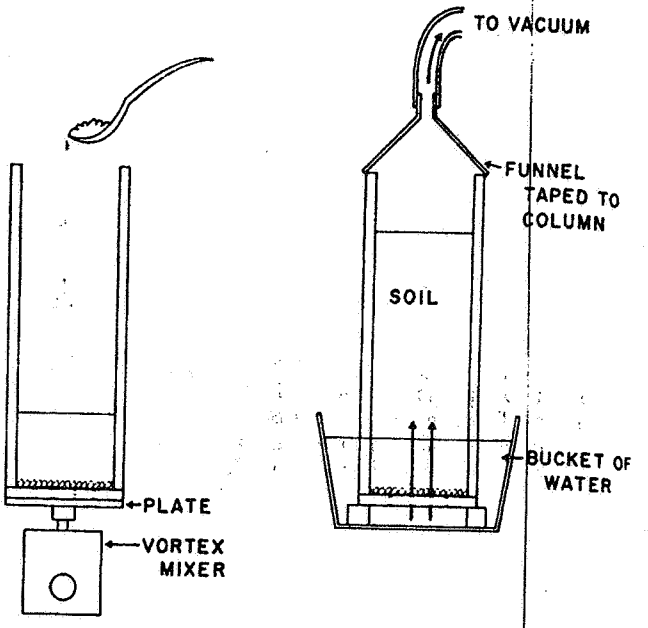


Figure 6. Preparation of hand-packed soil leaching columns: A. uniform packing of column by addition of small increments of soil and use of vortex-type mixer; B. prewetting of soil column by use of subirrigation and gentle suction.

Application of Water

For saturated flow studies, use plastic tape to connect a funnel to the bottom of the column and attach a piece of Teflon-lined tubing and a stopcock to regulate flow out of the column. (See A of Figure 3.) Place a glass wool mat or a disk of filter paper on the surface of the soil and use an Erlenmeyer flask filled with deionized water to maintain a constant head of water at the soil surface.

For unsaturated flow studies, tape a funnel to the bottom of the column as shown in B of Figure 3. Place a disk of filter paper on the soil surface and use a buret to regulate the rate of flow of deionized water through the column. (A more accurate flow rate can be achieved by use of a micropump and time clock arrangement.) The amount and frequency of watering should be commensurate with the rainfall or irrigation pattern for the area.

Water may be applied to the columns by adding a specific amount (usually 2 to 4 cm) per day for a specified time period (usually 30 to 45 days). At the end of the leaching

od the columns should be allowed to drain and dry out a day or two before the soil is removed from the columns.

MOVAL OF SOIL

Some soils may be removed from the columns by pushing entire soil core out of the column with a wooden plunger ing a diameter slightly smaller than the column interior. h other soils, a sample must be removed from the soil mn by use of a soil sampling tube (see Chapter 6) or h a long handled scoop. The soil column should be di- d into 5-cm sections. Each section should be placed a plastic bag, thoroughly mixed, a sample taken and ked for chemical or radiochemical assay, and the re- nder placed into small pots for herbicide bioassay.

PROCEDURES FOR HAND-PACKED SOIL COLUMNS

EPARING THE COLUMNS

Soil in these studies may be established at a specific soil sture level by adding an appropriate amount of water to sample, mixing, and storing overnight in a plastic bag ore the soil is put into the columns. If it is desired to es- lish columns at soil moisture levels approximating field acity, this may be accomplished by placing the columns in onized water and applying gentle suction to the top of the mn (see B of Figure 6).

If a natural soil profile is unobtainable, a simulated soil file can be a close approximation of the natural soil profile urring in the field. In using the method, soils collected n various depths are arranged in the proper sequence in soil column, as shown in B of Figure 3. Three types of mns which may be employed are shown in Figure 3. The d column, B, necessitates the removal of the soil from the mn for bioassay or chemcial analysis. The stacked cylin- column, C, allows for ease of separation of the various depths and analysis of the herbicide in each cylinder of soil column. The split column, D, provides a continuous column for herbicide analysis. The recently developed soil column and bioassay system shown in Figure 7 is a practical and simple system to measure herbicide (and r pesticide) leaching and bioactivity in soil.

The sample of soil from each depth should be sieved ugh a 2-mm screen, mixed, and uniformly packed into the columns. The soil should be used in field moist condition brought to a specified moisture level, as described pre- sly. Uniform packing can be accomplished by adding ll increments of soil to a column held in firm contact with rtex-type mixer set at a speed which has previously been d to result in the desired soil bulk density (see A of Fig- 6). Uniform packing and consistent soil moisture levels required for obtaining reproducible results from leaching mns (23).

When it is desired to compare herbicide movement ugh a uniform mixture of soil, it is necessary to use a ogeneous soil column. This technique permits compari- to be made between homogeneous soil samples taken various soil depths, and homogeneous soil samples rep- nting different soil types. The method is generally useful omparing the surface portion of cultivated soils down to plow layer. In cultivated soils the surface has been sub- tially disturbed and mixed by land preparation operations thus no longer has the characteristics of a virgin soil. soil is sieved, mixed, and uniformly packed into the soil mn as previously described.

