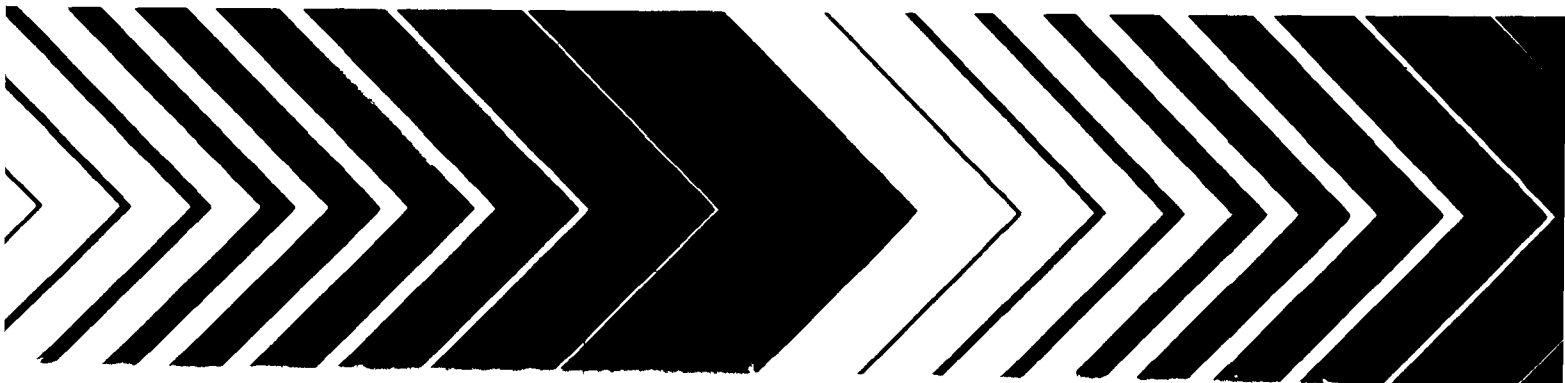




Proceedings of International Workshop on Research in Pesticide Treatment/Disposal/ Waste Minimization



PROCEEDINGS OF
INTERNATIONAL WORKSHOP ON RESEARCH IN PESTICIDE
TREATMENT/DISPOSAL/WASTE MINIMIZATION

February 26-27, 1991

Edited By:

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Cincinnati, Ohio 45268

and

Tennessee Valley Authority
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Muscle Shoals, Alabama 35660

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The following papers have been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication:

Tracking Small Quantities of Cancelled or Excess Pesticides
Containing Dioxins and Furans
by J. Paul E. des Rosiers

Waste Minimization for Non-Agricultural Pesticide Applicators:
EPA's Pollution Prevention Guide
by Teresa M. Harten

Pesticide Container Management in the United States
by Nancy Fitz

Pesticide Disposal in Guinea-Bissau: A Case History
by Janice Jansen

All other papers published in this Proceedings describe work that was not funded by the U.S. Environmental Protection Agency and therefore do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

The U.S. Environmental Protection Agency and the Tennessee Valley Authority's National fertilizer and Environmental Research Center have begun promoting cost-effective treatment techniques for pesticide disposal. In 1991, the two agencies co-sponsored a workshop on the pesticide waste minimization, treatment, and disposal. The workshop focused on current research in waste minimization strategies and cost-effective/disposal techniques as they effect applicators, fertilizer/agrichemical dealers and farmers.

These proceedings from the 1991 Workshop provide the results of projects recently completed and current information on projects presently underway. Those wishing additional information on these projects are urged to contact the author. It is hoped the conclusions and recommendations reached at this workshop will be the basis of a series of regional workshops to be held in 1992.

E. Timothy Oppelt, Director,
Risk Reduction Engineering Laboratory

ABSTRACT

The International Workshop on Research in Pesticide Management, Disposal, and Waste Minimization was held in Cincinnati, Ohio, February 26-27, 1991. The purpose of this workshop was to provide government officials, pesticide user groups, pesticide producers and farm organizations practical solutions to pesticide treatment and disposal problems. The workshop focused on how to destroy pesticides and their residuals at low cost by the applicators and dealers. The technical program included presentations by government researchers and regulators, university agricultural station professors, industry experts and individuals involved in pesticide disposal and treatment.

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AGENDA

TUESDAY, FEBRUARY 26, 1991

Plenary Session

- 9:00 **Welcome**
E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory
U.S. EPA
- John E. Culp, Director
Technology Introduction
National Fertilizer & Environmental Research Center
Tennessee Valley Authority
- 9:30 **U.S. EPA, ORD, RREL - An Overview**
Glenn M. Shaul
U.S. EPA
- 9:50 **Tennessee Valley Authority, National Fertilizer and Environmental
Research Center - An Overview**
Joe Gautney
Tennessee Valley Authority
- 10:10 **Break**
- 10:20 **Tracking Small Quantities of Canceled or Excess Pesticides
Containing Dioxins and Furans**
J. Paul E. des Rosiers
U.S. EPA
- 10:40 **Agrichemical Dealer/Applicator Site Assessment and Remediation**
Chris Myrick
National AgriChemical Retailers Association
- 11:00 **Keynote Address**
Robert Denny
Office of Pesticide Programs
U.S. EPA
- 11:30 **Lunch**
Caprice 1 and 4 (4th Floor)

AGENDA (continued)

Innovative Biological Treatment of Control of Pesticides

- 1:30 **The Evaporation/Degradation System for: Pesticide Equipment Rinsewater - A Practical Solution to a Pesticide Waste Management Problem**
Steven E. Dwinell
Florida Department of Environmental Regulation
- 2:00 **Pesticide Disposal Using a Demulsification, Sorption, Filtration, and Chemical and Biological Degradation Strategy**
D.E. Mullins, R.W. Young, G.H. Hetzel, and D.F. Berry
Virginia Polytechnic Institute and State University
- 2:30 **Break**
- 2:45 **Remediation of Herbicide Waste in Soil: Experiences with Landfarming and Biostimulation**
Alan Felsot and Kudjo Dzantor
Illinois Natural History Survey
- 3:15 **Open Discussion**
- 5:00 **Reception - Cash Bar**
Mezzanine Level above Palm Court

WEDNESDAY, FEBRUARY 27, 1991

Innovative Physical/Chemical Treatment for Control of Pesticides

- 8:30 **Removal of Pesticides from Aqueous Solutions Using Liquid Membrane Emulsions**
Verrill M. Norwood, III and Joe Gautney
Tennessee Valley Authority
- 9:00 **Field and Laboratory Evaluations of an Activated Charcoal Filtration Unit**
J.H. Massey, T.L. Lavy, and B.W. Skulman
University of Arkansas
- 9:30 **Preliminary Studies of Batch Chemical Oxidation of Wastewaters Containing Agrichemicals**
Claude E. Breed and Mike C. Crim
Tennessee Valley Authority
- 10:00 **Break**

AGENDA (continued)

- 10:15 Cleanup of Soil Contaminated with Pesticides Using Supercritical Carbon Dioxide Extraction**
G. Bradley Hunter
Tennessee Valley Authority

Waste Minimization Practices for Pesticide Products, Formulations and Applications

- 10:45 Pesticide Containment Systems**
Ronald T. Noyes
Oklahoma State University
- 11:05 Waste Minimization for Non-Agricultural Pesticide Applicators**
Teresa M. Harten
U.S. EPA
- 11:25 Pesticide Container Disposal in the U.S.**
Nancy Fitz
U.S. EPA
- 11:45 Lunch**
Caprice 1 and 4 (4th Floor)
- 1:30 Pesticide Disposal in Guinea-Bissau: A Case History**
Janice Jensen
U.S. EPA
- 1:50 Downstream Injection Equipment for Sprayers and Fertilizer Spreaders**
Stanley Weeks
Agway Farm Research Center
- 2:10 Evolution of the Pesticide Container**
C.G. Van Teeling and W. Inkpen
Alberta Environment
- 2:30 Break**
- 2:40 Retail Fertilizer Dealer Containment**
Michael F. Broder
Tennessee Valley Authority
- 3:00 Summary Discussion on Future Research and Technology Transfer**
Chaired by Patrick Eagan
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TREATMENT/DISPOSAL/WASTE MINIMIZATION

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INTRODUCTION

An international workshop on treatment, disposal, and waste minimization of pesticides and pesticide wastes was held in Cincinnati, Ohio on February 26-27, 1991. The purpose of this workshop was to work with government, pesticide user groups, pesticide producers, farm organizations and academia to define and offer practical solutions to pesticide users' treatment and disposal problems. The technical program included presentations by government researchers and regulators, academia, industry experts and individuals involved in pesticide disposal and treatment.

The workshop was sponsored by the following organizations:

U.S. Environmental Protection Agency
Office of Research and Development
Risk Reduction Engineering Laboratory
Cincinnati, Ohio 45268

and

Tennessee Valley Authority
National Fertilizer and Environmental Research Center
Muscle Shoals, Alabama 35660

The following people were on the workshop planning committee:

Glenn M. Shaul
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory

T. David Ferguson
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory

Edwin F. Barth
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Center for Environmental Research Information

Margaret M. Groeber
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Aside from the technical presentations, the workshop allowed for some discussion among the participants. Several issues/concerns were discussed by the attendees. The two issues which cause the greatest concern were site remediation and regulatory framework.

Discussions on site remediation were directed toward dealer sites. The focus on the cleanup was both soils and groundwater contamination. The largest problems identified with dealer site cleanup were costs and issues of how clean is clean enough. It was noted that many dealers could go bankrupt if costs were high. Also, very little remediation is being conducted because dealers feel that regulators can not give them cleanup levels that will hold true in the future.

Regulatory framework is also of great concern. There was much discussion over how to solve their problem. Suggestions included the following:

- 1) Prove technology then worry about the regulatory framework.
- 2) Regulatory framework needs to be looked at while technology is being developed--it can and does drive costs.
- 3) Policy people are not listening to research people.
- 4) Get the key players involved - Target State Regulators since they are closest to the problem - Get the concerns and scientific information to the pertinent regulatory people.

Another topic of discussion was waste minimization and education. It was agreed that many of the pollution prevention ideas would greatly decrease the number of future problems involving pesticides. These waste minimization techniques were generally low cost practical solutions to managing pesticides and pesticide wastes. It is important that these ideas become common practices by educating appropriate users and dealers of pesticides.

Tennessee Valley Authority,
National Fertilizer and Environmental Research Center

An Overview

by

Joe Gautney
Chemical Research Department
Muscle Shoals, Alabama 35660

ABSTRACT

The National Fertilizer and Environmental Research Center (NFERC) is a unique part of the Tennessee Valley Authority (TVA), a government agency created by an Act of Congress in 1933. The Center, located in Muscle Shoals, Alabama, is a national laboratory for research, development, education and commercialization for fertilizers and related agricultural chemicals including their economic and environmentally safe use, renewable fuel and chemical technologies, alternatives for solving environmental/waste problems, and technologies which support national defense. NFERC projects in the pesticide waste minimization/treatment/disposal areas include "Model Site Demonstrations and Site Assessments," "Development of Waste Treatment and Site Remediation Technologies for Fertilizer/Agrichemical Dealers," "Development of a Dealer Information/Education Program," and "Constructed Wetlands."

BACKGROUND AND INTRODUCTION

The National Fertilizer and Environmental Research Center (NFERC) is a unique part of the Tennessee Valley Authority (TVA), a government agency created by an Act of Congress in 1933 as part of President Franklin D. Roosevelt's New Deal for lifting the Nation from the Great Depression. Congress gave the new Agency a broad mandate for development of the Tennessee Valley region along with national responsibility for fertilizer research, development, and introduction. The Agency was also given responsibility for supporting national defense.

The Tennessee Valley Authority is a rather unique government agency. President Roosevelt described it as "a corporation clothed with the power of government, but possessed of the flexibility and initiative of a private enterprise." The Agency is headed by a three-person Board of Directors, each appointed to a nine-year term by the President of the United States with approval of the Congress. Organizationally (Figure 1), TVA consists of three operating groups: Generating, Customer, and Resource. The Generating and Customer Groups are associated primarily with TVA's power production operations. The Agency owns and operates the largest electric utility in the United States. The Resource Group includes the Agency's river basin operations, economic and community development activities, budget and business operations, and the National Fertilizer and Environmental Research Center (NFERC). Many of the organizations in the Resource Group receive core funding from Congressional appropriations. In contrast, TVA's power production operations are entirely self-supporting.

NATIONAL FERTILIZER AND ENVIRONMENTAL RESEARCH CENTER (NFERC)

The National Fertilizer and Environmental Research Center is located on a 1200-acre site in Muscle Shoals, Alabama. The Center has about 450 employees which include chemists, engineers, agronomists, soil scientists, and a highly skilled blue-collar staff for operation of pilot and prototype research facilities. The NFERC receives core funding from Congressional appropriations and during the last decade has come under increased pressure to supplement these appropriations with funds from outside contract work. The FY91 NFERC budget is \$54 million (\$33 million Congressional appropriations).

Fertilizer research and development was the main thrust of NFERC activities from its beginning until a few years ago. The Center conducted basic laboratory research with scale-up of promising technologies in pilot- and full-scale production facilities located at NFERC. Agronomic testing of the new fertilizer products was conducted in parallel with development of the production technology. Once developed, new fertilizer technologies were introduced across the Nation. This fertilizer orientation resulted in unparalleled technical improvements. NFERC technologies are involved in production of about 75 percent of the fertilizers in use today, and through the years NFERC has issued licenses to 400 companies for use of patented NFERC processes.

A few years ago NFERC began a shift more toward environmental research and development. This shift was prompted by growing public and regulatory concern over environmental pollution, particularly that from agriculture, and driven internally by NFERC staff and externally by NFERC's Executive Industry Review Group (EIRG). As a result of these internal and external forces, in January 1990 the Center was reorganized and its name changed from the National Fertilizer Development Center to NFERC. The mission of NFERC is to serve as a national laboratory for research, development, education, and commercialization for:

Fertilizers and Related Agricultural Chemicals Including Their
Economic and Environmentally Safe Use

Renewable Fuel And Chemical Technologies

Alternatives for Solving Environmental/Waste Problems

Technologies Which Support National Defense

The NFERC (Figure 2) is headed by Senior Vice President, John T. Shields. The Center has three divisions: Research, Development, and Technology Introduction. The Research division consists of Biotechnical, Chemical, and Agricultural Research departments. These departments conduct basic and applied research in their respective speciality areas. The Development division consists of Prototype Operations, Chemical Development and Project Management departments. The Prototype Operations Department maintains and operates NFERC's prototype facilities for testing and demonstrating new fertilizer and environmental technologies; the Chemical Development Department conducts bench- and pilot-scale research and development; and the Project Management Department is responsible for capital projects such as demolition of old full-scale production facilities, construction of new prototype facilities, and contractual projects which NFERC conducts for the U.S. Department of Defense. The Technology Introduction division consists of Field Programs, Marketing, and Engineering Services departments. The Field Programs Department works with industry and universities

through its field engineering staff and national network of area directors to introduce and test NFERC technologies and products. The Marketing Department is responsible for marketing NFERC technologies and products. The Engineering Services Department provides engineering design services to other NFERC organizations and outside clients. It also houses the NFERC environmental staff which is responsible for ensuring that NFERC projects and project activities meet environmental and regulatory requirements.

NFERC Projects in Pesticide Waste Minimization/Treatment/Disposal

NFERC currently has a number of projects in the pesticide waste minimization/treatment/disposal areas. Most of these projects are being pursued using interdisciplinary project teams which span division and department lines. The projects are "Model Site Demonstrations and Site Assessments," "Development of Waste Treatment and Site Remediation Technologies for Fertilizer/Agrichemical Dealers," "Development of a Dealer Information/Education Program," and "Constructed Wetlands."

Model Site Demonstrations and Site Assessments--

NFERC is establishing model demonstrations at fertilizer/agrichemical dealer sites across the United States to demonstrate secondary containment systems and other "best management practices" (BMPs) for minimizing fertilizer/pesticide losses to the environment. Selection of sites is made by a group composed of state fertilizer and agrichemical trade associations, individual dealers, TVA regional directors, and field programs staff. Under the program, NFERC provides--at no charge--technical assistance in planning and designing the containment system and recommends other BMPs based on existing and anticipated rules and regulations for that particular state. The participating dealer pays all construction costs associated with bringing the site into compliance and agrees to open his or her facility to visits by other dealers, regulators, and other interested parties. The NFERC plans to establish twenty model demonstration sites in fourteen states. Four sites have been completed.

NFERC also conducts site assessments on a fee basis for fertilizer/agrichemical dealers across the United States. Under this program NFERC environmental staff will conduct a "friendly" assessment of a dealer site and make written recommendations for secondary containment and other BMPs. NFERC also provides the dealer with information on applicable regulations, and depending on the fee, will provide either generic or customized drawings for secondary containment facilities, rinse pads, etc. To date NFERC has conducted approximately thirty environmental site assessments for dealers. The charge for a standard site assessment is \$3,500.

Development of Waste Treatment and Site Remediation Technologies for Fertilizer/Agrichemical Dealers--

The objectives of this project are to develop, introduce, and market waste treatment and site remediation technologies for fertilizer/agrichemical dealers. The project consists of four phases: Phase I - Define Problems, Phase II - Identify "Current State of the Art" for Waste Treatment and Site Remediation Technologies, Phase III - Evaluate/Modify/Research/Develop Waste Treatment and Site Remediation Technologies, and Phase IV - Introduce and Market Waste Treatment and Site Remediation Technologies.

In Phase I information to guide the project was collected from Federal and state regulatory agencies, nonregulatory agencies, universities, dealer and trade associations, and basic producer organizations. During Phase II which was conducted concurrently with Phase I, extensive literature reviews were conducted to identify waste treatment and site remediation technologies which are potentially applicable to waste treatment and remediation problems at fertilizer/agrichemical dealer sites. The information from Phases I and II was published in internal and external reports (TVA Circular Z-288) and in a series of three TVA bulletins (Y-213 - Y-215).

The project is currently in Phase III. In this phase research is being conducted on a number of promising waste treatment and site remediation technologies ranging from low to high technology. These projects are:

Supercritical Fluid Extraction of Pesticides From Soils

Bioremediation of Pesticide Contaminated Soils

Batch Oxidation of Pesticides in Rinsates

Best Management Practices Bioremediation of Pesticide Contaminated Soils

Development/Validation of Immunoassays for Pesticide Analysis

Solar Evaporation/Concentration/Degradation of Pesticides in Rinsate Wastes

Effects of Best Management Practices on "Natural" Remediation

Soil Washing To Remove Pesticides From Soils

Supercritical Water Oxidation of Pesticide Wastes

Remediation of Pesticide-Contaminated Soils by Application to Cropland

Promising technologies from Phase III will be demonstrated, introduced, and marketed in Phase IV. Many of the technologies developed in Phase III will likely be applicable (with modification) to the problems of other industries besides fertilizer/agrichemical dealers.

Development of a Dealer Information/Education Program--

The objectives of this project are to provide fertilizer/agrichemical dealers with information/education necessary to operate environmentally sound and profitable businesses. A dealer environmental checklist was recently developed in cooperation with the National Fertilizer Solutions Association and the National AgriChemical Retailers Association. More than 15,000 of these checklists have been distributed to dealers across the country. Other activities under this project include development of an environmental handbook, a video questionnaire for environmental self-assessment, and environmental workshops for dealers; and compilation of information on state-sponsored pesticide/household waste amnesty days (contract work for EPA). In addition, research is being conducted to evaluate different concretes and concrete additives, coatings, and liner materials for construction of load pads and other containment structures.

Constructed Wetlands--

The objective of this project is to develop a low-cost, low-technology solution to the treatment of contaminated waste waters from the agribusiness industry. Potential users of this technology include fertilizer/agrichemical dealers and food processors.

Constructed wetlands are generally rock filled, shallow cells which utilize plants and biological colonies that grow around their root system to absorb and/or destroy the contaminants in the waste water. A constructed wetlands research and development facility is scheduled for completion at NFERC in the Spring of 1991. The facility includes a greenhouse for conducting small-scale test work, 32 treatment test cells, and 2 larger nursery cells for propagating plants. Data from the greenhouse work and test cells will be used to install several demonstration test cells throughout the United States. These sites will be selected to demonstrate a variety of waste water compositions, flow patterns, plants, and climatic conditions.

Other NFERC Research Activities

Other NFERC research activities include production of ethanol and other chemicals from the cellulosic portion of municipal solid wastes, utilization of industrial and agricultural wastes in fertilizer production, development of controlled availability fertilizer materials, and development of improved fluid fertilizers.

Future Goals

NFERC plans to become a leader in environmental research and development-- it will continue to develop and introduce improved fertilizer technologies for the nation--develop and demonstrate technologies for converting cellulosic wastes to ethanol and other useful chemicals; remove old full-scale fertilizer production facilities and clean up the plant sites; design and operate prototype facilities for demonstrating fertilizer and environmental technologies; and upgrade staff to meet new job demands through training, affirmative actions, and hiring of new employees. In addition, NFERC will intensify its efforts to increase funding from nonappropriated sources by conducting contractual work for national defense agencies, other government agencies, and private firms.