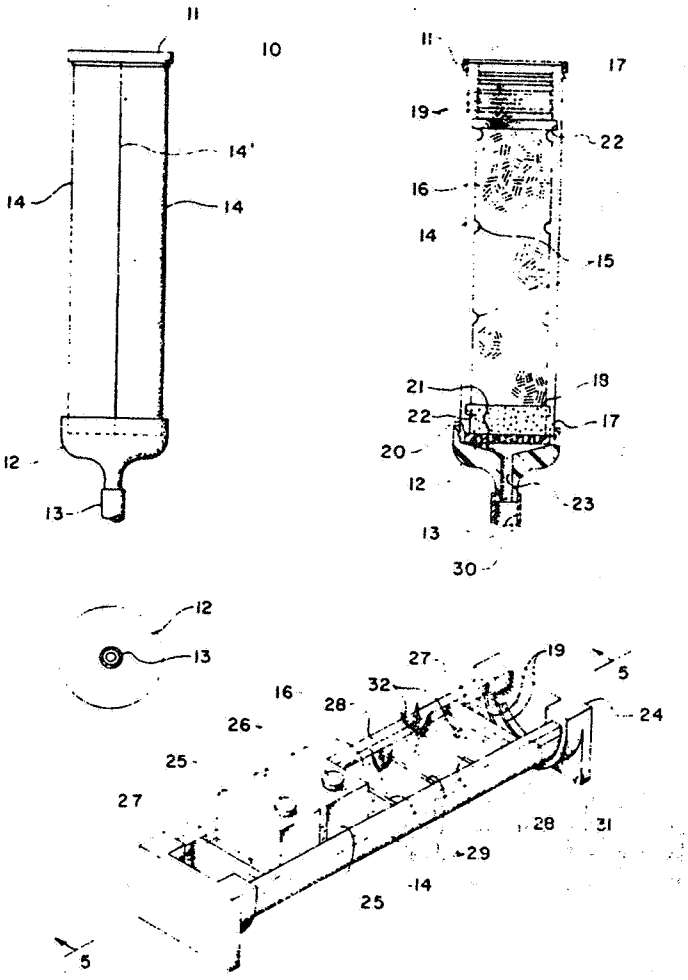


Figure 7. Herbicide soil leaching column and bioassay system. Two column halves (14) are joined together with silicone sealer (14'), a top ring (11) and a snap on funnel cap (12). Quartz sand is added to the bottom of the column on top of the screen (20). Surface soil (0 to 10 cm), and subsoil (10 to 20-cm and 20 to 30-cm samples) are added to the column to their respective sidewall marks (15). (The molded marks also prevent herbicide movement down the sidewalls.) Herbicide is applied and the column leached with water applied at 1-cm increments (19). After 30 days of leaching, the column halves are separated, the side rails (28) attached to one of the column halves and the end caps (24) snapped in place at each end. The column half is laid in a horizontal position. End plates (27) are installed to keep the soil in place. Soil dividers (29) are inserted into the soil at 2-cm increments. Seeds of sensitive plants are planted in between each soil divider to bioassay for the herbicide at each depth. Insect boxes (25) are used to bioassay for insecticides when they are leached.

APPLICATION OF WATER

The set-up for saturated or unsaturated flow studies or for adding specific amounts of water daily is the same as described for natural soil columns (see earlier section).

REMOVAL OF SOIL

Soil is removed from the solid column in the same manner as described for the natural soil column method. The stacked-cylinder soil column is disassembled by removing the tape at the joints, and cutting cross-sectionally through the soil core with a thin-bladed knife or sawing through with a piece of taut wire. Soil from each cylinder should be placed into a plastic bag, mixed, a sample removed and marked for

chemical or radiochemical assay, and the remainder returned to the cylinder for bioassay.

Removal of soil from the split column is accomplished by removing the tape from the joint and cutting the column in two longitudinally. Soil samples may be removed fr... one of the half columns and used for chemical or rad... chemical assay. The other column half may be used for bioassay of the herbicide as shown in Figure 5.

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APPENDIX C

HERBICIDE MOBILITY IN SOIL LEACHING COLUMNS (WEBER et. al., 1986)

Chapter IX

HERBICIDE MOBILITY IN SOIL LEACHING COLUMNS

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INTRODUCTION

The relative ease with which a herbicide moves vertically in soil is important in determining its efficacy, suitability for use as a selective herbicide, and potential for contaminating ground water or drainage effluent. Movement of a herbicide in soil is dependent on several factors, including chemical properties of the herbicide (5,17,18), soil properties (1,8,13,16), and intensity and frequency of applied water (12,17). The mobility of a given group of herbicides is generally inverse to their adsorptivity by soil as measured in Chapter 8 of this manual. Cationic herbicides, such as paraquat and diquat, are the least mobile because of their strong ionic bonding to the cation exchange complex of soil colloids. Water insoluble nonionic herbicides, such as trifluralin, are very immobile in the liquid state due to low solubility, but may be mobile in the vapor state due to moderate to high vapor pressure. Herbicides with basic properties, such as the s-triazines prometryn, prometon, and propazine are moderate to low in mobility and their mobility is dependent upon the pH of the soils. Higher mobility occurs under neutral or alkaline conditions than under acidic conditions. Acidic herbicides, such as picloram, bromacil, 2,4-D, and dicamba, and highly water soluble nonionic herbicides such as fenuron are highly mobile in soils because of this low adsorptivity to soil colloids. Mobility of a herbicide in soils is thus dependent upon: (a) ionizability, (b) water solubility, (c) vapor pressure, and (d) lipophilic nature of each compound. Chemical properties of soils that influence herbicide mobility include the kinds and amounts of each soil constituent (humic matter, type and amount of clay minerals, amount of iron and aluminum hydrous oxides) present, soil pH, soil permeability, porosity, and structure. Drying a soil may also delay the movement of a herbicide into the soil. In general, herbicides move faster and in greater amounts through coarse textured, sandy soils which are low in humic matter than they do through loamy soils containing moderate to high amounts of humic matter.

The intensity and frequency of applied water, whether it be from natural rainfall or by irrigation, greatly affects herbicide movement and distribution in the soil. Large amounts of water (51 cm) applied continuously, under saturated-flow conditions over a short period of time (3 h) can move as much as 81% of a relatively mobile herbicide, like tebuthiuron, completely through a soil column and out into the leachate (17). Application of the same total amount of water but in small amounts (1.2 cm/day), under unsaturated-flow conditions, over a long period of time (40 days) can result in as little as 2.5% of the same herbicide ending up in the leachate.

The relative mobility of selected herbicides has been determined by using: (a) soil leaching columns (4,5,10,12,13,14,15,16,17), (b) soil thin-layer chromatographic plates (2,6,7,8,9,18), and (c) soil thick-layer chromatographic trays (3,18).

The soil thin-layer plate technique utilizes a fine silty soil matrix applied to a glass plate as the supporting medium. Herbicides are spotted onto the soil matrix in a manner similar to that done when using routine silica gel coated TLC plates. One end of the plate is immersed in a small amount of water at the bottom of a closed glass chamber. The herbicides move up the plate and are separated and identified according to the principles of ascending chromatography (see Chapter 11). The technique is relatively rapid and the results are comparable with those obtained in adsorption studies, although of an inverse nature; i.e., immobile herbicides are strongly adsorbed and do not ascend the plate, while highly mobile herbicides are not adsorbed and move freely. The thin-layer plate technique also offers the advantage of allowing one to compare several herbicides at the same time under identical conditions.

The soil thick-layer chromatographic technique utilizes a shallow tray filled with soil and placed in a horizontal position with the herbicide-treated end at a slightly higher elevation than the other end (15% slope) (3). Herbicide is applied to the soil at one end of the tray and one end of a cloth wick is placed on the herbicide-treated soil, the other end of wick is placed into a dish of water. Water ascends the wick and diffuses into the soil carrying the herbicide along down the slope. After the soil has been wetted to the end of the tray, the soil is seeded with a plant species which is sensitive to the herbicide. The resulting injury to the bioassay plants is an indicator of herbicide movement. A much wider variety of soil textures can be examined using the soil thick-layer technique, as compared with the soil thin-layer technique. Both techniques are carried out under saturated-flow conditions.

The soil column technique, the method to be described herein, consists of filling a column with soil, preconditioning with water, mixing herbicide with the surface soil, applying a given quantity of water, allowing the soil to drain freely, and then determining the herbicide distribution in the soil column and in the leachate. Herbicide analyses may be done by radioassay, chemical assay, and/or plant bioassay, as described in other sections of this book. The technique has great flexibility, allowing one to compare: (a) relative mobility of many different herbicides through an unlimited number of soil types, (b) herbicide

mobility under saturated-flow conditions versus unsaturated-flow conditions, (c) herbicide mobility through moist versus air-dried soils, (d) herbicide mobility in reduced-tillage systems versus conventionally tilled systems, (e) herbicide mobility through undisturbed soil cores versus hand-packed soil columns, and (f) herbicide degradation product mobility through herbicide-treated, aged soil columns.

DESCRIPTION OF METHODS

Basically, there are two major types of columns used to investigate the leaching behavior of herbicides in soils: (a) natural soil columns, and (b) hand-packed soil columns. Two types of hand-packed soil columns are used, depending upon the kind of soil assays to be performed after the leaching is completed. They include: (a) stacked cylinder columns, and (b) split columns. Figures 1 to 4 illustrate these various kinds of soil columns.

APPARATUS, CHEMICALS, AND OTHER MATERIALS

Natural Soil Column Method

(A motorized, truck-mounted, column-driving unit would be useful if available.)

Columns (5 to 10 cm diameter by 35-cm long sharpened galvanized steel pipes)

Hardwood driving block

Sledge hammer

Shovel

Plastic bags

Marking pen

Cardboard box

Glass wool

Quartz sand

Erlenmeyer flasks, 4-L

Erlenmeyer flasks, 250-ml

Funnels (same diameter as columns)

Brass screen

Silicone sealer

Plastic tape

Deionized water

Rubber stopper

Glass tubing

Plastic tubing

NaCl

$AgNO_3$

Hand-Packed Soil Column Method

Soil sieve, 4-mm opening

1.0-cm diameter drill bit

Tubing connector, 1-cm

Marking pen

Silicone sealer

Vortex-type mixer

Plastic tubing

Quartz sand

Deionized water

Spatula

Plastic tape

Saw

PVC plastic pipe, 5- to 10-cm diameter

PVC cap

1-L buret (for saturated/unsaturated-flow) or 4-L flask with stopcock (for saturated-flow)

NaCl

$AgNO_3$

Erlenmeyer flask, 250-ml

Glass wool

PREPARATION AND USE OF COLUMNS

Natural Soil Columns

Five to 10-cm diameter, 14-gauge galvanized steel pipe is cut into sections 35 cm long (Figure 1). The bottom is sharpened for ease of soil penetration. To eliminate water flowing down the interior walls of the column, it would be desirable to use the divided-bottom technique of McNeal and Reeve (11). This technique provides a column within-a-column and only water moving down the center of the column is collected. This reduces boundary-flow errors resulting from water and herbicide moving down the walls. In many cases, however, natural channels in soil cores would probably contribute as much to herbicide movement as herbicide movement down the walls so the technique may not provide any clearer picture of herbicide movement and distribution than catching all of the water passing through the column. The soil must be removed from this column and transferred to plastic bags for chemical analysis or to small pots for plant bioassay.