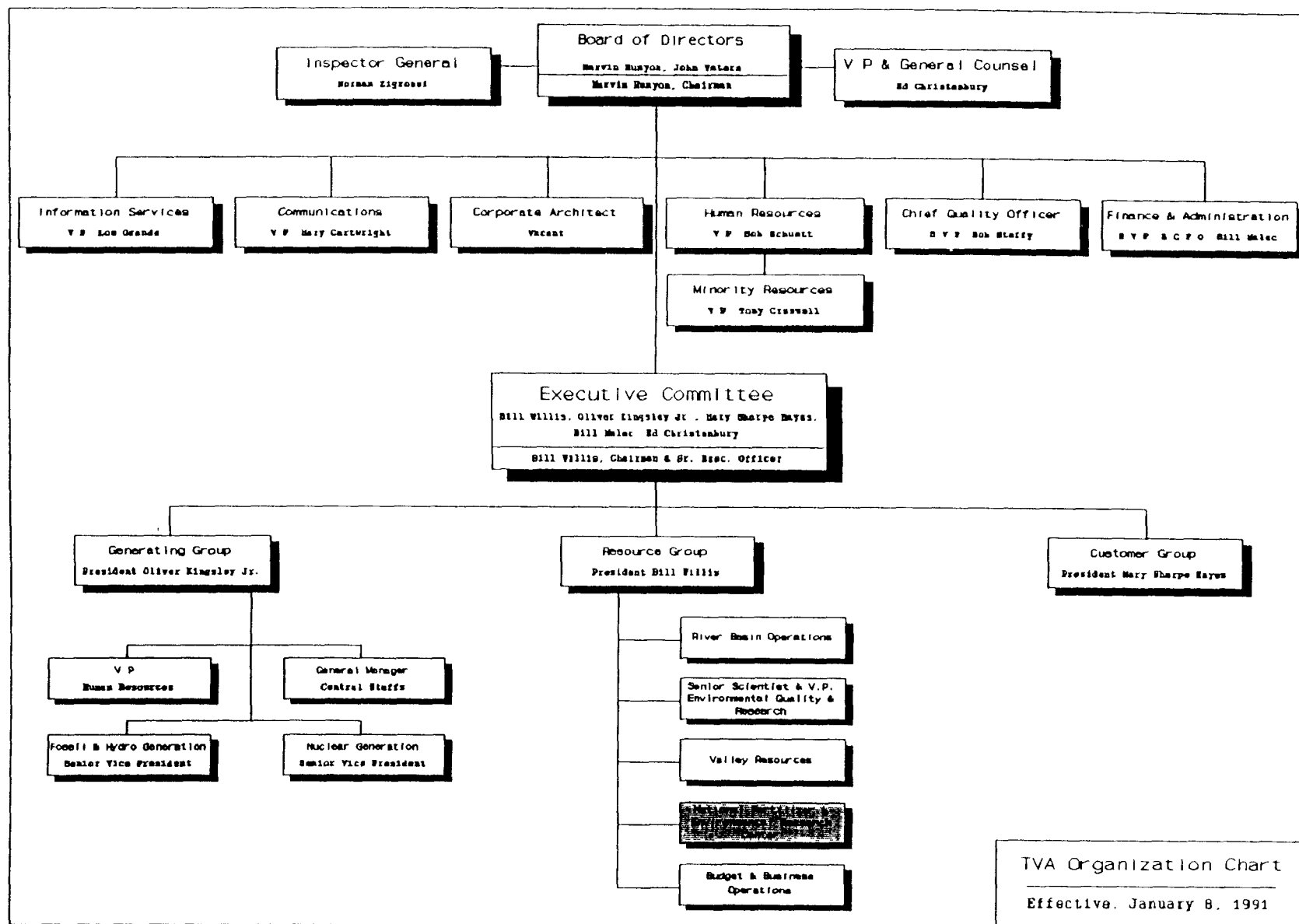


Figure 1. Tennessee Valley Authority

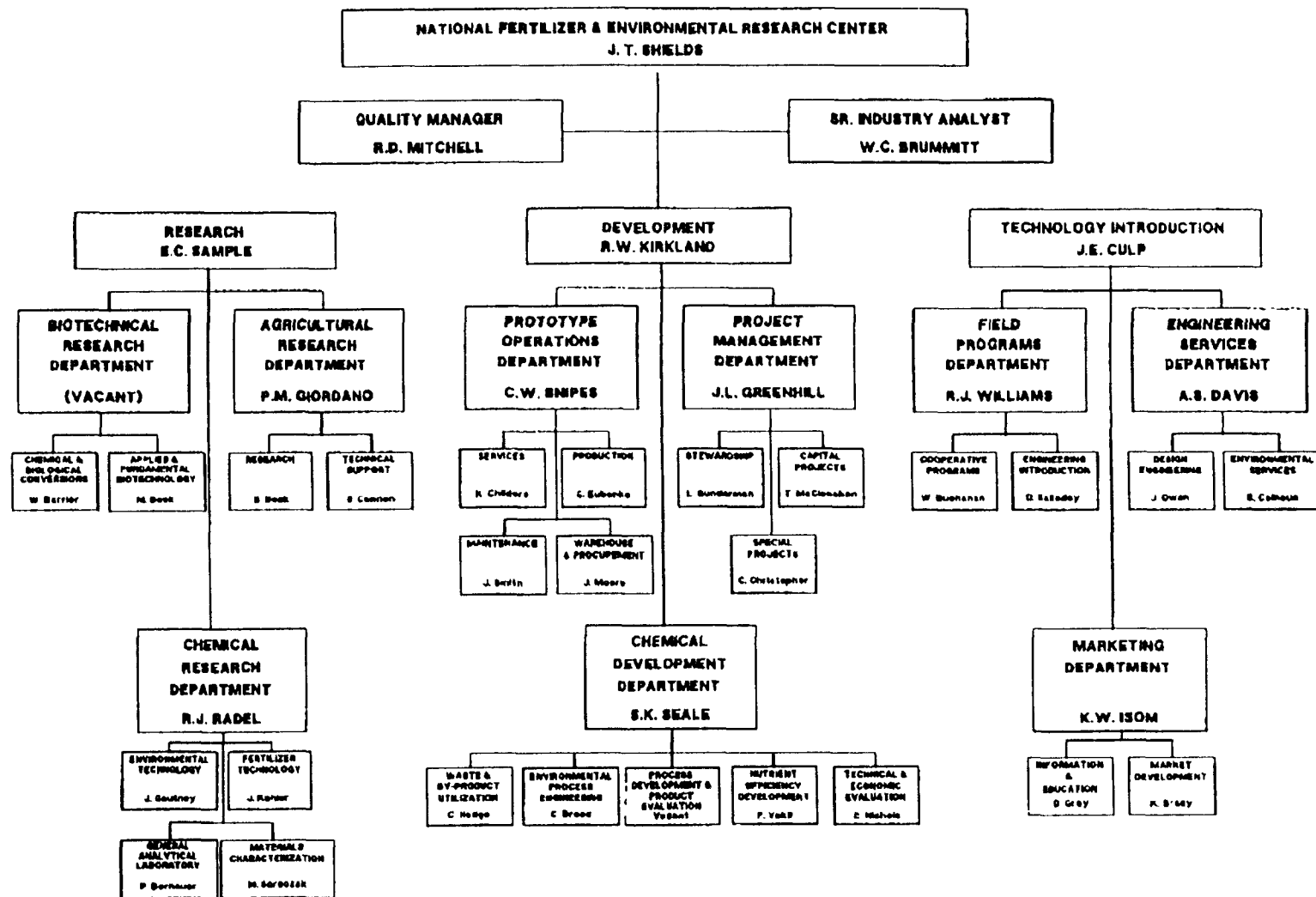


Figure 2. National Fertilizer and Environmental Research Center

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Tracking Small Quantities of Canceled or Excess
Pesticides Containing Dioxins and Furans

by

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ABSTRACT

Confusion currently exists regarding the treatment of suspended, canceled or excess, registered pesticides and their respective formulations under FIFRA, RCRA or CERCLA, particularly if soil and debris are contaminated by these chemicals.

The paper describes what options exist for pesticide-contaminated soil and debris or excess, registered pesticides, given that the former wastes are subject to the RCRA land disposal restrictions and must meet prescribed treatment standards and the latter formulations may be amenable to some creative interpretations of RCRA small quantity generator rules or may qualify under FIFRA for reuse and recycle by application as a pesticide according to label rates on label-approved crops or cropland.

Storage and Disposal Plans--Final Disposition

Confusion may exist regarding the treatment of suspended and/or canceled pesticides (e.g., endrin, heptachlor, chlordane, 2,4,5-T, 2,4,5-TP (Silvex), lindane, DDT, etc.) under FIFRA, RCRA or CERCLA particularly if soil and debris are contaminated by excess registered or suspended/canceled pesticides.

After the applicable effective dates, restricted waste may be land disposed only if it meets the prescribed RCRA treatment standards, or if it has been shown to a reasonable degree of certainty, that there will be no migration of hazardous constituents from the disposal unit for as long as the waste remains hazardous.

At present, a treatment standard is based on the performance of the best demonstrated available technology (BDAT) (51 FR 40578). Compliance with performance standards may be ascertained by determining the concentration level(s) of the principal organic hazardous constituent(s) (POHCs) in the waste, in the treatment residual, or in the extract of the waste or treatment residual.

The Agency has identified U, P (pesticide) and F waste for which proposed concentration-based standards have been changed to technology-based standards (e.g., incineration). (See Tables 1-3.)

Furthermore, soil and debris that are contaminated with prohibited waste are subject to the land disposal restrictions (LDRs) and must meet the treatment standard, as previously described, for the contaminating waste prior to land disposal. The Agency realizes, however, that there are certain sampling and analytical difficulties associated with regulating hazardous waste in soil and debris matrices. Because of such problems, the Agency is preparing a separate rule-making that will establish treatability groups and treatment standards for contaminated soil and debris. (See Table 4 and 5.)

If the pesticide contaminated soil and debris cannot be treated to meet the promulgated treatment standards, alternative treatment standards can be established under a site-specific variance from the treatment standards (see 53 FR 31221, August 27, 1988) or a full-scale variance (40 CFR 268.44). In order to be granted a site-specific variance from the treatment standard, the petitioner must demonstrate to the Agency that because the physical (or chemical) properties of the waste differ significantly from the waste analyzed and used to develop the treatment standard, the waste cannot be treated to specified levels (see 40 CFR 268.44).

Moreover, the Agency has established guidance levels for granting soil and debris treatability variance based on limited soil and debris treatment data and these can be found in Superfund LDR Guides #6A and 6B, July 1989 (U.S. EPA, 1989a and U.S. EPA 1989b).

Conceptual Approach under FIFRA

The soil that contains the pesticides should be viewed as a "new inert diluent" and, as such, comprises a carrier for the active ingredient(s) within the pesticide formulation. Representative soil samples should be analyzed by acceptable EPA methods to determine the concentration(s) of pesticide(s) of regulatory concern. This target pesticide (and others) should be used to calculate what an appropriate FIFRA-approved label rate would be for that particular pesticide. Once this rate is determined, the pesticide-soil may then be applied or redistributed at or below its "label rate" or agronomic rate for the type of crop grown on the receiving field in order to take advantage, during the active growing season or summer months, of natural or enhanced ultraviolet (UV) photolysis and controlled biodegradation by natural or special microorganisms. This approach is legal under RCRA because it represents recycle and reuse of a product; the approach should also be legal under FIFRA because the target pesticide(s) (those of most significance within the soil) is being applied according to label rates on label-approved crops.

The success of this approach will vary from location to location, based on specific active ingredient(s), concentration(s), and other factors, and this process should maintain the contaminated soil within the framework of FIFRA regulations and guidelines. If, however, RCRA becomes controlling, one option is to utilize the approach being used under CERCLA, i.e., obtaining a soil and debris treatability variance for remedial or removal actions (Superfund LDR Guides #6A and 6B). (See also Table 6.)

Excess Pesticides, Rinsates and Other Pesticides Containing Materials (FIFRA Part 165.62 *proposed* under Subpart D)

165.62 Allowable Practices and Procedures

- (a) Application as a pesticide (primary method of disposition)
 - (1) Pesticide in the material must be known; total amount of pesticide applied to the labeled site does not exceed the total amount allowed on the label; and other directions and conditions on the label are complied with.
 - (2) Any specific instructions on the label for application of excess pesticides, rinsates, another materials are complied with. For excess formulation or mixture of formulation and diluent, application as a pesticide to a labeled site at or below the rate of application allowed on the label is clearly within the provisions of the act.
- (b) Use as diluent--Pesticide-contaminated rinsates can be used as diluents for subsequent mixtures or the same pesticides. Rule-of-thumb--no more than 5-10% of the volume of a mixture can be composed of rinse water containing pesticide residues.
- (c) Recycle or recovery--Excess pesticides, rinse water containing pesticides and other pesticide containing materials can be offered for recycling or recovery under proposed regulation; but EPA Office of Pesticide Programs (OPP) definitions of each option differ from normally accepted definitions. For example, recycling involves returning of the pesticide to the manufacturer of the active ingredient for extraction of same; whereas, recovery is limited to combustion for energy value.
- (d) Storage as a pesticide--If excess pesticide, rinse waters, or other pesticide containing materials cannot be immediately applied as a pesticide, such as a diluent, or recycled and recovered, the material may be stored as a pesticide until it can be employed in one of those manners. However, it must be stored in compliance with applicable pesticide storage regulations (at the present time, the regulations do not specify a time limit for storage of these materials as pesticides.) The applicability limit set by FIFRA Subpart B is 11,000 pounds (5.5 tons or approximately 20 drums) and 60 days. The limit is also triggered by 1,350 gallons of rinsates.
- (e) Waste materials--If the excess pesticide, rinse waters, or other pesticide containing material cannot be used as stated previously, then these materials must be handled as wastes under RCRA, that is, if they cannot be handled in accordance with 40 CFR 165.62 (a)-(d) or if they contain any solvent other than the diluent specified on the label.

Practical Example and Potential Remedy

Waste containing chlorophenols are particularly difficult to address under RCRA and has often perplexed many during and after the implementation of the removal or remedial action phases (Collison, 1990). Not only are the current RCRA rules confusing, but EPA has added to the discomfort index by publishing the Final Rule on the Identification and Listing of Hazardous Waste (Wood Preserving) that delineates as hazardous waste, wastewaters, process residuals, preservative drippage, and discarded spent formulations from wood preserving processes at facilities that currently use or have previously used chlorophenolic formulations--F032 (55 FR 50450).

During the conduct of a routine environmental property audit at an agricultural chemical dealer, four 55-gallon leaking drums of pentachlorophenol-formulated pesticides were found. It could not be determined if the pesticide was "spent" or unused formulation. Chemical analyses showed it to contain the following constituents:

Pentachlorophenol	3.5%
Tetrachlorophenols	0.2%
Hexachlorobenzene	50 ppm
Polychlorodibenzoethers	100 ppm
TCDDs	ND
TCDFs	ND
PCDDs	5 ppb
PCDFs	20 ppb
HxCDDs	15 ppb
HxCDFs	30 ppb
HpCDDs	150 ppb
HpCDFs	320 ppb
OCDD	1000 ppb
OCDF	2000 ppb

One-hundred cubic yards of contaminated soil were found to contain approximately 0.5% PCP, and concentrations of dioxins and furans (CDDs and CDFs) were about ten percent of those indicated for the liquid pesticide. Because discarded, unused formulations of pentachlorophenol (PCP) and tetrachlorophenols (T4CPs) are considered RCRA-listed acutely hazardous F027 wastes, these waste pesticides must be treated according to the RCRA Land Disposal Restriction Rule (40 CFR 268.41) for "F" wastes, which requires treatment of the TCDDs, TCDFs, PCDDs, PCDFs, HxCDDs, and HxCDFs to < 1 ppb for each homolog and < 50 ppb, < 50 ppb, <100 ppb, and < 10 ppb for 2,4,5-TCP, 2,4,6-TCP, 2,3,4,6-TCP, and PCP, respectively. Two treatment methods currently can reduce this waste to below these limits--high temperature incineration and chemical detoxification (Fuhr and des Rosiers, 1988). However, no firm in the United States has the requisite RCRA permits to perform this service on a routine basis; besides, the total volume of four drums of liquid pesticide and 100 cubic yards of pesticide-contaminated soil is too small to justify the high cost of incineration (> \$1500 per drum for a relatively simple, hazardous waste).

There are options that have practical merit and have been recommended and employed, and these include: (a) on-site chemical detoxification under RCRA, and (b) land application as a pesticide under FIFRA.

(a) On-site chemical detoxification of the liquid pesticide.

The RCRA small quantity generator rule (40 CFR 161/162) (U.S. EPA, 1986) can be employed for the on-site treatment of < 1000 kg/month (see Table 7) without having to obtain a RCRA permit. Potassium polyethylene glycolate (KPEG) is used to detoxify (i.e., remove chlorine) the liquid pesticide. The KPEG agent is produced by reacting polyethylene glycol-400 (MW=400) with potassium hydroxide (85% purity), removal of aqueous waste, and dosing at 2.5 times the organochlorine content of the pesticide formulation. The temperature of the stirred reaction is maintained between 70-120° C for at least 24 hours. Byproducts produced are water soluble, biodegradable and have been shown not to be toxic to aquatic organisms (des Rosiers, 1986) (des Rosiers, 1989) (Taylor, et al., 1990). Composite analyses of POHCs and CDDs and CDFs are performed by a qualified analytical laboratory prior to and after detoxification to assure compliance with RCRA rules.

Regarding the 100 cubic yards of CDD-and CDF-contaminated soil, OSWER policy requires cleanup to RCRA standards if the 2,3,7,8-TCDD equivalency (TCDD_e) exceeds 1 ppb in residential areas or 20 ppb in industrial sites (desRosiers, 1988). (Note that this contaminated soil contains 15.7 ppb TCDD_e calculated using toxicity equivalent factors (TEFs) per the 1989 method) (Bellin and Barnes, 1989).

(b) Land application as a pesticide.

(This option has been previously discussed under Conceptual Approach under FIFRA.)

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Table 1. Pesticide Active Ingredients That Appear on the RCRA
 "Acutely Hazardous Commercial Products" Lists (RCRA P List)

Pesticide Active Ingredients	Hazardous Waste No.
Acrolein	P003
Aldicarb	P070
Aldrin	P004
Allyl alcohol	P005
Aluminum phosphide	P006
4-Aminopyridine	P008
Arsenic acid	P010
Arsenic pentoxide	P011
Arsenic trioxide	P012
Calcium cyanide	P021
Carbon disulfide	P022
p-Chloroaniline	P024
Cyanides (soluble cyanide salts)	P030
Cyanogen	P031
2-Cyclohexyl-4,6-dinitrophenol	P034
Dieldrin	P037
0,0-Diethyl S-[2-(ethylthio)ethyl] phosphorodithioate (disulfoton, DiSyston ^R)	P039
0,0-Diethyl _R 0-pyrazinyl phosphorothioate (Zinophos)	P040
Dimethoate	P044
0,0-Dimethyl 0-p-nitrophenyl phosphorothioate (Methyl parathion)	P071
4,6-Dinitro-o-cresol and salts	P047
4,6-Dinitro-2-cyclohexylphenol	P034
2,4-Dinitrophenol	P048
Dinoseb	P020
Endosulfan	P050
Endothall	P088
Edrin	P051
Famphur	P097
Fluoroacetamide	P057
Heptachlor	P059
Hydrocyanic acid	P063
Hydrogen cyanide	P063
Methomyl	P066
alpha-Naphthylthiourea (ANTU)	P072
Nicotine and salts	P075
Octamethylpyrophosphoramide (OMPA, Schradan)	P085

Table 1. Pesticide Active Ingredients That Appear on the RCRA
 "Acutely Hazardous Commercial Products" Lists (RCRA P List)
 (continued)

Pesticide Active Ingredients	Hazardous Waste No.
Parathion	P089
Phenylmercuric acetate (PMA)	P092
Phorate	P094
Potassium cyanide	P098
Propargyl alcohol	P102
Sodium azide	P105
Sodium cyanide	P106
Sodium fluoroacetate	P058
Strychnine and salts	P108
0,0,0,0-Tetraethyl dithiopyrophosphate (Sulfotepp)	P109
Tetraethyl pyrophosphate	P111
Thallium sulfate	P115
Thiofanox	P045
Toxaphene	P123
Warfarin	P001
Zinc phosphide	P122
Pentachlorophenol	F027
2,3,4,6-Tetrachlorophenol	F027
2,4,5-Trichlorophenol	F027
2,4,6-Trichlorophenol	F027
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	F027
2,4,5-Trichlorophenoxypropionic acid (Silvex)	F027
Chlorophenolic Formulations from Wood Preserving	F032
Creosote Formulations from Wood Preserving	F034
Inorganic Preservatives Containing Arsenic or Chromium	F035

Table 2. Pesticide Active Ingredients Contained on the RCRA
"Toxic Commercial Products" (RCRA U) List

Pesticide Active Ingredients	Hazardous Waste No.
Acetone	U002
Acrylonitrile	U009
Amitrole	U011
Benzene	U019
Bis(2-ethylhexyl)phthalate	U028
Cacodylic acid	U136
Carbon tetrachloride	U211
Chloral (hydrate)	U034
Chlordane, technical	U036
Chlorobenzene	U037
4-Chloro-m-cresol	U039
Chloroform	U044
o-Chlorophenol	U048
4-Chloro-o-toluidine hydrochloride	U049
Creosote	U051
Cresylic acid (cresols)	U052
Cyclohexane	U056
Cyclohexanone	U057
Decachlorooctahydro-1,3,4-metheno- 2H,5H-cyclobuta[c,d]-pentalen-2- one (Kepone, chlordecone)	U142
1,2-Dibromo-3-chloropropane (DBCP)	U066
Dibutyl phthalate	U069
S-2,3-(dichloroallyl diisopropyl- thiocarbamate) (diallate, Avadex)	U062
o-Dichlorobenzene	U070
p-Dichlorobenzene	U072
Dichlorodifluoromethane (Freon 12 ^R)	U075
3,5-Dichloro-N-(1,1-dimethyl-2- propynyl)benzamide (pronamide, Kerb)	U192
Dichloro diphenyl dichloroethane (DDD)	U060
Dichloro diphenyl trichloroethane (DDT)	U061
Dichloroethyl ether	U025
2,4-Dichlorophenoxyacetic, salts and esters (2,4-D)	U240
1,2-Dichloropropane	U083
1,3-Dichloropropene (Telone)	U084
Dimethyl phthalate	U102
Epichlorohydrin (1-chloro-2,3-epoxypropane)	U041
Ethyl acetate	U112
Ethyl 4,4'-dichlorobenzilate (chlorobenzilate)	U038
Ethylene dibromide (EDB)	U067
Ethylene dichloride	U077

Table 2. Pesticide Active Ingredients Contained on the RCRA
 "Toxic Commercial Products" (RCRA U) List (continued)

Pesticide Active Ingredients	Hazardous Waste No.
Ethylene oxide	U115
Formaldehyde	U122
Furfural	U125
Hexachlorobenzene	U127
Hexachlorocyclopentadiene	U130
Hydrofluoric acid	U134
Isobutyl alcohol	U140
Lead acetate	U144
Lindane	U129
Maleic hydrazide	U148
Mercury	U151
Methyl alcohol (methanol)	U154
Methyl bromide	U029
Methyl chloride	U045
2,2'-Methylenebis (3,4,6-trichlorophenol) (hexachlorophene)	U132
Methylene chloride	U080
Methyl ethyl ketone	U159
4-Methyl-2-pentanone (methyl isobutyl ketone)	U161
Naphthalene	U165
Nitrobenzene	U169
p-Nitrophenol	U170
Pentachloroethane	U184
Pentachloronitrobenzene (PCNB)	U185
Phenol	U188
Phosphorodithioic acid, 0,0-diethyl, methyl ester	U087
Propylene dichloride	U083
Pyridine	U196
Resorcinol	U201
Safrole	U203
Selenium disulfide	U205
1,2,4,5-Tetrachlorobenzene	U207
1,1,2,2-Tetrachloroethane	U209
Thiram	U244
Toluene	U220
1,1,1-Trichloroethane	U226
Trichloroethylene	U228
Trichloromonofluoromethane (Freon 11 ^R)	U121
Xylene	U239

Table 3. Pesticide Inert Ingredients Contained on the RCRA
"Toxic Commercial Products" (RCRA U) List

Pesticide Active Ingredients	Hazardous Waste No.
Acetone	U002
Acetonitrile	U003
Acetophenone	U004
Acrylic acid	U008
Aniline	U012
Benzene	U019
Chlorobenzene	U037
Chloroform	U044
Cyclohexane	U056
Cyclohexanone	U057
Dichlorodifluoromethane (Freon 12 ^R)	U075
Diethyl phthalate	U088
Dimethylamine	U092
Dimethyl phthalate	U102
1,4-Dioxane	U108
Ethylene oxide	U115
Formaldehyde	U122
Formic acid	U123
Isobutyl alcohol	U140
Maleic anhydride	U147
Methyl alcohol (methanol)	U154
Methyl ethyl ketone	U159
Methyl methacrylate	U162
Naphthalene	U165
Saccharin and salts	U202
Thiourea	U219
Toluene	U220
1,1,1-Trichloroethane	U226
1,1,2-Trichloroethane	U227
Trichloromonofluoromethane (Freon 11 ^R)	U121
Vinyl chloride	U043
Xylene	U239

Table 4. Predicted Treatment Effectiveness for Contaminated Soil *

Technology Treatability Group	Thermal Destruction	Dechlor- ination	Bioremed- iation ¹	Low Temp Thermal Desorption	Chemical Extraction & Soil Washing	Immobi- lization ⁴
Non-Polar Halogenated Aromatics (W01)	●	Δ	Δ ³	● Δ	Δ	Δ
PCBs, Halogenated Dioxins, Furans, and Their Precursors (W02)	●	Δ	Δ	● ¹	Δ	Δ ¹
Halogenated Phenols, Cresols, Amines, Thiols, and Other Polar Aromatics (W03)	● ³	Δ	Δ	Δ	Δ	Δ ³
Halogenated Aliphatic Compounds (W04)	●	Δ	Δ ²	●	Δ	Δ ²
Halogenated Aliphatics, Ethers, Esters, and Ketones (W05)	●	Δ ¹	Δ ¹	○ ¹	Δ ¹	Δ ¹
Nitrated Compounds (W06)	●	○ ¹	●	○ ¹	Δ	Δ ¹
Heterocyclics and Sample Non-Halogenated Aromatics (W07)	●	○ ²	●	●	Δ	Δ ²
Polynuclear Aromatics (W08)	●	○ ²	●	○	Δ ³	Δ
Other Polar Non-Halogenated Organic Compounds (W09)	●	○ ²	●	Δ	Δ	Δ
Non-Volatile Metals (W10)	○ ¹	○ ¹	○ X ¹	○ ¹	Δ	●
Volatile Metals (W11)	X ¹	○ ¹	○ X ¹	○ ¹	Δ	●

- Demonstrated Effectiveness
 ▲ Potential Effectiveness
 ○ No Expected Effectiveness (no
 expected interference to process)
 x No Expected Effectiveness (potential
 adverse effects to environment or process)
 * (Offut and Knapp, 1990).

¹ Data were not available for this treatability group.
 Conclusions are drawn from data for compounds with
 similar physical and chemical characteristics

² High removal efficiencies may be due to volatilization
 or soil washing

³ The predicted effectiveness may be different than the
 data imply due to limitations in the test conditions

⁴ These technologies may have limited applicability to high
 levels of organics

Table 5. Examples of Where RCRA-Listed Pesticides May Fit in Treatability Groups

Pesticide	Treatability Group
o-Dichlorobenzene	Halogenated Non-Polar Aromatic Compounds (W01)
Silvex, 2,4,5-T	PCBs, Halogenated Dioxins, Furans and their Precursors (W02) or Halogenated Phenols, Cresols, Amines, Thiols, and other Polar Aromatics (W03)
Pentachlorophenol	Halogenated Phenols, Cresols, Amines, Thiols, and other Polar Aromatics (W03)
1,2-Dibromo-3-chloro-propane (DBCP)	Halogenated Aliphatic Compounds (W04)
Endosulfan	Halogenated Cyclic Aliphatics/Ethers/Esters/Ketones (W05)
Toxaphene	Halogenated Cyclic Aliphatics/Ethers/Esters/Ketones (W05)
Dinoseb	Nitrated Aromatic & Aliphatic Compounds (W06)
Aniline	Heterocyclics and Simple Non-Halogenated Aromatics (W07)
Naphthalene	Polynuclear Aromatics (W08)
Acrolein	Other Polar Organic Compounds (W09)

Table 6. Alternate Treatability Variance Levels for Contaminated Soil and Debris.*

Structural Functional Group	Concentration Range (ppm) ^a	Threshold Concentration (ppm) ^a	Percent Reduction Range
Halogenated Non-Polar Aromatics	0.05 - 10	100	90 - 99.9
Dioxins	0.00001 - 0.05	0.5	90 - 99.9
PCBs	.01 - 10	100	90 - 99.9
Herbicides	0.002 - 0.02	0.2	90 - 99.9
Halogenated Phenols	0.5 - 40	400	90 - 99
Halogenated Aliphatics	0.5 - 2	40	95 - 99.9
Halogenated Cyclics	0.5 - 2	200	90 - 99.9
Nitrated Aromatics	2.5 - 10	10,000	90.9 - 99.99
Heterocyclics & Non-Halogenated Aromatics	0.5 - 20	200	90 - 99.9
Polynuclear Aromatics	0.5 - 20	400	95 - 99.9
Other Polar Organics	0.5 - 10	100	90 - 99.9

Structural Functional Group	Concentration Range (ppm) ^b	Threshold Concentration (ppm) ^b	Percent Reduction Range
Antimony	0.1 - 0.2	2	90 - 99
Arsenic	0.27 - 1	10	90 - 99.9
Barium	0.1 - 40	400	90 - 99
Chromium	0.5 - 6	120	95 - 99.9
Nickel	0.5 - 1	20	95 - 99.9
Selenium	0.005	0.08	90 - 99
Vanadium	0.2 - 22	200	90 - 99
Cadmium	0.2 - 2	40	95 - 99.9
Lead	0.1 - 3	300	99 - 99.9
Mercury	0.0002 - 0.008	0.06	90 - 99

* If the constituent concentration of the untreated waste is less than the threshold concentration, use the concentration range; if it is more than the threshold concentration, use the percent reduction range.

^a Total Waste Analysis

^b TCLP Analysis

Table 7. Categories of Hazardous Waste Generators
(40 CFR 161/162)

KEY: 1 barrel = about 200 kilograms of hazardous waste
which is about 55 gallons

Generators of No More Than 100 kg/mo	100-1000 kg/mo Generators	Generators of 1000 kg/mo or more
<p>If you generate no more than 100 kilograms (about 220 pounds or 25 gallons) of hazardous waste and no more than 1 kg (about 2 pounds) of acutely hazardous waste in any calendar month, you are a conditionally-exempt small quantity generator and the federal hazardous waste laws require you to:</p> <ul style="list-style-type: none"> • Identify all hazardous waste you generate. • Send this waste to a hazardous waste facility, or a landfill or other facility approved by the state for industrial or municipal wastes. • Never accumulate more than 100 kg of hazardous waste on your property. (If you do, you become subject to all the requirements applicable to 100-1000 kg/mo generators explained in this handbook. 	<p>If you generate more than 100 and less than 1000 kg (between 220 and 2,200 pounds or about 25 to under 300 gallons) of hazardous waste and no more than 1 kg of acutely hazardous waste in any month, you are a 100-1000 kg/mo generator and the federal hazardous waste laws require you to:</p> <ul style="list-style-type: none"> • Comply with the 1986 rules for managing hazardous waste, including the accumulation, treatment, storage and disposal requirements described in this handbook. 	<p>If you generate 1000 kg (about 2,200 pounds or 300 gallons) or more of hazardous waste, or more than 1 kg of acutely hazardous waste in any month, you are a generator of 1000 kg/mo or more and the federal hazardous waste laws require you to:</p> <ul style="list-style-type: none"> • Comply with all applicable hazardous waste management rules.

Research and Development Needs For Agrichemical Retail Dealership Site Assessment and Remediation

by

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INTRODUCTION

Why is research and development needed for the assessment and remediation of agrichemical dealerships?

Over the last few decades, many agrichemical dealers have slowly, and in most cases, inadvertently contaminated the soil at their dealerships with many different pesticide, fertilizer, and solvent products. As a result of this contamination, one of the most uncertain and ominous issues now facing the agrichemical industry is the cleanup of contaminated soils and water at retail agridealer facilities.

Currently, agridealers have very limited and expensive options available to them for the cleanup of contaminated soil and water. For example, if the soil at a dealership contains pesticide waste regulated under the Resource Conservation and Recovery Act (RCRA), estimates indicate that it could cost a dealer from three to five million dollars to cleanup his facility. In addition, a large data gap now exists with respect to the remediation of chemically contaminated soils and water at retail facilities that prohibits regulators from reviewing the viability of new and more cost effective procedures.

It is the goal of the agrichemical community to work in concert with federal and state regulatory officials as well as private and government research scientists to develop new and acceptable site assessment and remediation technologies that dealers can economically apply to their operations. Over the next few pages, I would like to review several areas of research and development that the agrichemical industry deems critical to addressing the site contamination problem.

RESEARCH AND DEVELOPMENT IN SITE ASSESSMENT

Development of Preliminary Site Assessment Procedures That Can Be Undertaken by a Retail Dealer

Today, an environmental consultant hired by a dealer to do a site assessment must report contamination, if found, to the State authorities. This requirement is currently prohibiting many dealers from moving forward with any corrective action because of the fear of bankruptcy and the high cost of a consultant.

It is the position of the National Agrichemical Retailers Association (NARA) that the development of visual as well as preliminary sampling procedures that can be carried out by retail dealers will help the industry move forward in discovering and correcting contaminated sites.

Specific Research Needs:

- Development of guidelines that can be used in a historical records check of a facility. These guidelines would help pinpoint specific practices or evidence that would indicate high probability of contamination.
- Development of guidelines for visual site assessment procedures based on vegetative state, soil decolorization, proximity to wells and ditches, etc.
- Development of preliminary sampling procedures that can be carried out by a retail dealer.

Development of Sampling Technology That Is Centered on the Unique Characteristics of Agrichemical Facilities

Sampling soils and water that may be contaminated with pesticides, fertilizers and solvents is a very complex task. Even though there is a minimal amount of research going on in this area at this time, much more research must be carried out in order to gain a better understanding of how to sample soils with a mixture or high concentration of wastes. Not only will sampling technologies have to concentrate on waste mixtures, they will also have to take into consideration soil type, hydrogeology and potential for constituent(s) to leach.

Specific Research Needs:

- Research aimed at establishing the validity of a variety of different extraction procedures and their relationship to constituent leaching potential.
- Research aimed at developing low cost procedures that are workable on soil containing a mixture of constituents. This sampling technology could accurately assess soils containing mixtures of Carbamates, Chlorinated Hydrocarbons, Triazines, Organophosphates, Organic Nitrogen Pesticides, Chlorophenoxy Acids, and other pesticide and fertilizer constituents.
- Development of standardized analytical procedure which would stimulate leaching or predict the degree of downward migration of agrichemical contaminants by actually testing soils from contaminated sites. This may be generically comparable to the E.P. Toxicity or TCLP procedure.

Development of Remediation Trigger Levels Based on Risk Assessment

It has been discovered through site assessment activities already undertaken that individual agrichemical facilities possess unique characteristics. These unique characteristics in many cases may require that regulators establish trigger levels on a facility by facility basis.

In the establishment of these individual trigger levels, regulators must now set them conservatively because of the limited amount of information regarding the risk that single or multiple waste mixtures present in different soil and hydrogeologic situations.

The development of remediation trigger level standards is of utmost importance to the entire agrichemical industry cleanup initiative.

Specific research needs:

- Development of risk assessment model which would accurately assess different constituents based on actual sampling, predicted leaching potential, and individual facility characteristics.
- Development of remediation trigger levels based on model predictions. These predictions would be based on health hazard constituent(s) present and potential to leach into ground water at each individual location.

Development of Micro-Economic Cost Analysis Formula That Can Be Used on a Site-By-Site Basis

The cost of site assessment activities are of great importance to the end goal of cleaning up contaminated sites. Agrichemical dealers typically operate on a small margin which leaves little funding for site assessment and remediation cost.

The development of micro-economic cost analysis formula that may be used by agrichemical dealers, consultants, and regulators would be of great benefit in determining whether a particular facility is financially capable of the cleanup recommended. This formula would also be very helpful when cleanup costs must be spread over a prolonged period of time.

Specific research needs:

- Development of site assessment cost data base which takes into consideration multiple site assessment technologies based on individual site characteristics.
- Development of linear programming model which considers basic facility characteristics and gives lowest cost site assessment procedure based on those characteristics.
- Development of financial data base which will be used to give lowest cost site assessment technology and individual facility financial capability.

RESEARCH AND DEVELOPMENT IN SITE REMEDIATION

Development of Soil Cleanup Levels

The discovery of soil and water cleanup levels that mitigate risk are important to the cleanup objectives of the agrichemical industry and regulators. Even though water cleanup levels are already specified through Maximum Contaminate Levels and Health Advisories in many cases, cleanup levels for soil are much more ambiguous.

Some basic research is already being conducted regarding the establishment of soil cleanup levels based on contaminate concentration, leaching potential, soil characteristics and hydrogeology. However, much more research must be conducted in order to gain a more accurate picture of the risk that different mixtures and concentrations of contaminants present under various conditions.

Specific Research Needs:

- Development of attainable soil cleanup levels (thresholds) that take into consideration individual constituents and constituent mixtures. These cleanup levels must meet risk/benefit analysis criteria that take into consideration the facility's ability to finance cleanup as well as the actual hazard that the waste present.

Development of Low Cost Remediation Technology

According to a review of literature on remediation technology, not much is known about the workability of current technology as it relates to agrichemicals. From preliminary cost estimates of technology currently being used however, it is evident that new in-situ low cost technologies must be developed in order for the agrichemical industry to cleanup contaminated sites and remain economically viable.

Because of the wide variety of chemical constituent mixtures currently present in dealership soils, researchers must take into consideration the regulatory implications of technological innovations. For example, waste regulated under RCRA cannot be treated in the same manner as waste that is not regulated under RCRA or special state laws. Research must be directed at finding low cost remediation technology that can be carried out by the dealer or consultant.

Specific Research Needs:

- Development of onsite remediation technologies that can be carried out by the agridealer under regulatory agency supervision. These remediation technologies must be proven capable of attaining the cleanup objectives of regulatory agencies while remaining low in cost.
- Development of a remediation technology data base that takes into consideration laws governing remediation activities.

Development of Micro-Economic Cost Analysis That Can be Used on a Site-by-Site Basis

As was the case for site assessment, the development of a Micro Economic cost analysis formula for the remediation of agrichemical facilities would be very helpful in projecting the short- and long-term cost of remediation activities.

Understanding remediation cost and weighing different remediation methods based on cost would be extremely helpful in insuring the continued financial security of the entire agrichemical industry.

Specific Research Needs:

- Development of a remediation cost data base which includes remediation cost information on contaminating constituents, leaching potential, soil and water cleanup objectives, and technology used.
- Development of linear programming model which can be used by individual dealers, regulatory officials, lending institutions, and insurance companies in determining the financial capability of a facility to successfully carry out remediation activities.

An Evaporation /Degradation System for Pesticide Equipment Rinse Water

by

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INTRODUCTION

In the 1985-86 a system for the evaporation/degradation was developed jointly by our Department and the University of Florida Agricultural Engineering Department to provide a viable option for the disposal of rinsewater from pesticide application equipment. This system was based on work done in the 1970's by Charles Hall and others at Iowa State University on pesticide degradation pits. This system does not use new technology but is an attempt to apply a workable technology in an environmentally acceptable manner in an economical way. It has almost been successful.

The system itself is quite simple. It consists of an above-ground tank (or, if the tank is below grade, a double tank), a covered wash down slab, and a system of transferring rinsewater containing pesticide residues from the slab to the tank. The tank contains a soil or gravel matrix and is covered with a clear fiberglass or glass roof. The pesticide rinsewater is adsorbed by the soil matrix, the liquid portion evaporated by sunlight, and pesticides in the rinsewater degraded by microorganisms in the matrix. There is no discharge from the system. A secondary containment system is used to protect against leaks. Attached are several figures and tables that describe the system. These figures are taken from the Institute of Food and Agricultural Sciences Bulletin 242.

The basic components of the system in Florida are:

- Above-ground or double walled tank.
- Clear roof over tank.
- Covered wash down slab.
- Transfer system for water from slab to tank with option for storage capacity.

The keys to successful operation in Florida are:

- Optimized evaporation.
- Containment of rinsewater discharged into system.
- Protection of evaporation/degradation tank from rainfall.

These are achieved by:

Evaporation

Maximizing surface area of tank and sizing tank for different parts of the state. The size of the surface area of the tank is decided based on the amount of water to be discharged to it. Tables 1 and 2 of Bulletin 242 provide the figures for calculating the appropriate surface area.

Using a clear roof. Clear fiberglass, glass, or other green house roof materials can be used.

Using a rinsewater distribution system that avoids film formation that could impede evaporation. This distribution system consists of a vertical pipe that conducts the rinsewater through the media to the bottom gravel layer of the tank. The rinsewater then moves up vertically through the media. (See Figure 2 from Bulletin 242).

Requiring setback from structures to aid airflow.

The evaporation/degradation tanks are required to be built a minimum of seventy-five (75) feet from other structures to avoid obstructions to air flow.

Containment

Above-ground tank for leak inspection. The tank must be a minimum of eight inches off the ground to allow for inspection for leaks. If the tank must be below grade, a double tank must be used with an automatic leak alarm and pump system.

Lined pad and sump. Both the wash down pad and the sump are lined to prevent leaks to underlying soil. The sump must also be pumped dry at the end of each day of operation.

Secondary containment. A berm is required around the evaporation /degradation tank to provide for secondary containment should the tank fail. The bermed area is also covered by a roof and is lined.

Alarm system. An alarm system and pump cutoff switch is required to prevent overfilling the tank when pumping water from the wash down slab to the tank.

Rainfall protection

Fixed roof over tank and secondary containment. A roof covers both the tank and the bermed area to prevent rain from filling this area.

Cover over slab - fixed or moveable. A low profile moveable cover - such as a swimming pool cover - can be used to prevent rain from getting onto slab, but a fixed roof is preferred.

Roof design - 30 degree overhang. The roof must have a minimum thirty degree overhang measured from the edge of the pad or the berm, in order to prevent rain from blowing into these areas in significant quantities. (See Figure 1 of Bulletin 242.)

Two questions that were addressed early on in the process of development of this system were air emissions and the rate of degradation of the pesticides added to the system. The question of air emissions was resolved based on data developed in the Iowa State studies that showed only very low detections of pesticides downwind from the degradation pit. Also, it was decided that air emissions from the degradation tank would have to be much less than air emissions from an application site, since the concentration of the pesticide solution discharged to the tank was two orders of magnitude less than the concentrations used in applications.

It was also decided that the degradation rate of the pesticides placed into the system was not important, since there was no discharge from the system, and, therefore, even slow rates were not a concern.

IMPLEMENTATION

The goal of implementation was to make this system economically feasible by minimizing permit and regulatory costs. In order to do this, it was important to: avoid high costs for permits, a requirement for a professional engineer seal, and high costs for compliance with applicable regulations. This was accomplished by:

- Obtaining an exemption from the RCRA facility permit initially
- Developing a general permit that
 - did not require engineer seal
 - did not require record keeping
 - did not require monitoring
- General permit did specify:
 - certain components
 - operation
 - closure requirements

Deviations from the components and specifications in the general permit not allowed.

A publication, Institute of Food and Agricultural Sciences (IFAS) Bulletin 242, was developed which described construction and operation in terms that average farmer could understand and use.

The state regulation allowing the construction and operation of these systems, DER Rule Chapter 17-28.822 was adopted in June 1988. The designation of this rule was changed in 1989 to Chapter 17-660.802, but language of the rule was not changed.

Currently there are three systems permitted under this rule - one each in 1988, 89, 90. Two of them are at research farms, one is at a golf course.

Experience

The systems have proven to be more expensive than originally estimated, with costs of about thirty to fifty thousand dollars per system. They have also been capable of handling more water than estimated, about double what was estimated. The pesticide users have found the systems to be very useful and helpful in their operations, and other applicators are interested in using these systems.

Regulatory Problems

In late 1989 we became aware that a new interpretation of RCRA exemption for waste water treatment units had been made. This new interpretation requires that treatment systems must have either a RCRA permit or Clean Water Act (known as a National Pollution Discharge Elimination System - NPDES) permit. Since the NPDES permits apply only to facilities that discharge, these systems can not obtain an NPDES permit. The Farmer's Exemption under RCRA also may not apply to these systems.

Current options for maintaining the economic feasibility of these systems are:

- Pursue RD&D permit through Technology Innovation Program
- Petition EPA for regulatory relief
- Petition Congress for exemption

CONCLUSION

The evaporation/degradation system is a promising technology and a good option for pesticide waste management that is being hampered primarily by current regulations and their interpretation, not because of environmental shortcomings. This is a system that can be utilized now, without years of research and development, but that will require innovative regulatory action to become a useful option for pesticide users.

Pesticide Disposal Using a Demulsification, Sorption, Filtration and Chemical and Biological Degradation Strategy

By

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ABSTRACT

Research concerning disposal of pesticide-laden solutions, including emulsions or particulate suspensions (wetttable powders and flowables), has focused on concentration and/or containment methods using biodegradable lignocellulosic sorbents. Contaminated sorbents are used as a matrix on which the pesticides are degraded in a composting environment. In laboratory studies, significant amounts of selected pesticides were removed from solutions (ranging in concentrations from 1,250 to 20,000 mg/kg) by a combination of demulsification, sorption and filtration in the presence of lignocellulosic materials. In other studies, high concentrations of diazinon and other pesticides were degraded rapidly in a nutrient-enriched lignocellulosic medium. Based on our research, a pesticide disposal system is currently under development that should prove to be practical, effective, safe and relatively inexpensive. It is envisioned that this pesticide disposal method will be useful in a variety of agrichemical situations.

INTRODUCTION

It is important that pesticide waste disposal methods be developed because inappropriate handling may result in soil contamination at mixing and pesticide handling sites. Failure to properly handle pesticides at these sites can result in groundwater contamination (Myrik, 1990; Norwood, 1990). Minimization of waste by rinsate recycling and spraying on treatable areas under many circumstances is a reasonable and effective means for rinsate disposal. However, there is still a need for practical, inexpensive, and effective methods for disposing of small volumes of concentrated and dilute pesticide wastes. A variety of potential technologies suitable for pesticide waste disposal have been examined, but few, if any, satisfactory methods are available to pesticide users. (Bridges, 1988; Norwood, 1990). It has been difficult to develop a general disposal method because many of the pesticidal materials that are available have unique chemical and formulated characteristics. As a result, development of "universal" disposal techniques is problematic.

According to Ware (1989), there are currently about 200 active pesticidal ingredients formulated in an estimated 37,000 formulations, and 75% of pesticides used are liquid sprays. Emulsifiable concentrates, wetttable powders, soluble liquids, and suspension concentrates represent the most common formulations used in liquid sprays (Ware, 1989; Seaman, 1990). Among these, emulsifiable concentrates, wetttable powders and soluble liquids are the most commonly used but

suspension concentrates, capsule emulsions, water-dispersible granules, emulsions in water and suspoemulsions may increase in usage at the expense of the more traditional formulations (Seaman, 1990). Future trends in formulation development and availability will be significantly influenced by regulatory pressures resulting from reassessment of inert ingredients used in formulations (Seaman, 1990; Thomas, 1990). Because of this, it would appear that development of pesticide waste disposal strategies must take into account current and future trends in pesticide formulation chemistry. The pesticide waste disposal strategy described here is designed to remove pesticides from a variety of aqueous formulations and dispose of them using chemical and biological degradation.

DISPOSAL STRATEGY

We have proposed a conceptual/functional model for pesticide wastewater disposal (Hetzel, et al., 1989). A modified version is presented in Figure 1. The disposal process is divided into a sorption and a disposal phase. The sorption phase includes addition of demulsification agents and lignocellulosic materials (peat moss, wood products). During this phase, solubilized pesticides are removed from the rinsate solution and concentrated onto the organic sorbents. We have found that addition of demulsifying agents facilitate the sorption process when treating various emulsifiable concentrate formulations (Judge et al., 1990). The disposal phase involves physical separation of the pesticide-laden sorbents and suspended pesticide particulates (derived from wettable powders, flowables, etc.) from the aqueous phase. The aqueous phase may then be recycled or discarded. The solid phase containing pesticides sorbed onto the lignocellulosic matrices and/or particulates removed from pesticidal particulates are then placed into a composting environment where the pesticides are chemically and biologically degraded. Lignocellulosic materials have been selected for use in disposal processes because they are relatively inexpensive, have been found to be highly sorbent, and may serve to support or enhance biodegradation activities. We have selected three such materials for study. Peat moss is a highly sorbent material which is readily available and relatively inexpensive. Because peat does not contain readily degradable carbohydrates, addition of high energy substrates (corn meal) is added to enhance solid substrate fermentation activities. Ground pine bark mulch is included in our studies because it has been found to sorb some pesticides effectively. Steam-exploded wood fibers (Overend and Chornet, 1987) were selected not only because of their potential as effective sorbents, but also because of their potential to support solid substrate fermentation with a reduced requirement of nutrient enrichment.

The effectiveness of composting as a means for hazardous waste management has been recently reviewed (Hart, 1991). Composting occurs widely in nature and as a process is being employed to dispose of municipal sewage sludge wastes (Hart, 1991; Parr, et al., 1978) and its potential to cleanup contaminated soil sites is being examined (Williams and Myler, 1990). The use of composting as a means for degrading pesticides is shown Figure 2. It illustrates a hypothetical situation where a pesticide contained in a composting environment can be degraded to relatively low levels. The degradation may be due to direct metabolism or cometabolism of the pesticide by the various composting microorganism populations. With time, the compost cycles from high to lower energy content, and microbial population dynamics will change reflecting the nutritional changes in substrate availability. In situations where the initial pesticide concentration is low, or where a pesticide is easily degraded, one feeding or

compost cycle may be sufficient to reduce the pesticide to low levels. However, under circumstances where the pesticide concentrations may be high, or under circumstances where they are not easily degraded, additional energy input may be required. Figure 2 includes three feeding cycles (nutrient addition) increasing the energy level of the compost at each addition. During each cycle as the temperature increases and then declines, the metabolic activities of thermophilic and mesophilic microbial populations will also cycle. The strength of solid substrate fermentation as a method of pesticide disposal is that it relies on a consortia of degrading microbes and not just one species. Under these conditions, rates of pesticide degradation are expected to be enhanced since the combined activities of a diverse microbial population is expected to be more efficient.

EXPERIMENTATION

Laboratory experiments have been conducted using approaches designed to reflect what is envisioned as applicable to development of a field prototype disposal unit. A variety of systems have been evaluated and the system selected for our studies includes mixing samples containing pesticide solutions and sorbents in an Erlenmeyer flask using a magnetic mixer or shaking table, followed by settling and filtration. In our initial experiments, pesticide-laden sorbent material was filtered through Whatman filter paper using a vacuum system. Currently, we are using a filtration system consisting of polyvinyl chloride (PVC) columns [3/4 in (dia) x 12 in (length)] fitted with a PVC coupling containing a stainless steel screen (40 mesh) 15 grams of fine sand and several layers of filter paper. Samples were taken at different stages of the sorption process and analyzed. Solvents used in this study were pesticide grade.

The general pesticide extraction and analytical procedures used are described by Walls (1981). Analytical standards were obtained from the U.S. Environmental Protection Agency Pesticide and Industrial Chemicals Repository MD-8, Research Triangle Park, NC. Depending upon the pesticide, several different solvents were used as extractants (ie. acetone, hexane, etc.). We also used sonication as a means to improve extraction efficiencies.

Following various purification and volume reduction procedures samples were analyzed using gas-liquid chromatography. Sorbents tested include sphagnum peat moss, steam-exploded yellow poplar wood fibers (1. water and alkaline washed; 2. bleached), and pine bark mulch. All lignocellulosic materials were ground in a Wiley mill using a 2 mm screen). Activated carbon (Calgon FiltrasorbR 200) was used as the comparison sorbent material (control).