Hand-Packed Soil Columns

Each of the following columns is fitted with a plastic pipe cap (Figures 2 and 3). A 1-cm hole is drilled in the center of the cap and the hole fitted with a tubing connector to which plastic tubing is attached. A 250-ml Erlenmeyer flask is placed beneath each column to catch the leachate.

Stacked-Cylinder Columns. Stacked-cylinder columns are prepared from 5- to 10-cm diameter plastic PVC pipe which has been cut into 5-cm sections (Figure 2). The 5-cm sections are fastened together with silicone sealer and plastic tape such that a 2- to 5-mm ridge of silicone sealer extends into the interior of the column at each section. The silicone sealer eliminates water and herbicide movement down the walls of the columns. The plastic PVC cap is also attached with silicone sealer to allow for easy separation at the termination of the study.

Split Columns. Split columns are prepared from desired lengths of plastic pipe (generally 40 cm), capped on one end (Figure 3). The columns are cut longitudinally down the pipe to the cap and then transversely. It is reassembled using silicone sealer, and reinforced by wrapping with tape. The ridges of silicone sealer are applied at 5-cm increments to the interior columns sections before the sections are joined together. The plastic PVC cap may be attached with PVC glue and left in place after column separation (Figure 3B).

APPLICATION OF HERBICIDE

When possible, herbicide should be applied to the soil in a manner analogous to that employed in the field. Herbicide may be mixed with water and applied to the surface or it may be incorporated into the top 2.0-cm of soil. In either case, the applied herbicide should be equilibrated with the soil for several hours before the leaching process is initiated.

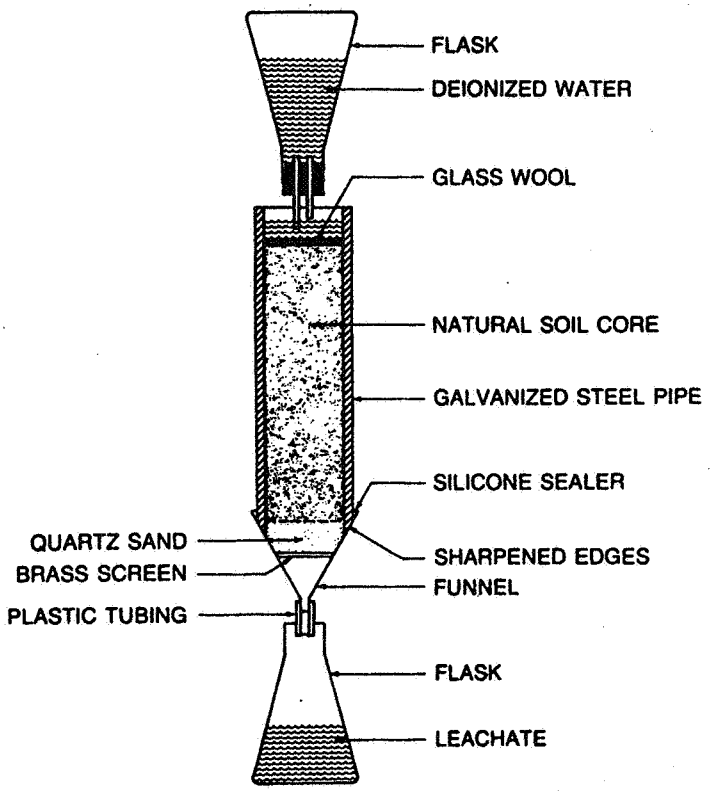

Figure 1. Cross-section of natural soil core, solid column, leaching system. Apparatus is set up for a continuous saturated-flow study. After leaching, soil must be removed from column for herbicide assay.

When ^{14}C-tagged herbicides are employed, mix formulated, non-radioactive herbicide and ^{14}C-tagged herbicide together to provide approximately 5 to 10 μCi of ^{14}C-activity at the desired application rate per soil column. It is also desirable at this time to add 2 ml of 1M NaCl to the top of the soil column and to test the leachate with a few drops of 1M $AgNO_3$ at 100 ml increments to determine the Cl^- ion breakthrough point. The Cl^- ion breakthrough point is useful for evaluating the relative mobility of herbicides with Cl^- ion to verify the performance of each column and to check the reproducibility between replicate columns. Glass wool is added to the top of the column to maintain the integrity of the surface.

PROCEDURE FOR NATURAL SOIL COLUMNS

Preparing the Columns

Select a representative site for obtaining the soil sample. Examine and describe surface cover conditions. Record the kind of crop and stage of growth, and any surface litter or mulch cover. Describe the surface conditions, freshly cultivated, cloddy, cracked, or crusted. Drive the 35-cm long steel column approximately 30 cm into the soil using the driving block and sledge hammer. Remove the soil from around the pipe to allow for easy removal of the column without disturbing the soil at the bottom of the core. At the same time collect soil samples in plastic bags, from various depths for soil moisture determinations. Examine and describe the soil profile at this time. Determine texture and soil structure and note any conditions that might influence water intake. Carefully remove the soil column from the earth, place it in a plastic bag and stand it upright in a cardboard box for transport back to the laboratory.