RESULTS AND DISCUSSION

Sorption phase

Table 1 summarizes information obtained when peat moss was mixed with various concentrations of Diazinon AG500 and Dursban 4E for 24 hours. Removal of diazinon from solution was effective at all concentrations tested, however, removal of chlorpyrifos, was not effective at the higher (20,000 & 10,000 mg/kg) concentrations tested (Hetzel, et al., 1989). Experiments with other emulsifiable concentrate formulations using similar protocols, provided variable

removal rates. During these preliminary studies, we observed that emulsions persisted after mixing the pesticidal emulsifiable concentrates with peat moss. Studies using a fluorescent probe, emulsifiable concentrate blanks and emulsifiable concentrate pesticide formulations (chlorpyrifos, diazinon, and malathion) revealed that addition of calcium hydroxide was an effective demulsification agent. We have found that the use of calcium hydroxide in the presence of peat moss greatly increased the rate of removal for several pesticide formulations from aqueous suspensions (Judge, et al., 1990).

Table 1. Sorption of Diazinon as Diazinon AG 500 and Chlorpyrifos as Dursban 4E at Several Concentrations after Mixing with Peat Moss for 24 Hours

Formulated Concentration mg/kg	Pesticide Remaining in Solution ^{1,2,3} (percent of initial concentration)				
	<u>20,000</u>	<u>10,000</u>	<u>5,000</u>	<u>2,500</u>	<u>1,250</u>
<u>Pesticide</u>					
Diazinon	1.4 ± 0.8	0.7 ± 0.1	1.0 ± 0.7	6.0 ± 0.8	3.0 ± 0.6
Chlorpyrifos	45 ± 6	19.0 ± 11	5.3 ± 5	2.4 ± 2.0	7.6 ± 4.6

¹ Actual initial concentrations for diazinon averaged 92 ± 6% of the intended formulation.

² 10 grams of sphagnum peat moss were mixed in 200 ml pesticide containing solution on a magnetic stirrer.

³ Percentage of remaining concentration represented as the mean ± standard error.

⁴ For details see Hetzel et al., 1989.

Table 2 contains information which we have obtained using a one-step demulsification, sorption and filtration process on 10 pesticide formulations and four sorbents. In an effort to represent what might occur in the field, we have used high initial pesticide concentrations (approximately 5000 mg/kg) in our laboratory experiments. Data provided in Table 2 indicates that in most cases, we were able to significantly reduce the amount of pesticide contained in test solutions using the demulsification, sorption, and filtration procedure. It is important to note that under certain circumstances, sorption may only contribute insignificantly to pesticide removal. Some of the pesticides are quite unstable in alkaline solutions (ie. captan, folpet, malathion, etc; Hartely and Kidd, 1987) and as a result may be degraded in the demulsification process. Extraction of the sorbent material indicated that this was the case for certain pesticides, since little material was recovered from the sorbents (data not shown). Also, large amounts of the pesticides formulated for use as particulate suspensions (wetttable powders and flowables), can be removed by filtration. When filtered

residues containing the particulate and sorbent phase obtained from experiments on these formulation types were extracted, measurable quantities of residues could be detected in these extracts (data not shown). Most of the pesticides tested are not very soluble in water, and as a result are sorbed onto hydrophobic sorbent sites if they are not physically removed (filtration) or chemically degraded (alkaline hydrolysis). Comparatively large amounts of metolachlor remained in solution after one step treatment (Table 2). Since metolachlor is somewhat soluble in water and not significantly transformed by alkaline treatment, additional treatment will be required for effective wastewater cleanup of this compound. It is possible that lignocellulosic materials could be modified in such a manner that they might be capable of binding more water soluble materials such as 2,4-D, metolachlor and alachlor. We are currently investigating the possibility of modifying steam-exploded wood fibers to improve specific sorptive properties in a manner similar to that described by MacCarthy and Djebbar (1986) for chemical modification of peat.

Table 2. Removal of Pesticides from Aqueous Suspensions of Various Pesticide Formulations Using Demulsification, Sorption, and Filtration

Compound/ Formulation	% Pesticide remaining ^{1,2,3}			
	Wood Fibers	Activated Carbon	Pine Bark	Peat Moss
Atrazine (EC)	1.0±0.6	0.6±0.4	1.2±0.6	1.2±0.2
Azinphos-methyl (WP)	0.0±0.0	1.3±0.1	-	
Captan (WP)	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
Carbofuran (F)	0.5±0.4	0.3±0.1	-	4.9±1.1
Chlorpyrifos (EC)	2.4±0.8	0.0±0.0	12±0.6	5.1±1.0*
Diazinon (EC)	1.5±1.3*	0.1±0.1*	2.1±2.2	2.0±1.4
Folpet (WP)	0.0±0.0	0.0±0.0	0.0±0.0	0.7±0.0
Lindane (EC)	0.2±0.1	0.0±0.0	-	0.1±0.1
Malathion (EC)	0.9±0.6*	0.0±0.0*	0.0±0.0*	0.0±0.0*
Metolachlor (EC)	9.9±2.8	5.9±1.1	13.6±8.7*	39.6±8.7

¹ Initial formulated concentration of pesticide solutions was approximately 5000 mg/kg, the percentages were calculated as changes from initial concentration after treatment. Means and standard errors are based on 3 replicates. Quantitation limits were set at 1 mg/kg.

² 100 ml of solution was mixed with 2.5 grams sorbent and 1 gram calcium hydroxide on a shaking table for 4 hours (or 24 hours as indicated by an asterik). The solution was allowed to settle (30 min) followed by filtration in PVC columns.

³ Formulations used were as follows: atrazine as AATREX[®] (50% ai), azinphos-methyl as Guthion[®] (35% ai), captan (49% ai), carbofuran as Furadan[®] (40.6%), chlorpyrifos as Dursban[®] (44.4% ai), diazinon (48% ai), folpet (50% ai), lindane as Ortho[®] (20% ai), malathion as Dragon[®] (50% ai) and metolachlor as Dual[®] (68.4% ai). Emulsifiable concentrates (EC), flowable (F) and wettable powders (WP).

Since applicators may choose to mix and apply some pesticides simultaneously, as in some orchard pest control operations, we conducted an experiment using an insecticide (azinphos-methyl) and a fungicide (captan) to examine the efficacy of the system we are developing to remove high levels of these two pesticides. The results of this experiment are shown in Table 3. The effects of alkaline addition on the stability of captan and azinphos-methyl are quite striking. When no calcium hydroxide was present about 1000 mg/kg of both pesticides remained in solution after filtration. Treatment of the pesticide-laden solution with calcium hydroxide essentially obliterates both of the pesticides (control with calcium hydroxide). When these pesticides are mixed with the demulsifying agent in the presence of sorbents, small amounts of captan were detected in the filtrate. It is possible that the presence of the sorbents influences the alkaline degradative process. Sorbents mixed with calcium hydroxide seem to have lowered the amount of azinphos-methyl retained in the filtrate. From these results it appears that the use of calcium hydroxide has utility in the one-step process even though both of the formulations were particulate suspensions.

We envision that acceptable levels of pesticide removal should be in low mg/l (0 to 9 mg/l) range and lower before the treated rinsate can be safely discarded. Since the system which we have been developing using a one-step process can reduce the levels of pesticide to a very low percentage of the initial concentration, (Table 2) we have begun to experiment with a two-step process. This process includes a first step similar to the one-step process where sorbent and a demulsifying agent are mixed with the pesticide waste solution. Instead of filtering the solution, it is then cycled through a column containing additional sorbent material. Table 4 includes data which was obtained from a experiment using a two-step demulsification/sorption process on a solution containing emulsified chlorpyrifos. It can be seen that significant reduction in chlorpyrifos concentration was achieved by first demulsifying (calcium hydroxide) and sorbing (steam-exploded wood) (first step), followed by additional exposure of the solution to one of three sorbents tested (second step). Although activated carbon did not remove as much chlorpyrifos as did two types of steam-exploded wood, the level was less than that found resulting from a one-step (24 hours of mixing) treatment.

We are in the process of applying the information which we have obtained to field studies. We have constructed a prototype which is designed to cleanup 30 to 40 gallons of pesticide-laden rinsate in a one-step process. Difficulties have been encountered in developing a suitable filtration system associated with the apparatus. We have found that to achieve good wastewater cleanup when using finely ground lignocellulosic sorbents, removal of these particulates by filtration is essential because pesticides sorbed to these particles remain suspended in solution as a part of the particulate phase. Filters have been found to be too porous to achieve good cleanup, or they become clogged with particulates, resulting in unacceptably slow filtration rates. Because laboratory findings suggest that a two-step process is more effective in wastewater cleanup, we are redesigning the prototype unit to field test this hypothesis.

Table 3. Removal of Pesticides From a Two Component Pesticide Mixture in One Step Using Demulsification, Sorption, and Filtration.¹

<u>Treatment</u>	<u>Captan</u>		<u>Azinphos-methyl</u>	
	<u>mg/kg</u>	<u>% of initial concentration</u>	<u>mg/kg</u>	<u>% of initial concentration</u>
Initial	7764 ± 1860	100	8377 ± 976	100
Control, no Ca(OH) ₂	983 ± 717	13	1000 ± 576	11.9
Control	0 ± 0	0.00	46 ± 22	0.5
Activated Carbon, with Ca(OH) ₂	0.7 ± 1.2	0.00	10 ± 17	0.12
Peat Moss	0 ± 0	0.00	12 ± 21	0.14
Wood Fibers	0.7 ± 1.2	0.00	12 ± 21	0.14

¹ Azinophos-methyl as Guthion® 35% WP and captan as a 49% WP in 100 ml were mixed with 2.5 grams sorbent and 1 gram calcium hydroxide for 4 hours. The solution was allowed to settle (30 min) and filtered using a PVC column. Means and standard errors based on 3 replicates.

Table 4. Removal of Chlorpyrifos¹ from Aqueous Solutions Using Two Steps: Demulsification and Sorption, and Column Sorption and Filtration

<u>Treatment</u>	<u>Concentration (mg/kg)</u>	<u>% of initial concentration</u>
Initial	4866 ± 146	100
4 hour mix, no filtration (first step)	2841 ± 152	56
24 hour mix + filtration ² (first step only)	116 ± 38	2.4
Activated carbon (second step)	72 ± 2	1.5
Wood fiber (second step)	7 ± 2	0.13
Bleached wood fiber (second step)	1 ± 0	0.013

¹ Chlorpyrifos as Dursban® 4E (44.4% ai) at approximately 5000 mg/kg (1500ml) was mixed with 37.5 grams of steam-exploded wood fiber and 15 grams calcium hydroxide for 4 hours. After mixing, 100 ml was filtered

² through 2.5 grams sorbent contained in glass columns. Means and standard errors based on 3 replicates. Data from a previous experiment (Table 2) using one step demulsification/sorption and filtration was included here for comparison.

Disposal Phase

Studies on chemical and biological degradation of pesticides in bioreactors using solid substrate fermentation have been conducted at several levels. A benchtop composting system has been employed to examine the rate and metabolic fate of chlordane and diazinon using radiolabeled materials (Petruska, et al. 1985). Field studies using large (6.7 cu ft) bioreactors have been used to demonstrate efficacy of biodegradation of diazinon, chlorpyrifos, metolachlor, atrazine, carbofuran and chlordane (Mullins, et al., 1989; Hetzel, et al., 1989). Some compounds are degraded quite rapidly in bioreactors containing peat moss that is enriched with corn meal. High levels of Diazinon AG500 (7.4 liters; at an estimated 66,000 mg/kg) were not detectable one year after the last addition of diazinon (Hetzel, et al., 1989). Recent studies using ten gallon bioreactors to examine degradation of carbofuran and atrazine using enrichment microbial culture have provided some interesting results (Berry, et al., unpublished data). Carbofuran sorbed onto peat moss (1771 ± 29 mg/kg) and mixed with corn meal (10:1) was degraded to 7 ± 3 mg/kg (0.4% of the initial concentration) in days. One metabolite, carbofuran phenol increased in concentration from 0 (initial) to 198 ± 108 mg/kg (35 days) to 0 (50 days) indicating that degradation of carbofuran metabolites may continue towards complete mineralization. Solid substrate fermentation of atrazine-laden lignocellulosic materials (1455 ± 11 mg/kg) in 10 gallon bioreactors resulted in a concentration reduction to 117 mg/kg (8% of the initial concentration) in 104 days. The concentration of a metabolite hydroxyatrazine reached 232 ± 82 mg/kg, and decreased to non-detectable levels at 104 days. This also demonstrates the potential obliteration of pesticide metabolites contained in composting environments (Berry, et al., unpublished data).

CONCLUSIONS AND FUTURE NEEDS

The pesticide wastewater disposal strategy using sorption and biodegradation as a potential method for pesticide applicators is supported by the information presented. We have demonstrated that one-step demulsification, sorption and filtration provides effective removal of pesticides having low water solubilities. The pesticides tested represented several types of pesticides and formulations. Aqueous solutions containing two pesticides also were reduced to low concentration levels by the one-step process. An experiment with chlorpyrifos using a two-step demulsification-sorption, and sorption-filtration process indicates effective wastewater cleanup can be achieved in this manner.

Comparison of results obtained using this method with other reports is encouraging. Dennis and Kolbyinsky (1983) were able to remove 7 pesticides (100 mg/kg, totaling 700 mg/kg) contained in 400 gallons using 45 lbs of Calgon F-300R activated carbon in a Carbolator. After a 21 hour treatment, concentrations ranged from 0.5 to 5.6 mg/kg. Somich, et al. found that treatment of a mixture of 4 pesticides (ranging from 17 to 82 mg/kg using ozone and biologically active soil columns, 1 to 20% of the pesticides remained. It should be noted that in our experiments, much higher initial concentrations (approximately 5000 mg/kg) have been used resulting in removal of significant quantities of the pesticides from the aqueous phase.

The advantages of the system under development includes its relative simplicity, reliance on low cost materials, safety, and potential for using microbial enrichment cultures for other purposes. It is likely that our batch demulsification, sorption and filtration system can be replaced by column demulsification, sorption and filtration system that will be less cumbersome to the operator. The use of lignocellulosic sorbents in the system show good promise because of their low cost and potential availability. Peat moss is currently quite readily available at low cost (\$0.05/lb). Steam-exploded lignocellulosic materials represent a new source of sorbent materials that have shown good potential in our experiments. Virtually any lignocellulosic material (wood products, crop residues, recycled newsprint/paper) can be steam-exploded. Cost estimates of bulk crude or unprocessed steam-exploded wood are in the range of (\$0.07/lb) which would make it competitive with peat moss. Additional processing to produce specialized sorbents for the more polar (soluble) pesticides would add to the cost, but this might not prove to be prohibitive. Calcium hydroxide was selected as a demulsifying agent because of its effectiveness, relatively inexpensive and available. In fact, calcium hydroxide is marketed as burn lime, and sold as an agrichemical at many agricultural supply stores. Cost estimates for the pesticide rinsate disposal prototype under development range between \$600 to \$900.

A major advantage of a sorption disposal process is that once the rinsate has been treated, the sorbed pesticide no longer represents a major contamination threat, should it be spilled. It can be collected and moved to a bioreactor quite easily. It should also be pointed out that as pesticide-degrading enrichment cultures are developed for a variety of pesticides, it is likely that these consortia could be used to degrade pesticides in contaminated soil. In situ, on site bioremediation may be possible by amending soils with lignocellulosic materials and pesticide-degrading microbes.

Several questions regarding the rinsate solution cleanup process need to be answered. Acceptable pesticide levels contained in treated rinsates destined for release in sewer systems, land application, etc. need to be established before the system can be approved and implemented. If alkaline demulsification is used, it will be necessary to neutralize the treated rinsate. Laboratory studies have indicated that small amounts of dilute solutions (0.2N) of hydrochloric acid can neutralize the treated rinsate. Hydrochloric acid (as muretic acid) is commonly used to cleanup masonry and is relatively inexpensive and available at most hardware stores. Another concern is what can be done with spent compost material when it is removed from bioreactors? It should be noted that during the composting process, the volume of lignocellulosic material will be reduced by as much as 20%. Ideally, if pesticides are effectively degraded in the bioreactors, there will be little pesticide residue remaining in the spent matrix. If this is the case, it would appear that the material could be land farmed or alternately, incinerated. It is also possible that spent compost could be reused as a sorbent. Studies are planned to evaluate these and other options which might be available for final disposal of this material.

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LEGENDS FOR FIGURES

Figure 1. Conceptual/Functional Model for Pesticide Wastewater Disposal using Organic Sorption and Microbial Degradation.

The process involves two phases: a sorption phase, and a disposal phase.

The sorbent phase involves mixing pesticide-laden waste solutions (or suspensions) with organic sorbents (lignocellulosic materials such as peat moss, processed wood products, etc.). During this phase, pesticides are removed from the aqueous solution by demulsification and sorption processes.

The disposal phase begins with the separation of the sorbed pesticide from the treated aqueous solution by filtration. The aqueous solution may then be discarded and the pesticide-laden sorbent added to bioreactors. Microbial populations native to the matrix will degrade the pesticide.

Figure 2. Pesticide Biodegradation Using Nutrient Enrichment and Microbial Consortia.

A hypothetical representation of pesticide microbial degradation in a situation where an organic matrix and nutrients are available to microbial populations. As the bioreactor cycles from higher to lower energy content, microbial populations will also cycle reflecting the changes in substrate availability. Pesticides which are more resilient to microbial degradation will require longer reaction times.

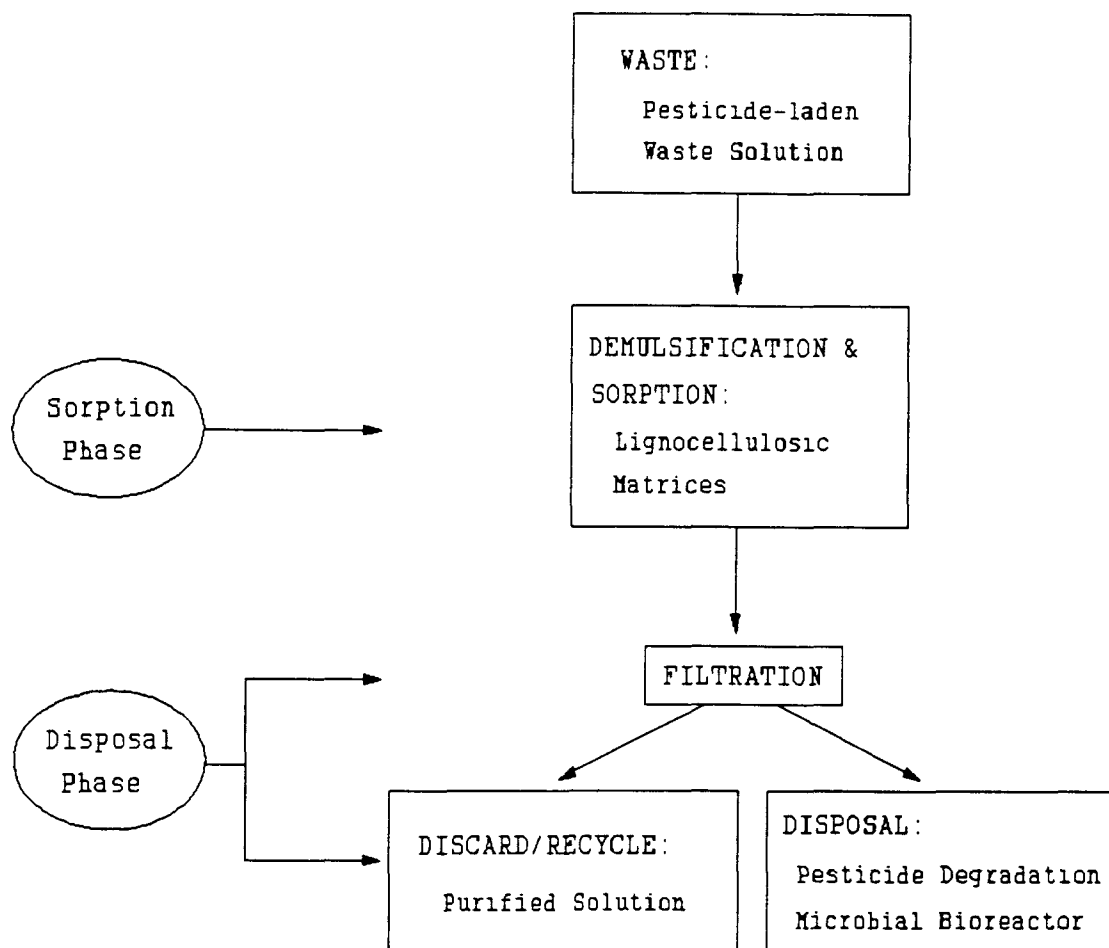


Figure 1. Conceptual/Functional Model for Pesticide Wastewater Disposal Using Organic Sorption and Microbial Degradation

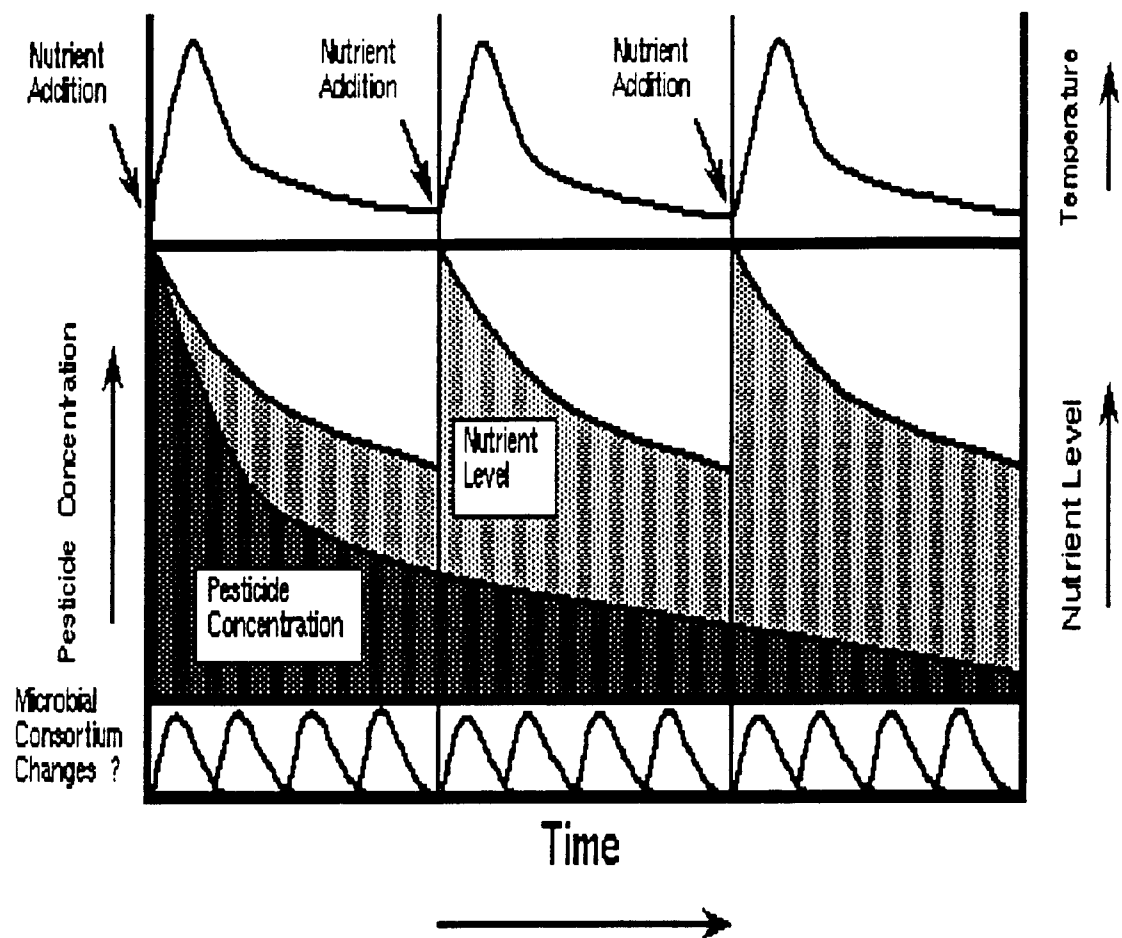


Figure 2. Pesticide Biodegradation Using Nutrient Enrichment and Microbial Consortia

Landfarming and Biostimulation for Decontaminating Herbicide Wastes In Soil

by

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ABSTRACT

The utility of landfarming for detoxifying pesticide waste in soil was examined at an agrichemical facility in Piatt County, Ill. Soil contaminated with the herbicides alachlor, atrazine, metolachlor, and trifluralin was excavated, and various amounts were applied to an adjacent field divided into corn and soybean plots. Dissipation of residues was monitored for nearly two years following application of the contaminated soil. Data from soil-treated subplots were compared to data from subplots in which herbicides were freshly sprayed. Herbicides did not dissipate significantly in excavated soil that had been stockpiled on the ground. After two years, alachlor and metolachlor concentrations in subplots with the highest application rate of contaminated soil were significantly greater than concentrations in the corresponding freshly-sprayed subplots. In subplots with the lowest application rate of contaminated soil, alachlor and metolachlor persistence did not differ significantly from persistence in plots freshly-sprayed with recommended application rates.