In preparing the column for leaching, remove the plastic bag and place the column into a funnel filled with quartz sand fitted with a brass screen (Figure 1). Apply silicone sealer along the joint where the column and funnel meet. Allow to harden and tape securely with tape. For most studies it is desirable to precondition the columns by wetting the column thoroughly and allowing to drain overnight to field capacity. This may be accomplished most easily by standing the columns in deionized water as shown in Figure 4B and allowing to drain free.

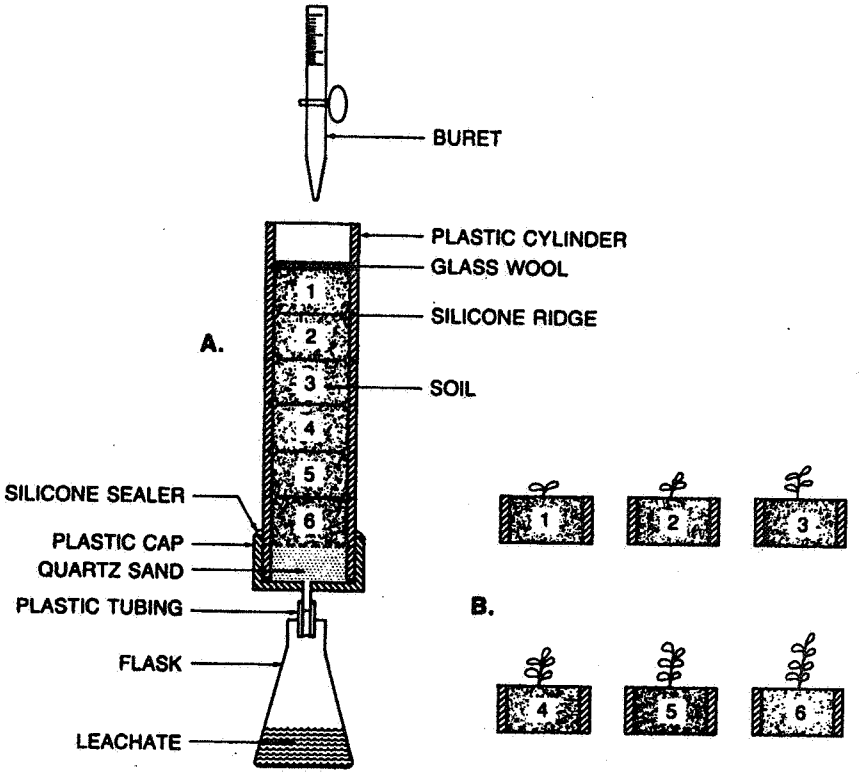

Figure 2. Cross-section of hand-packed soil column using stacked-cylinders. Apparatus is set up for incremental additions of water in saturated/unsaturated-flow studies (A). Cylinders are fastened together with silicone sealer and plastic tape. After leaching, cylinders are bioassayed independently according to soil depth (B).

Application of Water

For saturated-flow studies arrange the soil column as shown in Figure 1. Using the flask of deionized water and stopper arrangement shown, a small head (2 cm) of water can be maintained over the course of the leaching period (generally 50.8 cm of water applied over a 2 to 4 h period). Place a small mat of glass wool on the top of the column and a 250-ml Erlenmeyer flask under the funnel to catch the leachate before initiating the leaching cycle.

For saturated/unsaturated-flow studies, arrange the column as shown in Figure 2A. Place a mat of glass wool on the soil surface, and a 250-ml Erlenmeyer flask under the column. Using a buret, apply deionized water in an amount equivalent to the desired rainfall rate (generally 1.2 cm/column/day) and allow the water to leach through the column and collect in the leachate flask. For a 10 cm diameter column, a 1.2 cm/day addition of applied water will result in approximately 100 ml/day of leachate.

For continuous, unsaturated-flow studies, arrange the column as shown in Figure 3A. Place a mat of glass wool on the soil surface and a 250-ml Erlenmeyer flask under the column. Using the stopcock and flask of water apparatus shown, adjust the flow of water such that water drips onto the glass wool mat with no head of water.

Removal of Soil and Herbicide Assay

Some soils may be removed from the column by pushing the entire core out of the column with a wooden plunger having a diameter slightly smaller than the column interior. With other soils, a sample must be removed from the soil column by use of a soil sampling tube or with a long handled scoop. The soil column should be divided into 5-cm sections. Each section should be placed into a plastic bag, thoroughly mixed, a sample taken and marked for chemical or radiochemical assay, and the remainder placed into small pots for herbicide bioassay.