In the laboratory, soil amendment with 2% w/w ground corn or soybean residues or sewage sludge enhanced the degradation of 100 ppm alachlor compared to the degradation in unamended controls. Soil amendment with the crop residues at the rate of 10% w/w did not significantly increase the rate of alachlor degradation over that observed at the 2% level of amendment, however 10% sewage sludge significantly accelerated alachlor degradation when compared to the 2% amendment. Addition of 1000 ppm inorganic N in the form of NH_4NO_3 significantly inhibited alachlor degradation in both unamended and crop residue-amended soils compared to the degradation in soils without N or with 10 ppm N.

In two soil types alachlor disappeared fastest in water-saturated soils that were left unamended or amended with 2% w/w ground corn residue. Under the saturated conditions, alachlor was transformed into an unidentified nitrogen-containing product that was not detected under unsaturated conditions.

Soil inoculation with an alachlor-cometabolizing fungus produced a transient and marginal increase in alachlor degradation rate over the degradation rate in uninoculated soils. Combinations of 2% w/w corn residue amendment and fungal inoculation did not increase alachlor degradation over that caused by corn amendment alone.

INTRODUCTION

There is increasing recognition that soils at many agrichemical facilities and farms have been contaminated with high concentrations of pesticides through accidental spills or improper rinsing and discharge procedures (Long, 1989). High concentrations of ordinarily biodegradable pesticides can be extremely persistent in soil partly because they inhibit soil bioactivity (Wolfe et

al.,1973, Staiff et al.,1975, Davidson et al.,1980, Winterlin et al.,1989, Felsot and Dzantor 1990a, Dzantor and Felsot 1991). High concentrations of many pesticides are more mobile than low concentrations (Davidson et al.,1980). The combination of prolonged persistence and greater mobility increases the risk of surface and groundwater contamination by high pesticide concentrations and emphasizes the need for their expeditious cleanup.

The usual methods of disposing of waste contaminated soils are excavation and subsequent landfilling or incineration. These methods are expensive in economic and environmental terms, yet they do not always address the problem of contaminant detoxification. As more contaminated sites are discovered, it is becoming increasingly important to seek cleanup technologies that are permanent and duly cognizant of the widespread nature of the waste problem. More permanent solutions could involve decontamination by landfarming (also known as land application or land treatment), biological treatment (bioremediation), or combinations thereof.

Typical problems faced by agrichemical facilities were demonstrated at the Galesville Chemical Co. (GCC) in Piatt County, Ill. (Felsot et al. 1988). Soil to a depth of 1m along a railroad-right-of-way at the GCC facility had been found by the Illinois EPA (IEPA) to be contaminated with unacceptably high levels of herbicides (e.g. 24,000 ppm alachlor in the top 10 cm, 100 ppm at a depth of 60 cm). The herbicides were discharged to this area as a waste stream arising from the mixing, loading, and cleaning operations of GCC. Pesticide residues were detected in the ditches lining the streets of Galesville (population <500), and trace levels were detected in two water wells. IEPA ordered excavation and clean-up of the site.

To avoid obtaining a special waste permit and hauling contaminated soil to a municipal landfill, the Illinois Natural History Survey collaborated with IEPA and the management of GCC to landfarm the contaminated soil in corn and soybean plots on an adjacent farm. The soils were excavated and stored on the ground in piles, which were sampled to determine residue levels and microbial activity. After application of contaminated soil to soybean and corn plots, herbicide residues were monitored in the soil for nearly two years. Along with the landfarming studies, laboratory experiments were performed to identify factors that influence the degradation of alachlor, the prevalent chemical at the contaminated site, and determine how they may be manipulated to maximize degradation of the herbicide. We wish to present our observations on the dissipation of herbicides after landfarming of contaminated soils. In laboratory studies, we also show how degradation of alachlor is affected by nutrient amendment, soil moisture content, and microbial inoculation.

METHODOLOGY

Landfarming Experiment

Site Description--

GCC drained waste water from loading and tank rinsing operations onto a railroad right-of-way along the eastern edge of its property. Soil in this area, which covered approximately 1,215 m², was excavated and stored on the ground at the site in four piles designated as "waste pile soil" 1-4.

After excavation, the site was backfilled with soil from an adjacent fence row that was at a higher elevation and presumed not to be contaminated from the waste-water discharges. Waste-pile soil 2, which contained the highest levels of herbicides, was excavated from the top 60 cm of an area encompassing 122 m² and was used in subsequent land application experiments. Contaminants included alachlor, atrazine, metolachlor, and trifluralin.

During the spring of 1986, a four-acre field adjacent to the railroad right-of-way and to the north of the waste piles was divided into two, 2-acre fields for land application of waste-pile soil 2. The field had been planted to corn in 1985 and chisel plowed in the fall. In 1986, the southern half of the field was designated for corn production and the northern half was designated for soybeans. The soil was a mixture of Ipava silt loam and a Sable silty clay loam with an organic carbon content of 3.1 percent and moisture content of 22.6 percent w/w at 0.3 bar. Waste-pile soil had an organic carbon content of 5.6 percent and a moisture content of 30.3 percent w/w at 0.3 bar.

The corn and soybean plots were further subdivided into three replicated blocks containing six subplots, (12.3m x 12.3m or 40 ft x 40 ft), that were treated with contaminated soil or freshly sprayed with herbicides (see below for details of the treatments). Each plot was surrounded by a 6.2m x 6.2m untreated buffer zone. Corn and soybeans were planted within one week of soil and spray applications. Each plot contained 16 crop rows spaced 76 cm apart.

After the crop was harvested in 1986, the plots were left untilled, and benchmarks placed so that plots could be re-established in the same positions during the 1987 crop year. In May, the field was treated with paraquat to burn down perennial weeds. On June 10, 1987, the field was prepared by chisel plowing in a north-south direction, parallel to the old crop rows. Untreated border areas around each plot prevented soil from one subplot from contaminating an adjacent subplot. Corn and soybeans were planted along the north-south direction on the same day. No further applications of soil or herbicides were made.

Application of waste-contaminated soil--

Persistence of herbicides in landfarmed, contaminated soil was compared to persistence of herbicides that were freshly sprayed with amounts calculated to yield concentrations in soil similar to those in waste-pile soil 2. Rates of application were determined on the basis of the alachlor concentration since it was the most prevalent contaminant. Treatments were designated by the following codes:

1. CHECK: untreated soil;
2. 1x-N: herbicide spray mixture applied in 1986 at the rate normally recommended for alachlor, 3.36 kg active ingredient [a.i.]/ha; the mixture consisted of alachlor, atrazine, metolachlor, and trifluralin in proportion to the concentrations found in waste-pile soil 2 in May, 1986 (74, 48, 17, and 3 mg herbicide/kg oven-dry soil [ods], respectively, Felsot et al. 1988);
3. 5x-N: herbicide spray mixture applied in 1986 at 18.6 kg a.i./ha, five times the recommended alachlor rate;
4. 1x-S: contaminated soil from waste-pile 2 applied at the equivalent alachlor rate of 3.36 kg a.i./ha;
5. 2.5x-S: waste-pile soil applied at the equivalent alachlor rate of 8.4 kg a.i./ha;

6. 5x-S: waste-pile soil applied at the equivalent alachlor rate of 18.6 kg a.i./ha.

Soil was applied with a manure spreader. The spreader was filled by using a front loader that was calibrated by weighing the entire loader with and without a full load of soil. Within 24 hours after application of contaminated soil and herbicide sprays, all plots were disked twice in two directions to incorporate the pesticides and soil. Buffer zones were also disked, which served to clean equipment and minimize cross-contamination between treatment plots.

Soil sampling, preparation, storage--

Soils were collected from field plots with a 5-cm diam. bucket auger during 1987 and early 1988. Two subsamples of soil from depths 0-15 cm and 15-30 cm were collected from each replicated subplot. The subsamples were combined in the field and returned to the laboratory on the same day. The auger was washed with methanol between subsamples taken by soil depth and between different subplots. Soils were sieved through a 3mm mesh screen and stored at 2°C for up to one month prior to extraction. Herbicide residues remained stable under these conditions for at least four months (Felsot et al. 1988).

Extraction and Analysis--

Fifty grams of soil were slurried with 20 mL of distilled water and extracted twice with 90 mL of ethyl acetate as described by Dzantor and Felsot (1989) for methyl carbamate insecticides. All herbicides were qualitatively analyzed by packed column gas-liquid chromatography (GLC, Packard Model 328) with nitrogen-phosphorus specific detection. Residues were separated isothermally at 190°C on a 90 cm x 0.2 mm i.d. glass column packed with 5% Apiezon + 0.1% DEGS. Residues were quantified by the method of external standards, which were used to calibrate the GLC response each day of analysis.

Biostimulation and Bioaugmentation Experiments

Soil Incubation--

The soil used in most of the experiments was collected from untreated experimental plots at the Galesville landfarming site. Freshly collected soil was air dried to about 20% moisture content, passed through a 2mm sieve, and stored at 5°C until needed. All experiments were performed in triplicate with 30 g ods in 250 mL erlenmeyer flasks. An emulsifiable concentrate of alachlor (Lasso, 4EC; 45.1% a.i) was added as a dilution in water to give 100 mg ai/kg in soil. After treatment, soils in individual flasks were brought to desired moisture tensions by additions of distilled water. The flasks were covered with parafilm and the soils were incubated at 25°C for specified periods of time. The soils were aerated once a week. At the start of each experiment and at specified intervals during the incubation period, three flasks from each treatment were frozen (-10°C) for chemical assay. Soil in three flasks from each treatment were slurried with 15 mL of water and extracted twice by stirring with 90 mL of ethyl acetate. Parent alachlor was determined by packed column gas-liquid chromatography as described above.

Effect of nutrient amendments on alachlor degradation--

To determine the effect of organic amendments on alachlor degradation, bulk soil samples were weighed into large plastic bags and mixed thoroughly with either corn plant residue, soybean plant residue or municipal sewage sludge at the rate of 20 or 100g/kg ods (2 or 10% w/w) before distribution into flasks. The amendments had been ground to pass a 2 mm sieve. Soils without organic amendment served as controls.

To examine the effect of inorganic nitrogen on alachlor degradation, soils were amended with NH_4NO_3 to yield 10 or 1000 mg N/kg ods. Soils without NH_4NO_3 served as controls. Combinations of the crop residue amendments and inorganic N were also tested.

Effect of fungal inoculation on alachlor degradation--

To examine the effect of microbial inoculum on alachlor degradation, soils were inoculated with an alachlor-cometabolizing *Fusarium* sp. (Felsot and Dzantor 1990a). The inoculum was grown in a peptone-yeast extract-alachlor (100ppm alachlor) medium on a rotary shaker at 25°C. After three days, growth was harvested by centrifugation at 13,000 rpm (25931 x g) for 10 mins. The cells were washed once and resuspended in autoclave-sterilized phosphate buffer containing 100ppm alachlor. Washed cells were stored at 2°C until needed. Soils were inoculated within 24h of harvest and within one to two hours after addition of alachlor.

RESULTS AND DISCUSSION

Landfarming Study

During the planning of the landfarming experiment, we developed four criteria for successful remediation of the herbicide-contaminated soils: (1) no significant difference after one growing season between herbicide residues in soil from waste-treated plots and freshly sprayed plots; (2) no contamination of shallow groundwater above maximum contaminant levels (MCLs) suggested by U.S. EPA; (3) no significant residues in grain; (4) no significant toxicity to crops as measured by phytotoxicity assays in the field or greenhouse and by comparison to yields from the untreated check plots. The extent to which criteria 2-4 were met has been presented elsewhere (Felsot and Dzantor 1991), so this discussion will be limited to herbicide dissipation during landfarming.

Herbicide residues in soil--

Soil samples collected within a day after application of waste-pile soil and herbicide sprays afforded a comparison of the initial concentration of herbicides found in all experimental plots compared to the theoretical amounts corresponding to the various rates of application. On the basis of a 3.36 kg a.i./ha application rate (i.e., 1x treatment), the soil to a depth of 15 cm should have contained theoretically 1.71, 4.28, and 8.55 ppm of alachlor for a 1x, 2.5x, and 5x application rate, respectively. The percentage of theoretical recovery ranged from 33.6% for the 5x-S soybean treatment to 110% for the 1x-N corn treatment. Percentage of theoretical recovery for all treatments combined was 66.5+/-23.0%.

Another concern was the initial concentrations of herbicides in soil treated plots compared to the corresponding treatments in sprayed plots. With the exception of the 5x-S and 5x-N alachlor treatments in the soybean plots, there were no significant differences in recovery of herbicides between soil-applied and sprayed herbicide on day 0 in the top 15 cm of the profiles (Fig. 1, 2). Nearly twice as much alachlor was recovered from the 5x-N treatment in the soybean plot as from the 5x-S treatment. This difference may reflect sampling error because concentrations of alachlor recovered later from the 5x-S treatment were much higher than the initial recoveries (Fig. 1).

During the first 140 days of sampling, high variability precluded the detection of significant differences between corresponding rates of application of fresh herbicide and contaminated soil. By days 380 and 520, however, significantly more alachlor and metolachlor were recovered from 5x-S treatments than from 5x-N treatments (Fig. 1, 2). No statistically significant differences were seen between 1x-N and 1x-S or 2.5x-S treatments, although the latter two were often numerically greater than the 1x-N treatment (data not shown). Recovery of the other herbicides did not differ significantly among treatments on these sampling days. Residues at the 15-30 cm depth did not differ among treatments.

The three-to-10 fold greater recoveries of alachlor and metolachlor from the 5x-S treatment than from the 5x-N treatment suggested that the residues in the aged, contaminated soil were less available to microbial degradation. The residues recovered 1.5 years after application were more than half of what would be expected after a recommended application rate of 3.36 kg ai/ha. The prolonged persistence of alachlor and metolachlor in waste-pile soil and in the field plots is not characteristic of the comparatively rapid degradation of these compounds when used at normal rates of application. Alachlor half-life generally ranges from 2-4 weeks (Sharp 1988), and it is less persistent than metolachlor, whose half-life is highly variable (13-108 days) depending on moisture and temperature conditions (LeBaron et al. 1988). On the other hand, several studies have shown that high concentrations of pesticides, which are characteristic of waste, are unusually persistent (Davidson et al. 1980, Stojanovic 1972, Junk et al. 1984, Schoen and Winterlin 1987, Wolfe et al. 1973). In our study, alachlor and metolachlor were still found in waste-pile 2 at concentrations of 23 and 17ppm, respectively, two years following excavation.

Two hypotheses were developed to explain the prolonged persistence of alachlor and metolachlor in the waste-pile soils and in the field plots. First, studies of high concentrations of pesticides in soil have shown that microbial populations can be severely reduced, which may be the critical factor for explaining the prolonged persistence of those chemicals (Stojanovich 1972, Davidson et al. 1980, Dzantor and Felsot 1991). We therefore hypothesized that the microbial populations in the waste-pile soils were reduced as a result of exposure to toxic concentrations of the herbicides.

The inhibition of microbial populations, however does not explain adequately the prolonged persistence of the herbicides after mixing waste-pile soil with uncontaminated soil during land application. The herbicides in waste-pile soil could be considered to be aged (Smith et al. 1988), i.e., the chemicals were in contact with the soil for an extended period of time. Aged residues have been shown to be less desorbable (McCall and Agin 1985, Steinberg et al. 1988) and in some cases seem to degrade more slowly than freshly-applied chemicals (Steinberg et al. 1988, Byast and Hance 1981). Thus, a second hypotheses, but

not mutually exclusive of the first, ascribes the slow degradation of the herbicides to a lack of pesticide bioavailability upon aging in the soil.

Biostimulation Study

The prolonged persistence of alachlor after contaminated soil had been spread on cropland suggested that landfarming alone may not be sufficient for remediating all contaminated soils regardless of contaminant composition, concentration, or age. We previously reported that amending soils in the laboratory with 2% corn or soybean residues enhanced the degradation of 100 ppm but not 1000 ppm of freshly applied alachlor (Felsot and Dzanter 1990a). If degradation of up to 100 ppm of herbicide can be thus accelerated in the field, then biostimulation may be the strategy for detoxifying high concentrations of contaminants after they have been diluted by landfarming, or for detoxifying moderately high concentrations of pesticides in situ. Successful application of this strategy depends on the understanding of the soil environmental factors that control degradative processes. In our continuing efforts to stimulate the degradation of alachlor in soil, we have further investigated the effects of types and levels of nutrient amendments, soil moisture content, combinations of moisture and nutrient amendments, and bioaugmentation with fungal inoculation.

Effect of nutrient amendments on alachlor degradation--

Similar to our previous observations, 100 ppm of alachlor degraded more rapidly in corn or soybean residue-amended (2% w/w) soils than in unamended soil (Fig. 3,4). Soil amendment with 10% of either type of crop residue produced only marginal increases in alachlor degradation over that observed with 2% amendment. In a more recent experiment we observed that alachlor degraded at similar rates in soils that were amended with either 2% corn residue or 2% municipal sewage sludge. But unlike corn residues, soil amendment with 10% sewage sludge caused a significant enhancement in alachlor degradation over that observed at the 2% level of amendment (Fig. 5). Within 28 days, <12% of the initial 100ppm dose of alachlor was recovered in soils amended with 10% sewage sludge. In contrast, about 40% of the initial dose was recovered in the soils amended with 2% corn residue or sewage sludge; the unamended soil still contained approximately 70% of the added alachlor after 28 days. Since the enhancement of the rate of alachlor degradation did not appear to be a linear function of the level of sewage sludge, we are now attempting to determine the minimum sewage sludge application rate at which degradation is optimized.

In a preliminary experiment, we observed that addition of NH_4NO_3 to soil to give 1000 ppm N appeared to inhibit the stimulatory effect that crop residue amendment had on the degradation of 100 ppm alachlor (Felsot and Dzanter 1990 b). Recoveries of the herbicide in residue amended soils that were also treated with N were not significantly different from recoveries in unamended soils. Because we did not determine the effect of inorganic N on alachlor degradation in unamended soil in preliminary experiments, a follow up experiment was performed to examine the effect of different levels of inorganic N with or without crop residue amendments on the degradation of 100 ppm alachlor.

After 56 days, alachlor recoveries were highest (>80% of initial dose) in unamended soils that were also treated with 1000 ppm N (Fig. 6); the lowest recoveries of the herbicide (4-5 %) were from crop residue-amended soils that were treated with 0 or 10 ppm N. The 1000 ppm N addition reduced the stimulatory effect of organic residue amendment, as we have had observed in preliminary

studies, but alachlor dissipation was still significantly faster than in all unamended soils (Fig. 6). Other researchers have shown that certain forms and levels of inorganic N inhibit degradation of some pesticides. For example, the degradation of parathion in soil was inhibited by 100 ppm N in the form of $(\text{NH}_4)_2\text{SO}_4$ but not as NH_4NO_3 (Ferris and Lichtenstein 1980). However, at 182 ppm N equivalent, NH_4NO_3 also significantly reduced degradation of parathion. The inhibition of pesticide degradation by high concentrations of inorganic N may be quite important. Operations at many agrichemical facilities and farms may involve nitrogen fertilizers as well as pesticides; it is quite likely that soils contaminated by pesticides at some of these sites may also be contaminated by high levels of N fertilizers.

Effect of Soil Moisture Tension on Degradation of Alachlor--

Figures 7 and 8 show the effects of soil moisture content on the degradation of 100 ppm of alachlor in two soil types that were either left amended or amended with 2% ground corn residue. The second soil type, coded as soil 52, was collected from part of an experimental field at the Illinois Natural History Survey. It is a Drummer-Catlin mixture with an organic carbon content of 2.0%, and moisture content of 24.7% w/w at 0.3 bar. Alachlor degradation was investigated at soil moistures ranging from wilting coefficient (15 bar), corresponding to 11.6 and 12.1% w/w for GCC soil and soil 52, respectively to saturation (0 bar) or 100% w/w moisture content in both soil types.

Alachlor recovery from both soil types decreased as soil moisture content increased (decreasing moisture tension) (Fig. 7); the combination of 2% corn residue amendment and increasing moisture content stimulated further dissipation of parent alachlor from both soils (Fig. 8). Several workers have demonstrated enhanced degradation of chlorinated pesticides in anaerobic soils amended with organic materials. For example, degradation of pentachlorophenol in flooded soils was enhanced by addition of anaerobic sewage sludge (Mikesell and Boyd 1988), and DDT degraded significantly faster in anaerobic soils amended with 1% w/w glucose (Parr et al 1970) or rice straw (Mittra and Raghu 1986). Also, gamma-hexachlorocyclohexane degraded significantly faster in flooded soils with green manuring compared to unamended soils. (Drego et al., 1990).

In this study alachlor also dissipated rapidly in unamended soil 52 under saturated conditions (Fig. 7). But the rapid disappearance of parent alachlor under saturated conditions may be misleading because, as we have observed in this and other unpublished experiments, the loss of parent alachlor under these conditions was accompanied by the appearance of an unidentified nitrogen-containing metabolite that was not detected under non-saturating conditions. Effective bioremediation would ideally require that transformation products be removed as rapidly as parent compounds.

Effect of Fungal Inoculation on Alachlor Degradation--

We have previously reported that inoculation of soil with an alachlor-cometabolizing fungus at the rate of 0.015% w/w ods caused a transient marginal increase in the rate of degradation of 100 ppm alachlor, compared to the rate of degradation in uninoculated controls (Felsot and Dzantor 1990a). The small and temporary nature of the increase in degradation caused us to question the efficiency and competitiveness of the fungus once it has been reintroduced into the soil. In an attempt to answer this question, we examined the effect of a higher level of fungal inoculation (0.045%) on the degradation of alachlor in soils that were left unamended or amended with 2% corn residue.

Figure 9 shows that within 28 days in unamended soil, significantly more alachlor was recovered from uninoculated treatments than from inoculated ones. During the same period, soils inoculated at the rate of 0.045% w/w showed a slightly higher rate of alachlor loss than those inoculated at the rate of 0.015%. By day 56, alachlor recoveries from all unamended treatments were practically identical, indicating that the stimulation in degradation rate by the fungal inoculum had waned over time. Amending soils with 2% corn residue completely masked the effect of fungal inoculation (Fig. 10)

CONCLUSIONS

Landfarming and biostimulation are becoming practical strategies for detoxification of wastes in soils. The procedures involved are environmentally more desirable than traditional "out of sight - out of mind" disposal methods such as landfilling. The technologies are also more readily affordable by small scale operations than the more expensive and less accessible methods such as incineration. However, these waste cleanup methods have certain limitations that require careful evaluation prior to implementation. Our landfarming experiments revealed that herbicides applied as waste soil generally degraded more slowly than fresh applications, particularly at high loading rates. Another concern is the potential for crop phytotoxicity when the waste soil contains a diverse mixture of herbicides. A combination of excessively high levels of contamination and space limitation may necessitate higher than normal loading rates during landfarming. Prolonged persistence and the possibility of crop phytotoxicity may restrict the use of landfarming.

The strategy of biostimulation is based on the so called principle of microbial ubiquity (Mathewson and Grubbs 1989) which assumes that the requisite degrader microorganisms are present at all contaminated sites and only their appropriate stimulation is necessary to accelerate the degradation of each contaminant. However, soils do differ in their abilities to be stimulated to degrade individual compounds (Dzantor and Felsot 1990). Often, these differences are related to differences in microbial profiles and accompanying specificities to degrade different compounds. Differences in microbiological profiles also imply that soil manipulations that may stimulate degradation of one compound may not necessarily act on a different compound; finding the right conditions that will accelerate degradation of pesticide mixtures may be difficult. Even if the requisite organisms are present at a contaminated site, it may be impractical to stimulate them to overcome toxic effects of certain chemicals if concentrations are too high.

Our fungal inoculation experiments have demonstrated to us the difficulty of using bioaugmentation alone to decontaminate soils. First the procedures for obtaining individual or consortia of microorganisms to degrade specific parent compounds and their metabolites may be tedious and time-consuming; thus, the approach may not be amenable for contaminated sites that require immediate cleanup. More importantly, this approach may not be feasible because of poor competitiveness of laboratory-obtained degrader microorganisms once they have been reintroduced into soil, as our results have suggested.

In summary, our results suggest that no one strategy alone may be sufficient to clean up all contaminants regardless of composition, concentration or age. The limitations have been discussed to stimulate debate rather than to diminish the enormous potential of landfarming and bioremediation. We have yet

to explore all the combinations of landfarming, biostimulation, or bioaugmentation necessary to accelerate contaminant detoxification. An understanding of the microbial ecology of biodegradation may be the key to the successful use of these strategies to decontaminate wastes in soils.

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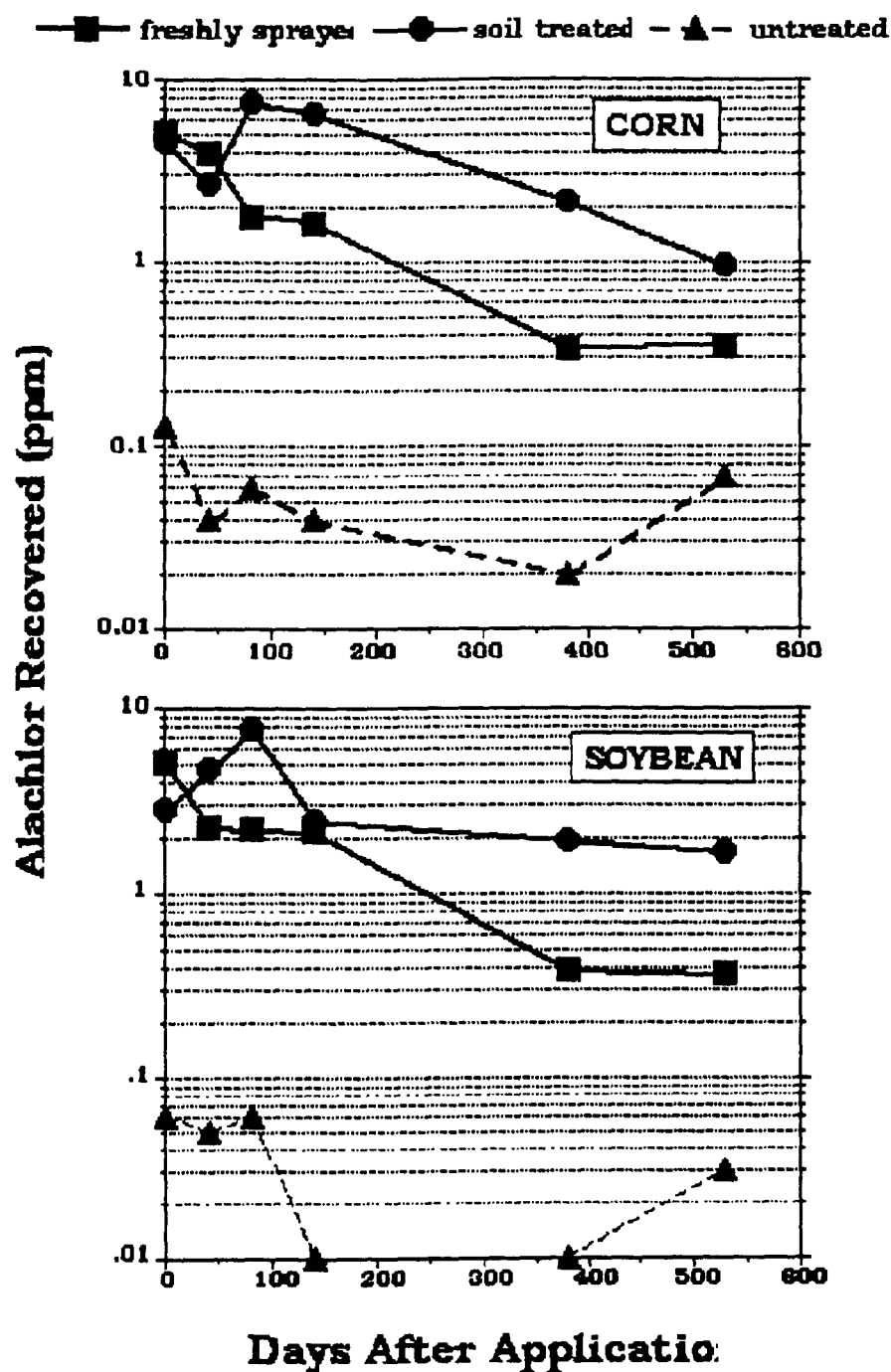


Figure 1. Alachlor residues in corn and soybean plots treated with fresh herbicide sprays or with herbicide-contaminated soil at the equivalent rate of 16.8 kg a.i./ha.

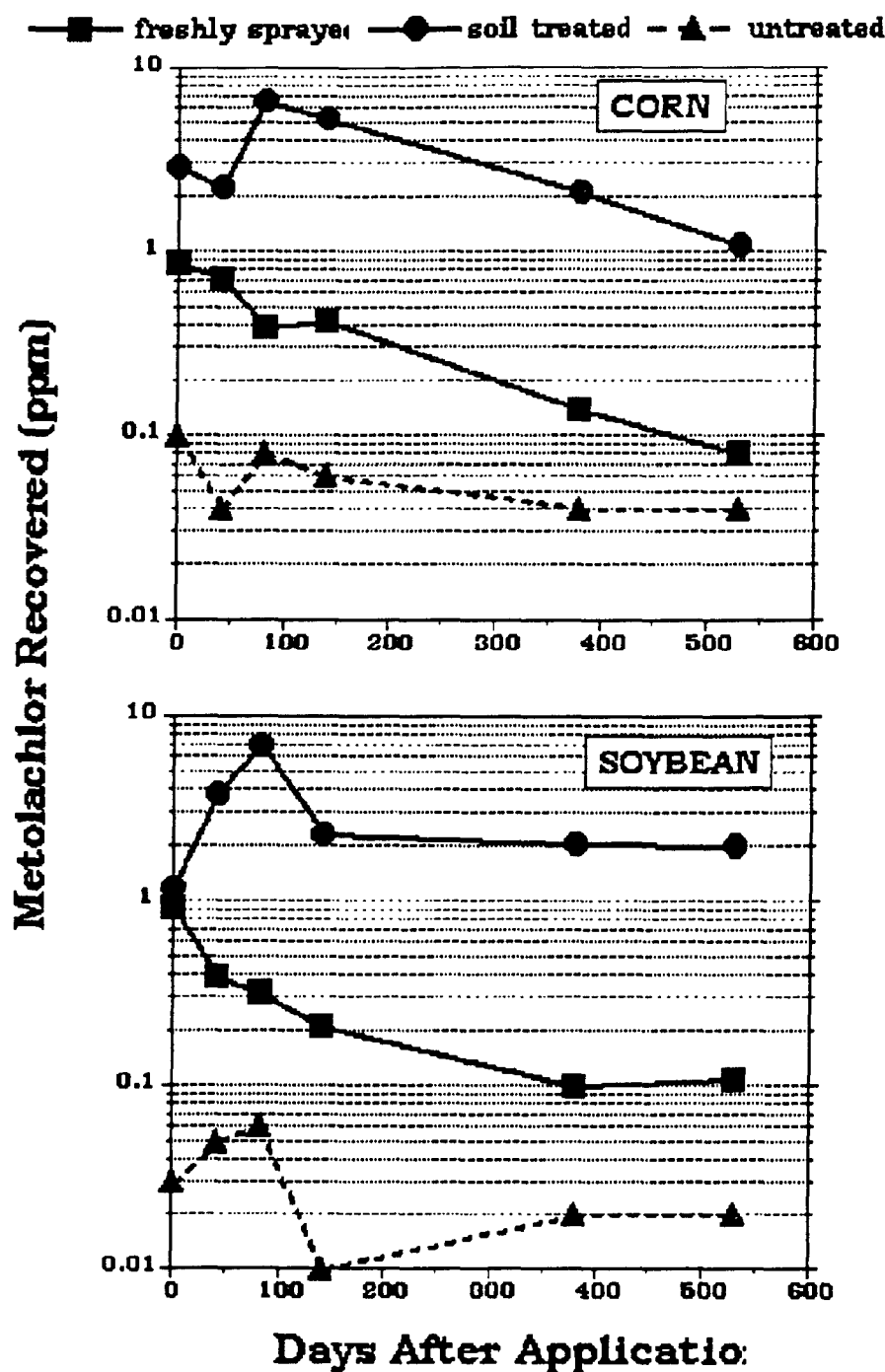


Figure 2. Metolachlor residues in corn and soybean plots treated with fresh herbicide sprays or with herbicide-contaminated soil at the equivalent rate of 2.85 kg a.i./ha.

Figure 3. Effect of Corn Residue Amendment on Degradation of 100 ppm Alachlor in GCC Soil

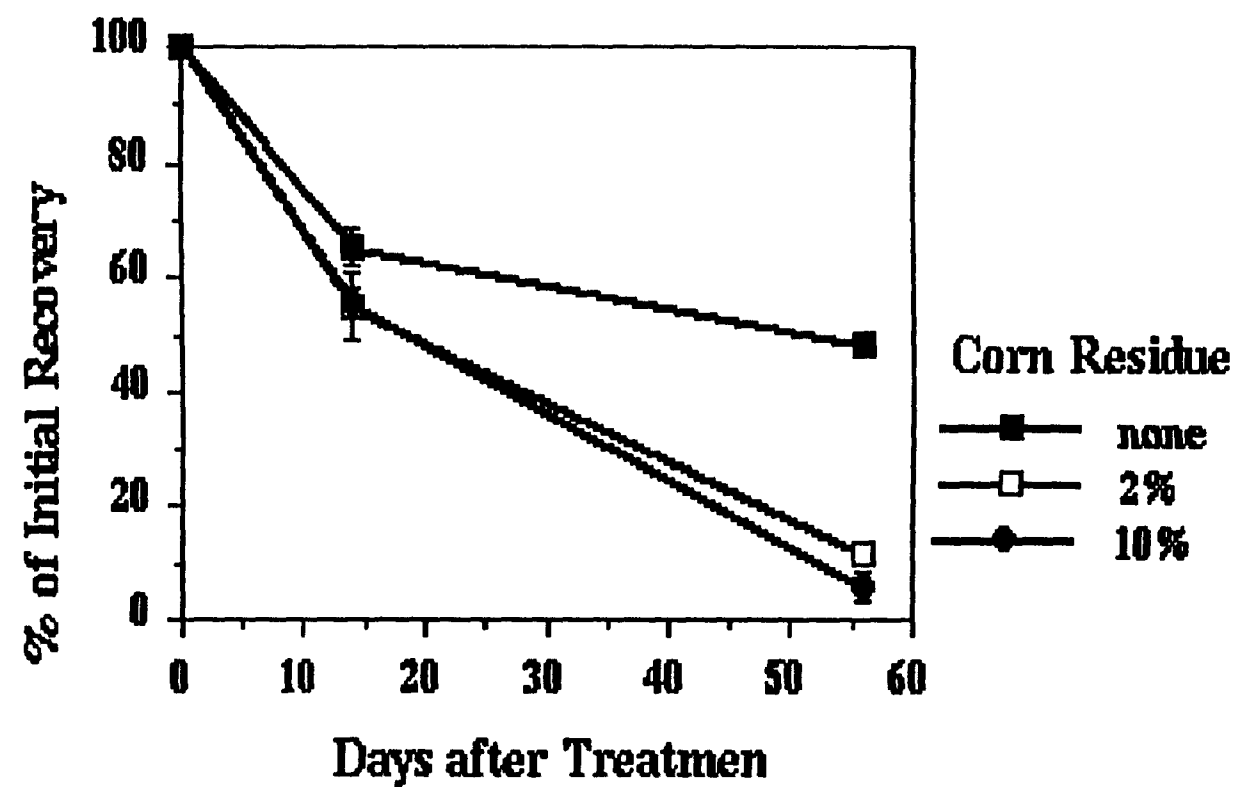


Figure 4. Effect of Soybean Residue Amendment on Degradation of 100 ppm Alachlor in GCC Soil

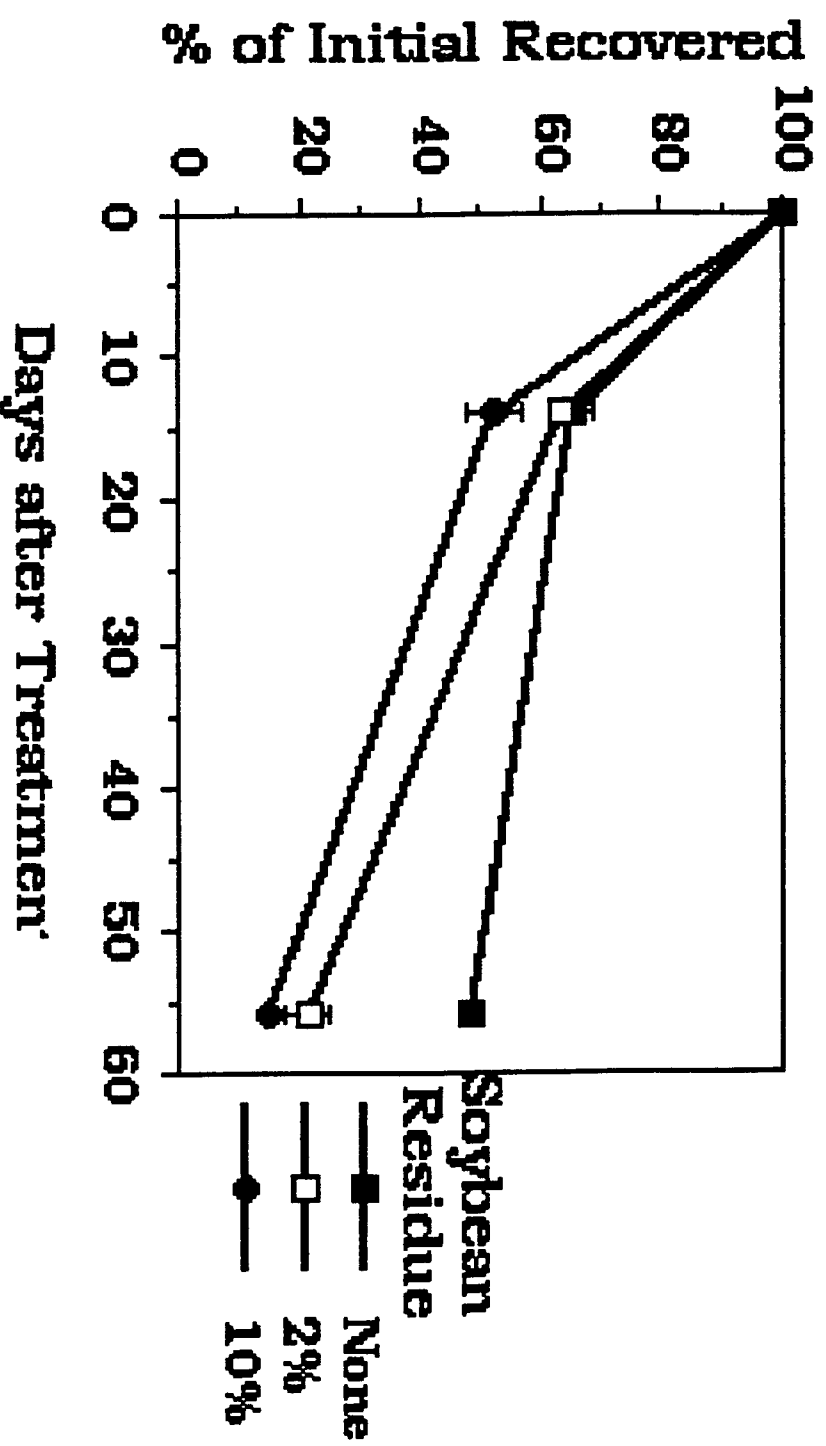


Figure 5. Effect of Type and Level of Amendment on Degradation of 100 ppm Alachlor in GCC Soil

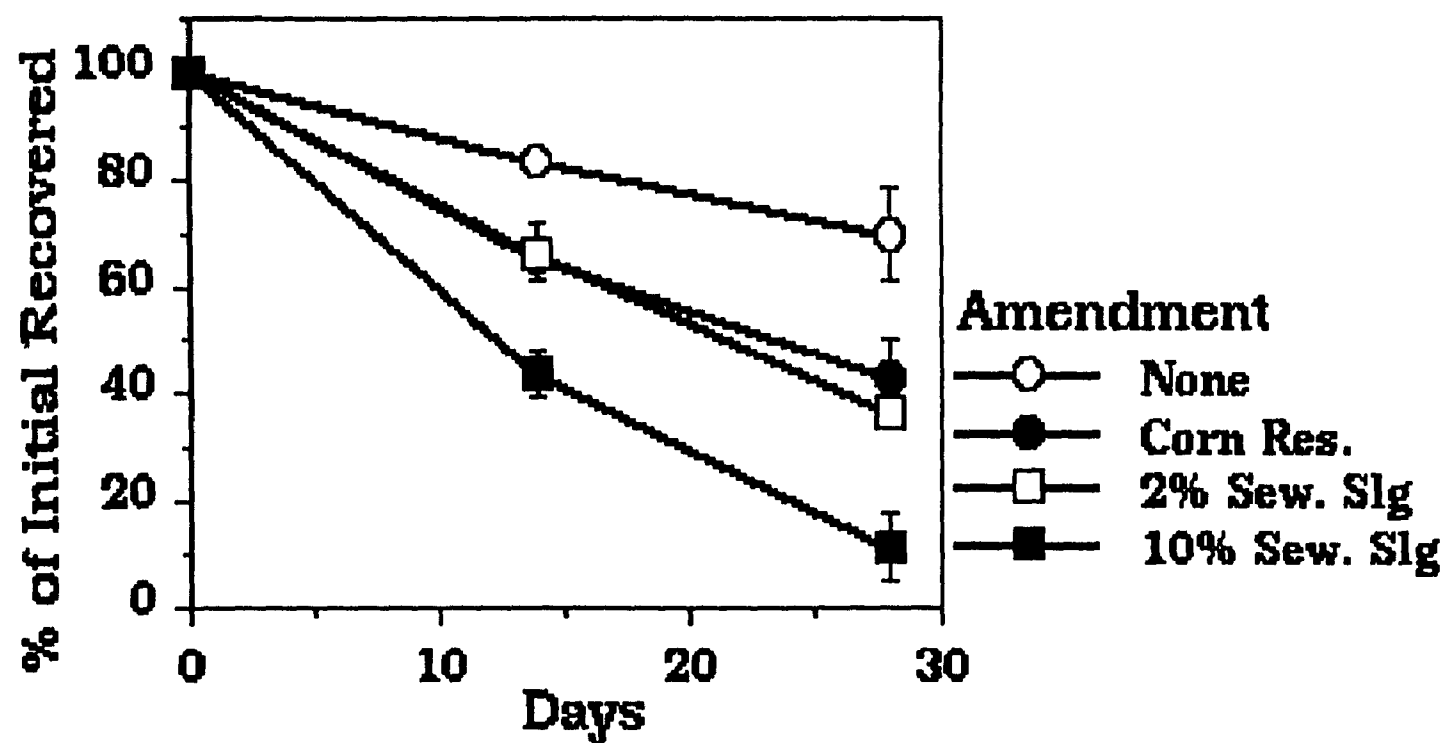


Figure 6. Effect of Inorganic N on Degradation of 100 ppm Alachlor in GCC Soil

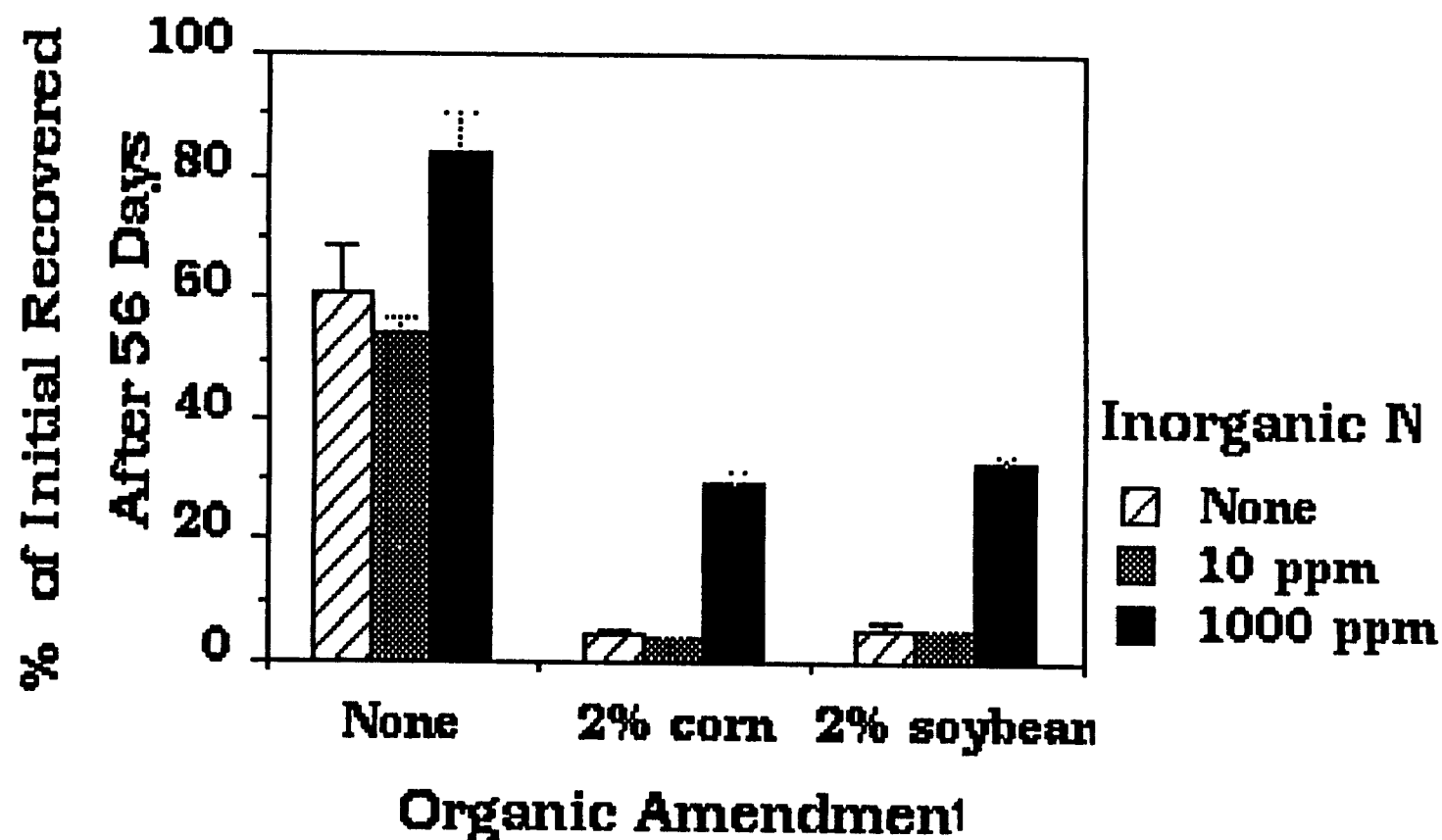


Figure 7. Effect of Moisture Tension on Degradation of 100 ppm Alachlor in 2 Soil Type