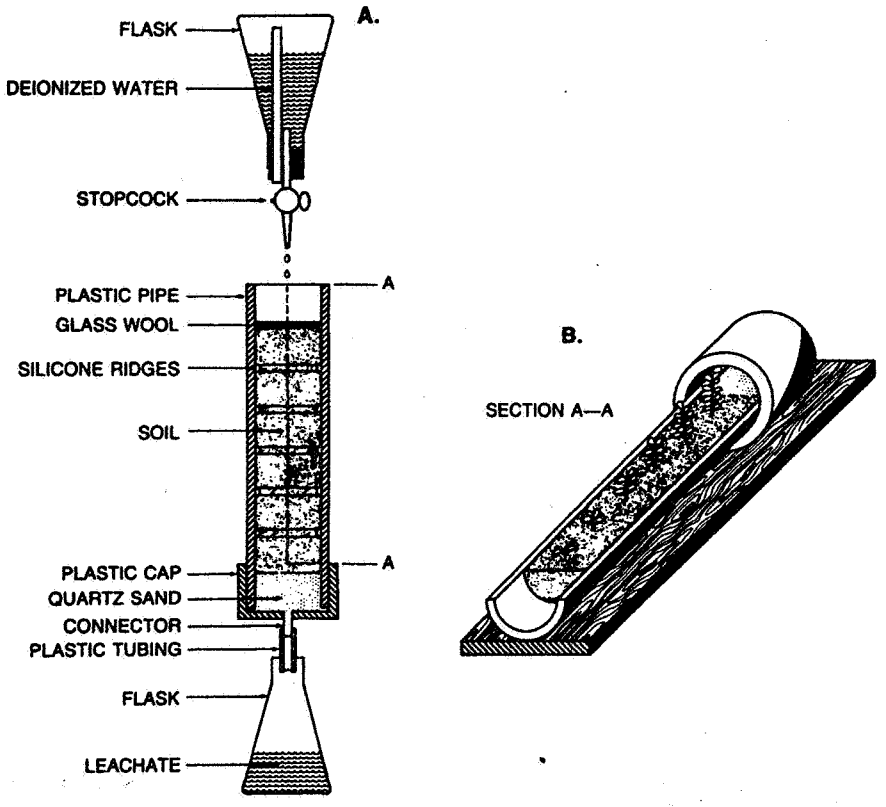

Figure 3. Cross-section of hand-packed soil column using a split-column system, apparatus is set up for unsaturated-flow studies (A). After leaching, column may be divided longitudinally to provide two continuous half-columns, one for chemical or radiochemical assay and one for plant bioassay (B).

PROCEDURES FOR HAND-PACKED SOIL COLUMNS

Preparing the Columns

Soil in these studies may be utilized in a field-moist or air-dried condition. A field-moist condition is preferred if the soil contains significant amounts of organic matter or expanding-type clay minerals which generally shrink and contract greatly when dried. It is generally desirable to precondition the column before initiating leaching by saturating the soil and allowing the column to drain to field capacity. This may be accomplished by placing the column in deionized water as shown in Figure 4B.

Soil from each 5-cm depth should be sieved through a 4-mm screen, mixed, and uniformly packed into the soil columns if it is desirable to establish a "simulated" soil profile. It is generally satisfactory to take soil from the plow layer (0 to 15 cm depth) and from the 15 to 30 cm suboil zone, but more commonly soil is taken from the 0 to 15 cm depth and used throughout the 0 to 30 cm of soil in the column. Uniform packing can be accomplished by adding small increments of soil to a column held in firm contact with a vortex-type mixer as shown in Figure 4A. The mixer should be set at a speed which has previously been found to result in the desired soil bulk density (generally 1.5 g/cm^3 for a sandy soil).

Uniform packing and consistent soil moisture levels are required for obtaining reproducible results from leaching columns (19).

Application of Water

The set-up for saturated-flow, saturated/unsaturated-flow or continuous, unsaturated-flow studies is the same as described for natural soil columns (see earlier section).