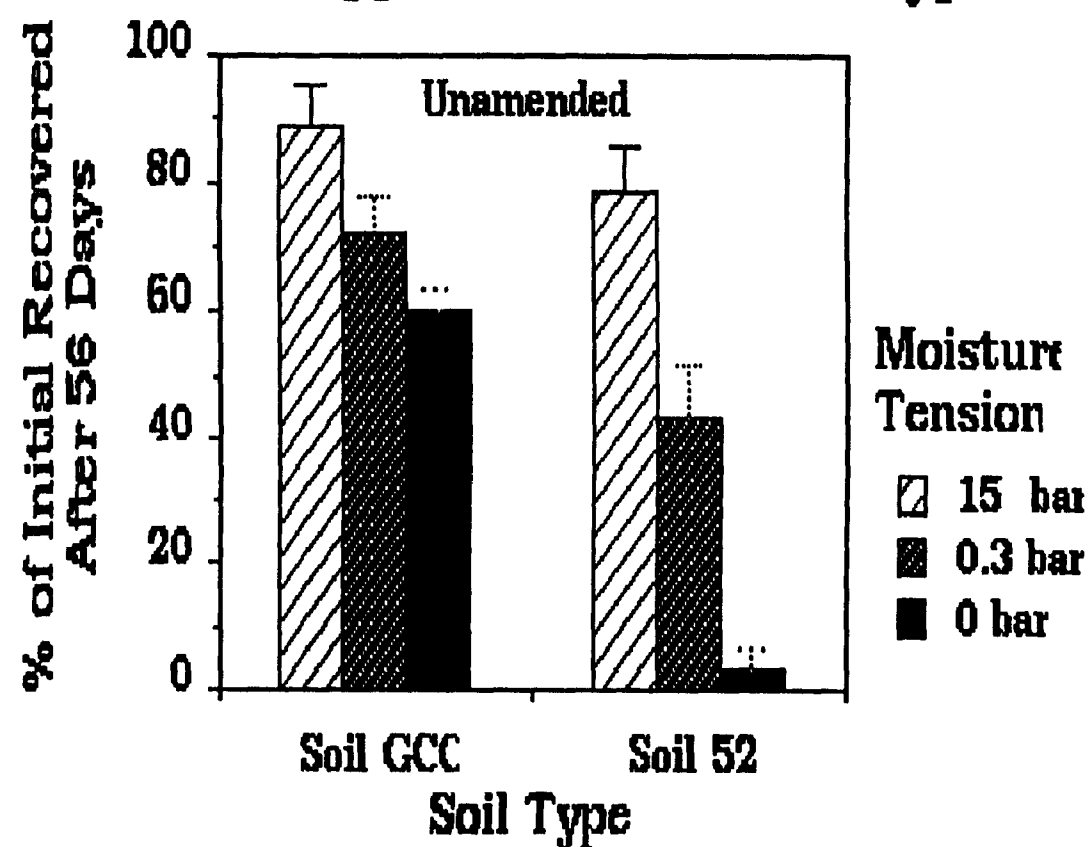


Figure 8. Effect of Moisture Tension on Degradation of 100 ppm Alachlor in 2 Soil Types

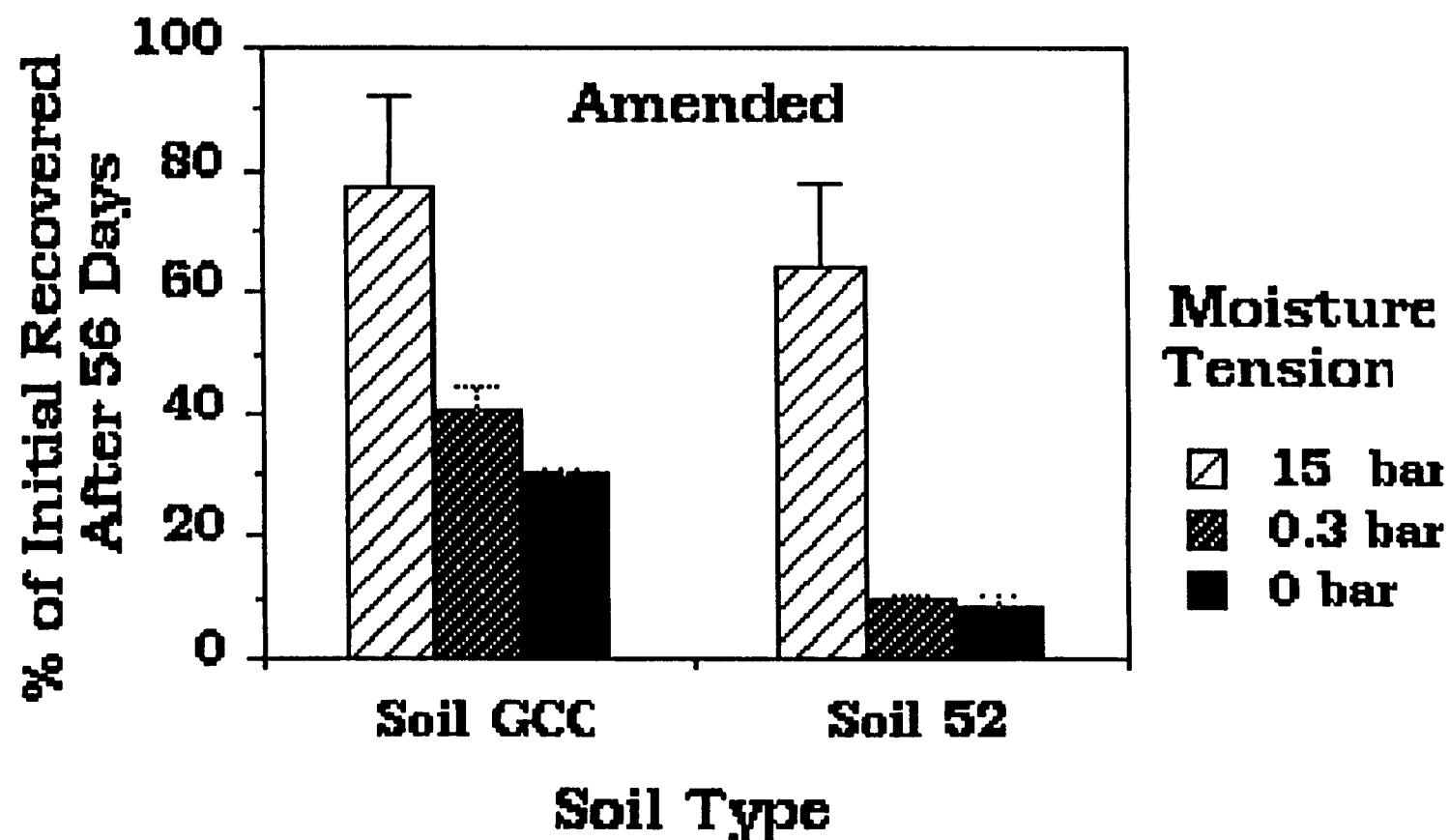


Figure 9. Effect of Fungal Inoculation on Degradation of 100 ppm Alachlor in GCC Soil

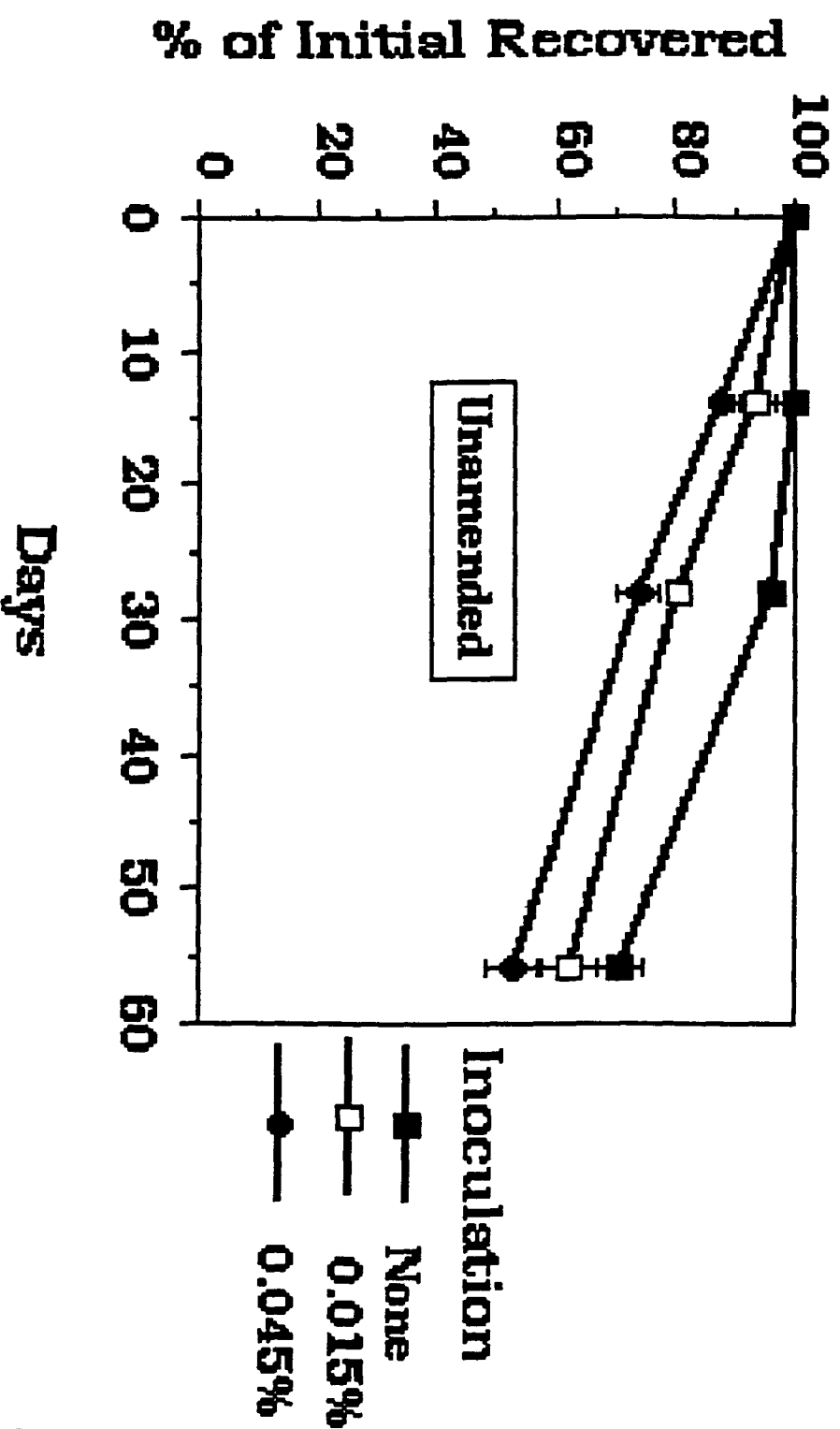
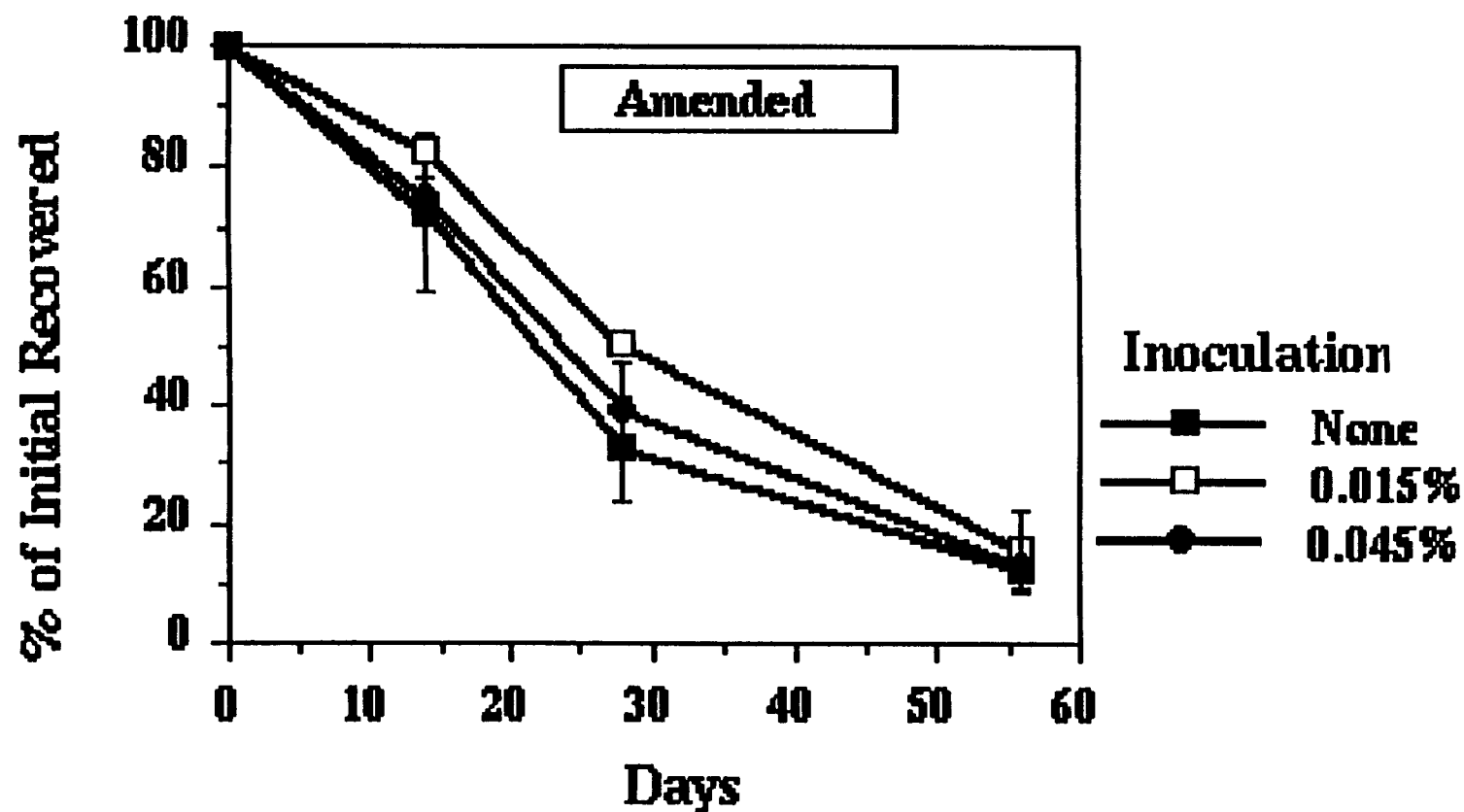


Figure 10. Effect of Fungal Inoculation on Degradation of 100 ppm Alachlor in GCC Soil



Removal of Pesticides From Aqueous Solutions Using Liquid Membrane Emulsions

by

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ABSTRACT

Extractive liquid membrane technology is based on a water-in-oil emulsion as the vehicle to effect separation. An aqueous internal reagent phase is emulsified into an organic phase containing a surfactant and optional complexing agents. The emulsion, presenting a large membrane surface area, is then dispersed in an aqueous continuous phase containing the species to be removed. The desired species is transferred from the continuous phase through the organic liquid membrane and concentrated in the internal reagent phase. Extraction and stripping occur simultaneously rather than sequentially as in conventional solvent extraction.

Liquid membranes have been used to extract phenol, acetic acid, other weakly ionized acids and bases, and various metallic species from aqueous solution with high efficiency. In this work, experiments were conducted to assess the feasibility of using liquid membranes to extract pesticides from rinsewaters typical of those generated by fertilizer/agrichemical dealers. A liquid membrane emulsion containing 10% NaOH as the internal reagent phase was used to extract herbicides from aqueous solution at a continuous phase:emulsion ratio of 5:1. Removals of 2,4-D, MCPA, Carbaryl, Diazinon, and Atrazine were 85.4, 61.2, 80.2, 73.9, and 92.9%, respectively, after 15-20 minutes mixing time.

INTRODUCTION

There are over 14,000 agricultural chemical dealers ("dealers") in the United States. Dealers sell fertilizers and/or pesticide products; they also custom mix and apply these products. Incidental spillage of fertilizer/pesticide products may occur during handling and can result in the accumulation of hazardous chemicals in the soil, surface water and groundwater. Chemicals can also accumulate in these media when tanks and application equipment are rinsed with water and the rinsewater is not disposed of or recycled properly. As dealers continue their efforts to contain, collect, and recycle their wastes and spills, there will be an increased need for technologies to treat that portion of the wastes and spills that cannot be recycled.

The National Fertilizer and Environmental Research Center (NFERC) has recognized that the waste treatment problems currently facing dealers are real and cannot be ignored. Therefore, in March 1990, a multidisciplinary NFERC project team was organized to identify, research, develop, and demonstrate waste treatment and site remediation technologies for dealers. The work reported in this paper was undertaken as part of the research phase of this program.

OBJECTIVE

The primary objective of this research project was to assess the feasibility of using liquid membrane emulsions to remove herbicides from aqueous solutions similar to the rinsewaters generated at dealer sites. Several experiments were also run with aqueous solutions of phenol or acetic acid to gain experience in the experimental techniques involved in the preparation and handling of liquid membrane emulsions.

The five herbicides investigated in this study were:

- (1) 2,4-D (2,4-dichlorophenoxyacetic acid)
- (2) MCPA (4-chloro-0-tolyloxyacetic acid)
- (3) Carbaryl (1-naphthyl N-methylcarbamate)
- (4) Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine)
- (5) Diazinon (O,O-diethyl-O-[2-isopropyl-4-methyl-6-pyrimidyl]phosphoro-thioate)

BACKGROUND

General Description of Liquid Membranes: Liquid membranes were invented by Norman N. Li in 1968 (1-3). Liquid membranes are made by forming an emulsion of two immiscible phases (the membrane and internal phases) and then dispersing the emulsion into a third phase (the continuous phase). Usually, the internal phase and the continuous phase are miscible. If the liquid membrane emulsion is to remain stable, the membrane phase must not be miscible with either the internal or the continuous phase. To maintain the integrity of the emulsion during an extraction experiment, the membrane phase usually contains certain surfactants, additives as stabilizing agents, and a base material which is a solvent for all the ingredients. Since the compositions of the membrane and the internal phase can be varied, liquid membranes can be tailor-made to meet specific requirements for a given application (4-7).

When the liquid membrane is dispersed by agitation in the continuous phase, many small globules of emulsion are formed (Figure 1). Their size depends on the nature and concentration of the surfactants in the membrane, the emulsion viscosity, and the mode and intensity of mixing. In general, the globule size is controlled in the range from 0.1 to 1 millimeter in diameter. A large number of globules of emulsion are formed to produce a large membrane surface area for rapid mass transfer for species from the continuous phase to the internal phase of the emulsion. In addition, many smaller droplets, typically 1 micron in diameter, are encapsulated within each globule. A variety of chemical species can be trapped and concentrated in the internal phase and subsequently disposed of or recovered for reuse or recycle.

Liquid Membrane Separation Technologies: Liquid membrane technology is very promising for a variety of applications. Examples of these applications include: the separation of hydrocarbons (8, 9) and metal ions from water (10-25); hydrometallurgy (10-25) and wastewater treatment applications (13, 26-36); and biochemical engineering, such as the encapsulation of enzymes and bacteria (37, 38). Liquid membrane technology currently has two commercial applications; one in zinc extraction and recovery (4) and the other in oil production as a well control fluid (39, 40).

Liquid Membrane Extraction Mechanisms: The effectiveness of the liquid membrane process can be enhanced by utilizing "facilitated transport" mechanisms to maximize both the flux through the membrane and the capacity of the internal phase for trapping and concentrating the diffusing species (7). One type of facilitated transport consists of carrying the diffusing species across the membrane by incorporating liquid ion exchange reagents in the membrane. This type of carrier-mediated transport can be illustrated by the separation of metal ions from wastewater or ore-leaching solutions. A conceptualized drawing of a liquid membrane "capsule" for extracting copper ions from wastewater is given in Figure 2. Extraction of copper ions occurs at the membrane/continuous phase interface. A liquid hydroxyoxime-type ion-exchange reagent specific for copper ions is incorporated in the membrane phase. Stripping of copper ions from the ion-exchange reagent occurs at the membrane/internal phase interface by 10% H₂SO₄. The overall reaction represents an exchange of a copper ion for two hydrogen ions. The copper is effectively trapped in the interior of the liquid membrane by the large excess of hydrogen ions (16-21).

One important advantage of the liquid membrane process for metal extraction lies in the concurrent extraction and stripping in a single stage rather than in two separate stages as required by solvent extraction. In addition, by concurrently extracting and stripping, the liquid membrane process drives the extraction by removing the complexed ions as they are formed, thereby removing the equilibrium limitation inherent in solvent extraction. Another benefit resulting from the nonequilibrium feature of the liquid membrane process is the significant reduction of the reagent inventory required for the extraction process.

The second type of facilitated transport is illustrated by the removal of oil-soluble contaminants such as ammonia (26, 30, 32-34), phenol and other organic acids such as acetic acid (32-36) from aqueous solution. In these cases, the membrane phase does not contain a liquid ion-exchange reagent. Rather, the extraction is driven by minimizing the concentration of the diffusing species in the internal phase. This is accomplished by reacting the diffusing species with a reagent in the internal phase to form a product(s) incapable of diffusing back through the membrane.

This type of facilitated transport can be illustrated by the separation of phenol from wastewater (Figure 3). In this case, sodium hydroxide (10% NaOH) is encapsulated inside the internal phase as the reagent which reacts with phenol. The phenol first dissolves in the membrane phase from the continuous phase and then diffuses to the interface between the membrane phase and the internal phase. At this interface, the phenol reacts with 10% NaOH to form sodium phenolate that is insoluble in the membrane phase. As a result, the concentration of phenol at the membrane/internal phase interface is maintained at zero, allowing a continuous driving force for permeation through the membrane. In addition to phenol, contaminants which can be removed by reaction with sodium hydroxide in the internal phase are cresols, carboxylic acids, and hydrogen sulfide.

In principle, the liquid membrane extraction process should be broadly applicable to many acidic species containing an ionizable chemical functional group(s). These species include many types of herbicides. Two of the five herbicides investigated in this study are representative of these acidic species, i.e., 2,4-D and MCPA. The other three herbicides, i.e., Carbaryl, Diazinon, and Atrazine, were chosen for study because each are soluble in organic solvents and, furthermore, each are known to hydrolyze rapidly in alkaline solution.

EXPERIMENTAL

Preparation of the Liquid Membrane Emulsion: The membrane phase consisted of a mixture of surfactant (4%) and solvent (96%). The surfactant was ECA 4360 (Paramins Co., Paramus, NJ), a polyamine with an average molecular weight of 1500. The solvent used was Low Odor Paraffin Solvent (LOPS); this solvent is an isoparaffin hydrocarbon (Exxon, Houston, TX). All the herbicides were analytical grade and used as received (ChemService, Inc., West Chester, PA).

Liquid membrane emulsions for use in bench-scale batch tests were prepared by extensive mixing of the membrane and internal phase (10% NaOH) in a Waring blender. The internal phase was mixed with the membrane phase on a 1:1 weight ratio to form a water-in-oil emulsion. The mixing was accomplished at 10,000 rpm for 6 minutes to ensure complete encapsulation. The resulting emulsion was mixed with the continuous phase (aqueous solutions of phenol, acetic acid, or herbicides) at a continuous phase:emulsion ratio of 5:1 in a baffled 2-liter resin kettle. Mixing was accomplished with 2 marine-type propellers attached to a variable speed stirrer via a 1/4 inch stainless steel stirring rod. The mixing speed ranged from 400 to 600 rpm for the phenol experiments and 420-440 rpm for the acetic acid and herbicide experiments. The mixing speed was monitored by a hand-held digital tachometer (Shimpo Model DT-201). The length of all experiments was 20 minutes. Samples were taken at 1, 5, 10, 15 and 20 minutes via a stopcock at the bottom of the resin kettle. All experiments were conducted at ambient temperature.

RESULTS AND DISCUSSION

Phenol and Acetic Acid Solutions

Extraction of Phenol from Aqueous Solution (35,36): Figure 4 shows data from an experiment to assess the effect of mixing speed (rpm) on the extraction of phenol. Three observations can be noted:

- (1) The percent extraction values at the 1 minute sampling time decrease as the mixing speed decreases.
- (2) The maximum extraction value of each curve shifts to longer sampling times as the mixing speed decreases.
- (3) The slopes of the extraction curves after about 5 minutes increase from nearly zero at the low rpm to larger negative values as the mixing speed increases.

As the mixing speed increases two phenomena occur: (1) the emulsion globule size decreases, and (2) the rate at which globules are broken increases. A smaller globule size will lead to more interfacial transfer area between the continuous phase and the liquid membrane, thus allowing the extraction to occur at a higher rate. In addition, the higher rate of shear and subsequent higher rate of breakage of globules at the higher rpm values allows more leakage of the phenolate ion back into the continuous phase from the internal phase of the liquid membrane emulsion.

Extraction of Acetic Acid from Aqueous Solution (36): Aqueous solutions of acetic acid (5000, 3000, and 1000 ppm) were used as the continuous phase for the three extraction runs shown in Figure 5. Percent extraction values are plotted versus mixing time. The results shown in Figure 5 indicate that as the

concentration of acetic acid in the continuous phase increases the extraction rate decreases. This did not appear to be the case in the experiments described above where phenol was the pure component in the continuous phase. The difference in the results from the acetic acid and phenol extraction runs is most likely due to the difference in the partition coefficient values of the components between the membrane and continuous phases. In the case of acetic acid, its solubility in the membrane phase is likely the controlling factor.