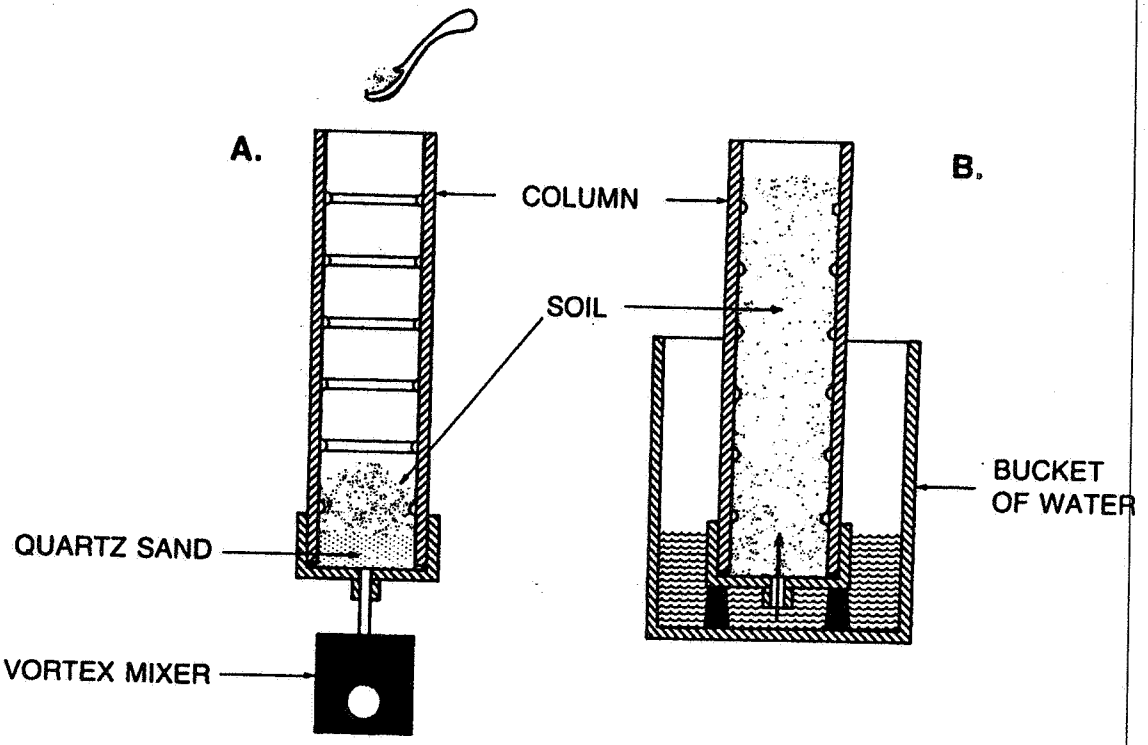

Figure 4. Preparation of hand-packed soil leaching columns: A. Uniform packing of column by addition of small increments of soil and use of Vortex-type mixes; B. Prewetting of soil column by use of subirrigation.

Removal of Soil and Herbicide Assay

The stacked-cylinder soil column is disassembled by removing the tape at the joints, and cutting cross-sectionally through the soil core with a thin-bladed knife or sawing through with a piece of taut wire. Soil from each cylinder should be placed into a plastic bag, mixed, a sample removed and marked for chemical or radiochemical assay, and the remainder returned to the cylinder for bioassay (see Figure 2B). Bioassay standards should be included to determine the approximate herbicide concentrations in each soil cylinder.

Removal of soil from the split column is accomplished by removing the tape from the joint and cutting the column in two longitudinally. Soil samples may be removed from one of the column sections and used for chemical or radiochemical assay. The other section may be used for a bioassay of the herbicide as shown in Figure 3B. Bioassay standards should be included.

EXAMPLE AND METHOD OF COMPUTING RESULTS

Constructing Column

Construct a hand-packed soil column system using a split column with a 10-cm diameter and 40-cm length, as described previously and shown in Figure 3A. Place quartz sand in PVC cap portion of the column to a depth of 5 cm followed by approximately 3600 g of sandy loam soil to a depth of 30 cm and bulk density of 1.5 g/cm^3 (3600 g/2355 cm^3) as shown in Figure 4A. Place soil column in bucket of water overnight to precondition as shown in Figure 4B. Remove column from water and allow to drain free.

Applying herbicide

Mix 5 μCi of ^{14}C-labeled atrazine (0.3 mg of ^{14}C-atrazine with sp act. = 25.0 μCi/mg) with formulated atrazine (4.16 mg of 80WP atrazine) to achieve a rate of 4.5 kg ai/ha (based on soil surface area of column of 78.5 cm^2) in 5 ml of water and apply with a pipet in a cross hatch pattern to the soil surface. Add 2 ml of 1M NaCl to the top of the soil column.

Application of Water and Sampling

Set up apparatus shown in Figure 3A to provide for a continuous unsaturated-flow study. Apply water in a continuous drop fashion until 4-L have passed through the soil column. Sample each 100 ml of

leachate and test for Cl^- ion by adding several drops of 1M $AgNO_3$ (watch for a white, cloudy precipiate of AgCl). Record the volume of leachate when Cl^- ion is first detected (normally detected in the first 400 to 600 ml of leachate). Radioassay each 200 ml of leachate by placing 1 ml of leachate into 10 ml of liquid scintillation cocktail [16.5 g 2,4-diphenyloxazole (PPO), 0.5 g 1,4-bis [2-(4-methyl-*S*-phenyloxazoyl] benzene (POPOP), 1-L Triton X-100, and 2-L toluene] and placing into a liquid scintillation spectrophotometer. Record cumulative volume (or weight) of leachate and cumulative amount of atrazine (% of applied) for each 200 ml volume of leachate until all applied water has passed through the column. See Table 1 for example of ^{14}C-activity (atrazine) distribution in leachate.

Allow column to drain overnight, then remove plastic tape and silicone sealer. Split soil column by pulling a taut wire down the longitudinal slot. Lay column sections side by side on a table. Remove approximately 40 to 50 g of soil from each 0 to 5 cm section, place into separate plastic bags, mark bags, and knead and mix each sample thoroughly.

Remove a 10 g sample from each 0 to 5 cm zone and determine soil moisture content as described in Chapter 8. Remove 10 subsamples (1 g each) from each bag, place into separate 50 ml beakers and dry at 110 C overnight. Mix each dried sample thoroughly, and remove a 1-g sample for ^{14}C determination by placing into a Harvey Biological Oxidizer (OX-300) programmed to burn at a temperature of 900 C for 4 minutes and trap the $^{14}CO_2$ in liquid scintillation cocktail containing Harvey No. 161 CO_2 trapping solution. Counting efficiencies will range from 70 to 80%. Convert disintegration/min/g to % of ^{14}C-activity applied and record as shown in Table 2. The soil samples can also be extracted with methanol and the extracts separated by TLC to obtain the amount of atrazine parent and metabolites present. Radiochemical chromatographic methods are described in another section of this manual.

Table 2 illustrates the ^{14}C-activity (atrazine) distribution in the soil after leaching a 30-cm Norfolk soil column continuously with 50.8 cm of water under unsaturated-flow conditions. The total amount

Table 1. ^{14}C-activity distribution in leachate from Norfolk sand treated with ^{14}C-atrazine and leached continuously with 50.8 cm (4-L) of water under unsaturated-flow conditions

Cumulative volume of leachate	Cumulative ^{14}C-activity
(ml)	(% of applied)
0	0
600	0.00[1]
800	0.06
1000	0.48
1200	0.87
1400	1.27
1600	1.58
1800	1.89
2000	2.40
2200	3.08
2400	3.84
2600	4.49
2800	5.13
3000	5.99
3200	6.83
3400	7.54
3600	8.18
3800	8.82
4000	9.94
Total	9.94

[1] Cl^- ion first detected.

Table 2. ^{14}C-activity distribution in Norfolk sand treated with ^{14}C-atrazine and leached continuously with 50.8 cm (4-L) of water under unsaturated-flow conditions

Soil depth	^{14}C-activity
(cm)	(% of applied)
0 - 5	12.0
5 - 10	11.5
10 - 15	14.8
15 - 20	15.2
20 - 25	11.4
25 - 30	7.5
Total	72.4

recovered (% of applied in leachate + % of applied in soil) in this case amounts to 9.94 + 72.4 = 82.34. It will normally range from 70 to 105% ± 5 to 10%.

Effect of Herbicide Type

Herbicides move through soils differently depending on the chemical properties of both the herbicides and the soil. Table 3 shows the distribution of three herbicides with high (bromacil), moderate (atrazine) and low (diuron) mobility through a Lakeland sand when leached with 36 cm of water, at 1.2 cm/day for 30 days, under unsaturated-flow conditions. The acidic, highly water soluble bromacil is much more mobile than the less soluble atrazine and diuron.

Effect of Soil Type

Soil humic matter content, clay type and content, soil pH, and other factors greatly affect the mobility of herbicides through different soil types. Some herbicides bind to both organic (humus) and inorganic (clay) soil colloids, while others bind to one of the soil colloids and not to the other. Table 4 shows the distribution of a relatively mobile herbicide, tebuthiuron, through three different soil types. Movement of the herbicides was controlled primarily by the humic matter content and the clay content of the soils.

Effect of Column Size

Many different diameter leaching columns have been used to measure the relative mobility of herbicides through soils. They have ranged in size from as small as soda straws to as large as field sized

Table 3. ^{14}C-labeled herbicide (bromacil, atrazine, diuron) distribution in Lakeland soil treated with ^{14}C-herbicide and leached with 1.2 cm/day for 30 days (36 cm of total water applied) under unsaturated-flow conditions [Weber and Whitacre (17)]

	^{14}C-herbicide		
Soil depth	Bromacil	Atrazine	Diuron
(cm)	(% of applied)		
0 - 5	7.3	72.2	107.3
5 - 10	13.2	25.3	0.3
10 - 15	18.5	16.9	0.0
15 - 20	20.4	0.8	0.0
20 - 25	17.0	0.0	0.0
25 - 30	10.4	0.0	0.0
Total	86.8	114.2	107.6

Table 4. ^{14}C-activity distribution in three soils treated with ^{14}C-tebuthiuron and leached with 1.2 cm/day for 40 days (48 cm total) under unsaturated-flow conditions [Weber and Whitacre (17)]

Soil depth	Portsmouth sandy loam	Rains silt loam	Davidson clay
(cm)		(% of applied)	
0 - 5	47.9	50.9	2.4
5 - 10	19.0	11.4	4.3
10 - 15	12.1	8.5	6.7
15 - 20	6.7	5.0	7.6
20 - 25	3.4	2.6	9.2
25 - 30	1.1	1.0	10.2
Total	90.1	79.4	40.4

lysimeters. Table 5 shows the relative distribution of the very mobile herbicide picloram through a 30-cm long column of Norfolk sandy loam (Typic Paleudult; fine-loamy, siliceous, thermic, 0.2% HM 0.5% OM, 2% clay) using columns with diameters of 2.5, 5.0, and 10.0 cm and leaching continuously with 50 cm of water under saturated-flow conditions. No differences in picloram distribution in the soils or total recovered in the leachate occurred between columns with diameters of 5.0 or 10.0 cm. The soil distribution of picloram and the % recovered in the leachate of the 2.5 cm diameter column was significantly different from the two larger columns. More consistent results would probably be obtained if leaching columns of 5.0 to 10.0 cm in diameter or larger were used. The larger columns also provide more soil for chemical, radiological, and biological assays.

Table 5. Effect of column diameter on ^{14}C-picloram distribution in Norfolk sandy loam and in leachate when leached continuously under saturated-flow conditions with 50 cm of water (30 cm soil profiles)

Soil depth	Column diameter (cm)[1]		
	2.5	5.0	10.0
(cm)		(% of applied)	
0 - 5	1.5	0.6	0.7
5 - 10	2.2	1.2	1.1
10 - 15	2.7	1.6	1.5
15 - 20	3.2	2.0	1.9
20 - 25	3.5	2.4	2.2
25 - 30	3.9	2.7	2.6
Total	17.0	10.5	10.0
Lsd (0.5) = 0.2 (columns), 0.3 (depth)			
Total in leachate	87.3	90.3	89.2
Lsd (.05) = 3.0 (columns)			
Total accounted for	104.3	100.8	99.2

[1]Columns contained 245, 975, and 3900 of soil, respectively.

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