Herbicide Solutions

2,4-D: Table 1 contains data from the first extraction run where an aqueous solution containing approximately 100 ppm 2,4-D was used as the continuous phase. After 1 minute mixing time, the concentration of 2,4-D decreased from 96.8 to 30.7 ppm, a reduction of 68.2%. After 20 minutes mixing time, the amount of 2,4-D extracted from the continuous phase by the liquid membrane increased to a value of 85.4%. Based upon the results summarized in Table 1, no leakage of 2,4-D from the internal phase of the membrane back into the continuous phase occurred during this experiment.

MCPA: Table 2 contains data from the second extraction run where an aqueous solution containing approximately 100 ppm MCPA was used as the continuous phase. After 1 minute mixing time, the concentration of MCPA decreased from 96.1 to 67.4 ppm, a reduction of only 29.9%. However, after 15 minutes mixing time, the amount of MCPA extracted from the continuous phase increased to 61.2%. Unfortunately, some leakage of the MCPA from the internal phase of the liquid membrane emulsion back into the continuous phase occurred during this experiment based on the fact that the concentration of MCPA in the continuous phase increased from 37.3 ppm at 15 minutes to 41.4 ppm at 20 minutes total mixing time.

Diazinon: Table 3 contains data from the third extraction run where an aqueous solution containing approximately 30 ppm diazinon was used as the continuous phase. After 1 minute mixing time, the concentration of diazinon decreased from 28.3 to 14.7 ppm, a reduction of 48.1%. After 15 minutes mixing time, the amount of diazinon extracted from the continuous phase by the liquid membrane emulsion increased to a value of 73.9% and thereafter remained essentially constant. No significant leakage of diazinon from the internal phase of the membrane back into the continuous phase is indicated by the data given in Table 3.

Carbaryl: Table 4 contains data from the fourth extraction run where an aqueous solution containing approximately 30 ppm carbaryl was used as the continuous phase. After 1 minute mixing time, the concentration of carbaryl decreased from 31.3 to 10.3 ppm, a reduction of 67.1%. After 20 minutes mixing time, the amount of carbaryl extracted from the continuous phase increased to a value of 80.3%. No leakage of carbaryl from the internal phase of the membrane into the continuous phase was indicated by the experimental data.

Atrazine: Table 5 contains data from the fifth and final extraction run where an aqueous solution containing approximately 30 ppm atrazine was used as the continuous phase. After 1 minute mixing time, the concentration of atrazine in the continuous phase decreased by 64.9%. However, after 15 minutes mixing time, the amount of atrazine extracted from the continuous phase by the liquid membrane increased to a value of 92.9%. Some leakage of atrazine from the internal phase back into the continuous phase is indicated by the data given in Table 5 at the 20 minute mark.

SUMMARY

The major results obtained from this study may be summarized as follows:

- (1) More than 99% of phenol can be extracted from aqueous solution after approximately 1 minute with a liquid membrane emulsion containing 10% NaOH as the internal reagent phase.
- (2) Acetic acid can also be extracted by the liquid membrane emulsion but at a slower rate (5-10 minutes mixing time).
- (3) The liquid membrane emulsion containing 10% NaOH as the internal reagent phase can extract herbicides from aqueous solution at a continuous phase:emulsion ratio of 5:1. Removals of 2,4-D, MCPA, Carbaryl, Diazinon, and Atrazine were 85.4, 61.2, 80.2, 73.9, and 92.9%, respectively, after 15-20 minutes mixing time.

CONCLUSION

Based upon the exploratory work reported in this paper, it appears that liquid membrane technology can be used to extract herbicides from aqueous solution. The types of herbicides that can be extracted by the particular membrane composition reported in this paper are limited to those that will form an ionized species or hydrolyze in alkaline solution. Further work is required to determine whether other types of herbicides are amenable to extraction from aqueous solution by different liquid membrane compositions. Also, it will be useful to analyze the composition of the internal reagent phase, after the liquid membrane emulsion is broken, to perform a material balance calculation and identify degradation products.

Table 1. Extraction of 2,4-D from Aqueous Solution

<u>Mixing Time (min)</u>	<u>Concentration (ppm)</u>
0	96.8
1	30.7 (68.2% Removed)
5	16.6
10	14.9
15	16.3
20	14.1 (85.4% Removed)

Table 2. Extraction of MCPA from Aqueous Solution

<u>Mixing Time (min)</u>	<u>Concentration (ppm)</u>
0	96.1
1	67.4 (29.9% Removed)
5	62.2
10	52.4
15	37.3 (61.2% Removed)
20	41.4

Table 3. Extraction of Diazinon from Aqueous Solution

<u>Mixing Time (min)</u>	<u>Concentration (ppm)</u>
0	28.3
1	14.7 (48.1% Removed)
5	10.3
10	9.3
15	7.4 (73.9% Removed)
20	7.6

Table 4. Extraction of Carbaryl from Aqueous Solution

<u>Mixing Time (min)</u>	<u>Concentration (ppm)</u>
0	31.3
1	10.3 (67.1% Removed)
5	14.7
10	11.3
15	9.4
20	6.2 (80.2% Removed)

Table 5. Extraction of Atrazine from Aqueous Solution

<u>Mixing Time (min)</u>	<u>Concentration (ppm)</u>
0	29.8
1	10.5 (64.9% Removed)
5	6.3
10	4.1
15	2.1 (92.9% Removed)
20	4.6

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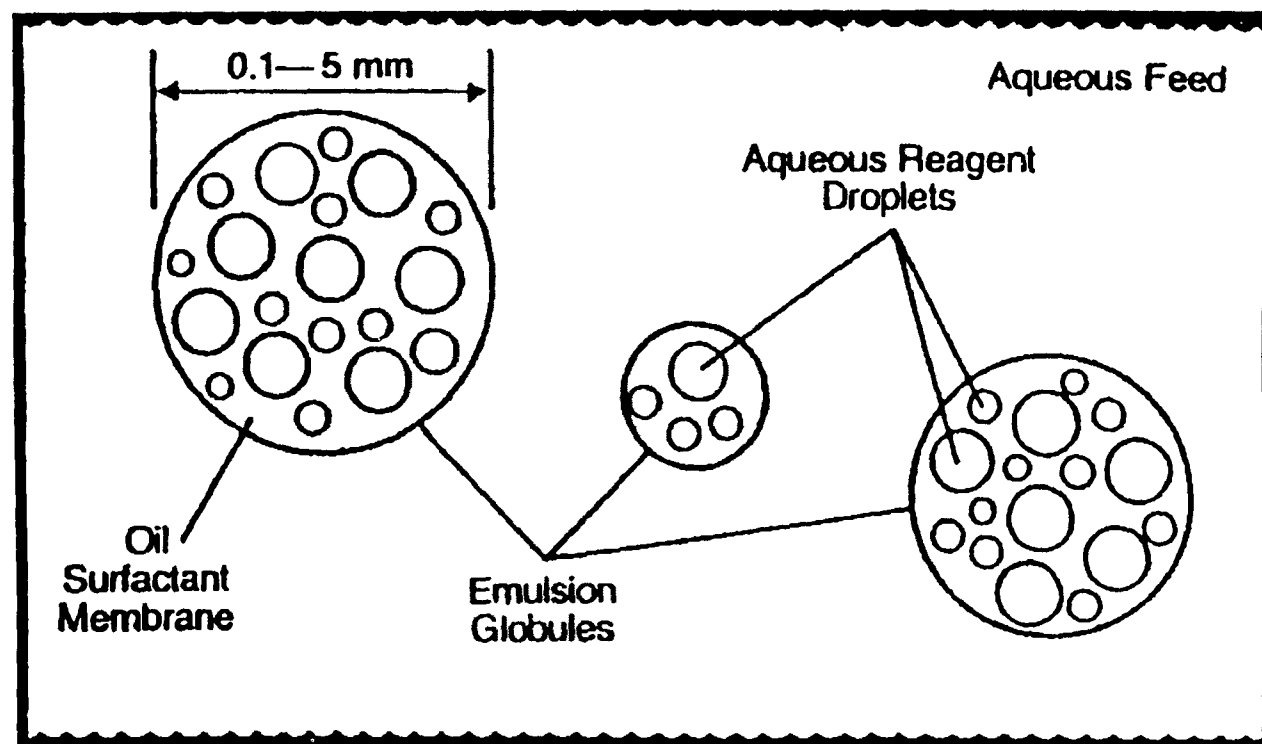


Figure 1. Dispersion of Liquid Membrane Emulsion²⁰

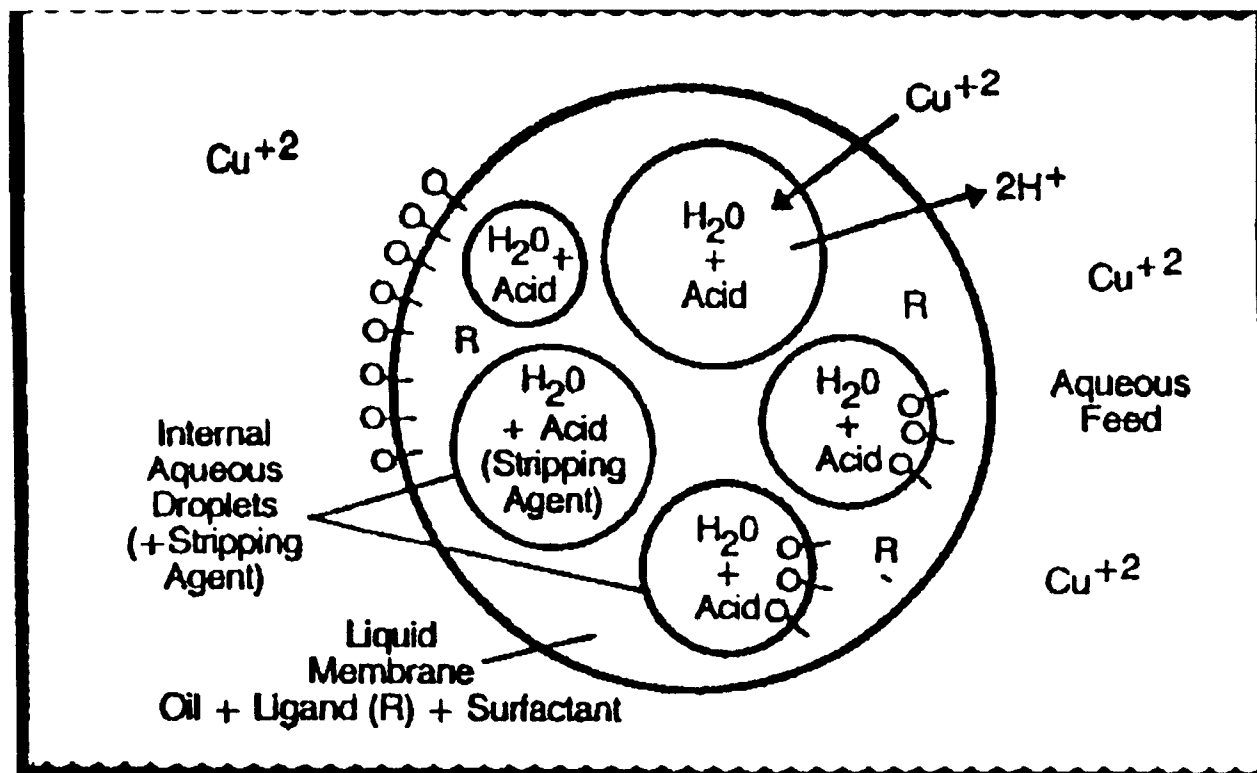


Figure 2. Cooper Transfer in a Liquid Membrane Globule ²⁰

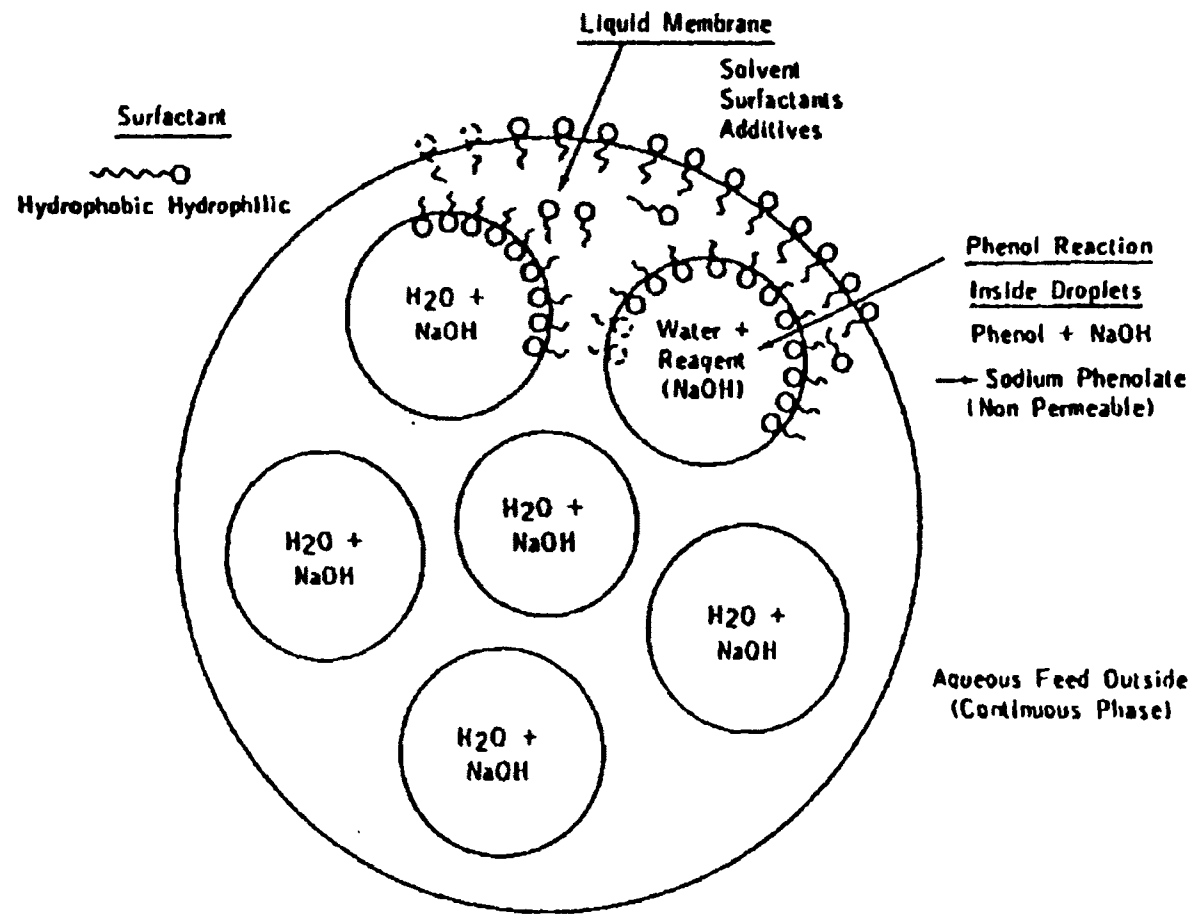


Figure 3. Liquid Membrane System for Phenol Removal ²⁰

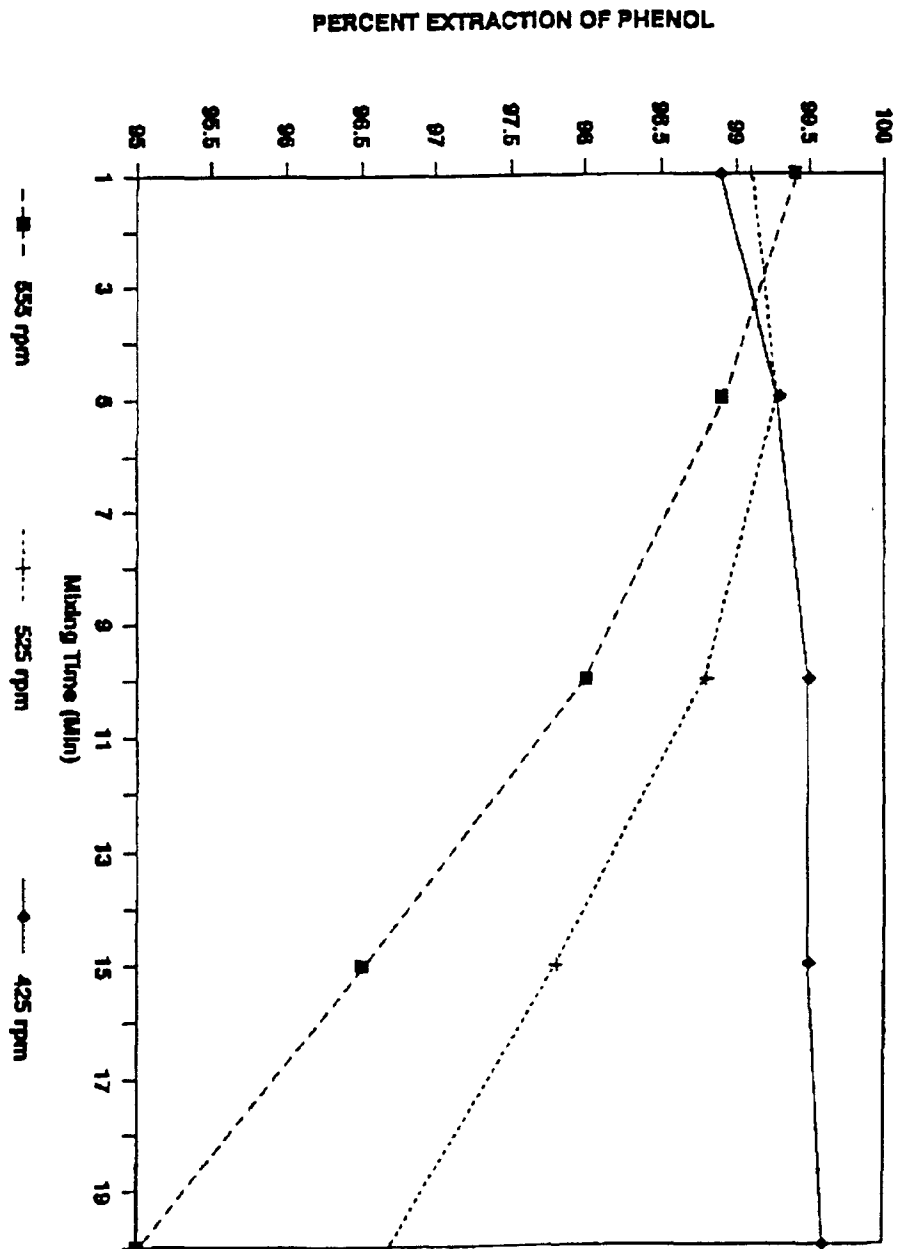


Figure 4. Effect of Mixing Speed on the Extraction of Phenol

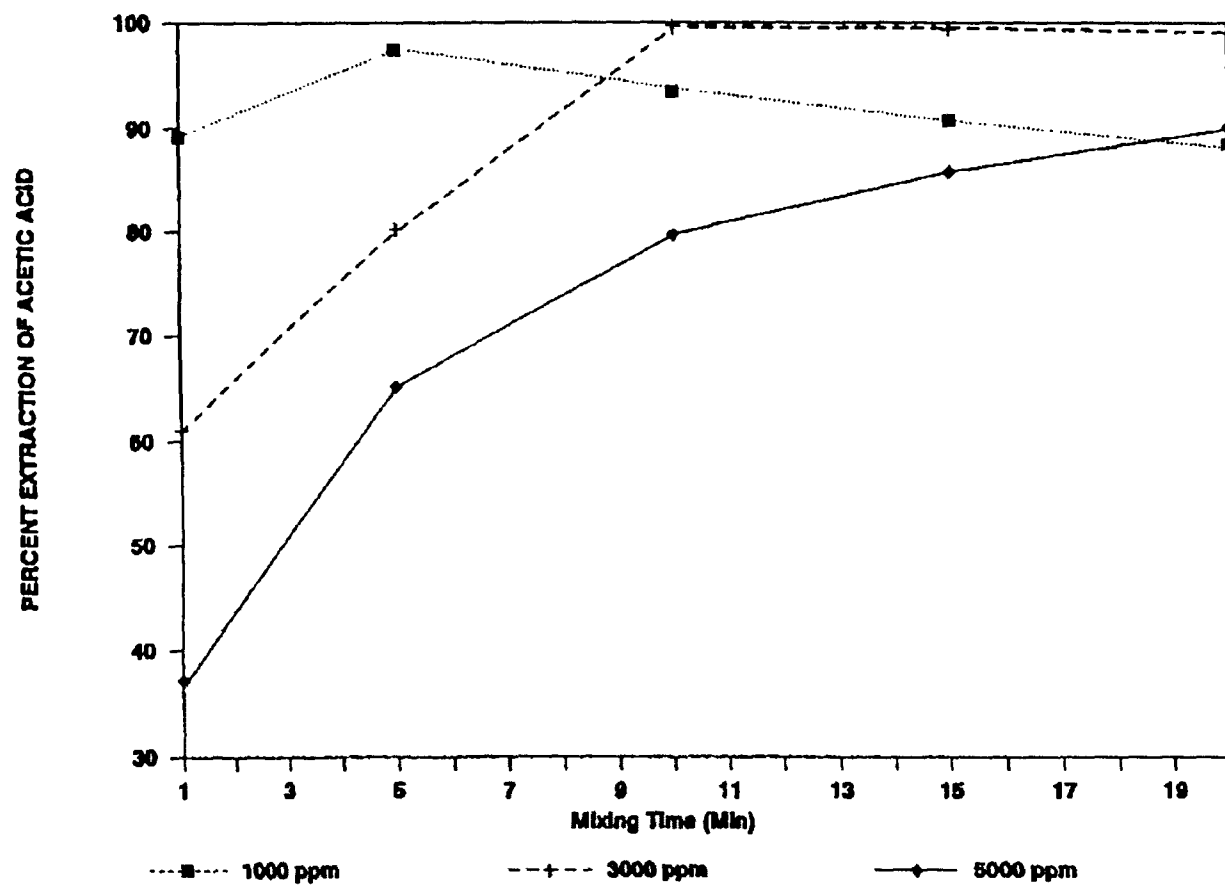


Figure 5. Effect of Concentration on the Extraction of Acetic Acid

Field and Laboratory Evaluations of an Activated Charcoal Filtration Unit

by

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ABSTRACT

An activated charcoal filtration unit was designed to remove pesticides from leftover pesticide solutions and rinsates generated under farm-like conditions. The system, fabricated for less than \$1200 using readily available components, effectively removed the pesticides atrazine, benomyl, carbaryl, fluometuron, metolachlor, and trifluralin from wastewater. A total of 2253 L of wastewater were treated using the system. Of these 1768 L were generated from washing out the spray tank while 485 L stemmed from leftover pesticide solutions that were mixed, but not applied. Typical initial pesticide concentrations in the wastewater were on the order of 300 to 1000 parts per million (ppm). The final pesticide concentrations remaining after charcoal filtration were generally less than 10 ppm. Approximately 1514 L of wastewater were treated with 23 kg of charcoal before the charcoal was replaced. This resulted in an estimated pesticide loading rate of 0.05 to 0.10 kg pesticide active ingredient per kg activated charcoal. Incubation of alachlor-treated charcoal with a mixed culture of microorganisms resulted in approximately a 50% loss of alachlor after 50 d. These results suggest that the degradation of alachlor sorbed to charcoal does occur but more research is needed to determine if it is a feasible alternative to incineration for spent charcoal. A reduced adsorption of methylene blue and alizarin red dye with increasing amounts of trifluralin sorbed to charcoal occurred. Activated charcoal treated with more than 200 mg/g trifluralin adsorbed considerably less of these dyes than the control where no trifluralin was added. The adsorption of malachite green dye was less affected by these trifluralin concentrations. These results suggest that methylene blue or alizarin dye might be used to rapidly assess the remaining adsorptive capacity of a activated charcoal used to treat pesticide-laden wastewater.

INTRODUCTION

Several researchers have successfully used activated charcoal to remove pesticides from leftover solutions and rinsates. Nye (1988) developed a flocculation/sedimentation and filtration process that reduced 18925 L of wastewater to 379 L of sludge and 91 kg of spent carbon. Dennis (1988) built a similar system based on the CARBOLATOR 35 water purification unit. After 20 h of filtration with 18 kg of Calgon-300 charcoal, 4 out of 6 pesticides initially present in 1552 L of water were not detectable.

In each of these systems, pesticides were filtered from wastewater using granular activated charcoal (GAC). After filtration, the wastewater could be reused as a diluent or returned to the environment with minimal impact. Although activated charcoal has proven to be quite effective at removing many different pesticides from wastewater, more research is needed in order to optimize the charcoal adsorption process.

One major drawback of activated charcoal filtration is that the pesticides are adsorbed, not destroyed, and contaminated charcoal is produced. This contaminated charcoal presents the problem of proper disposal in order to prevent environmental contamination. While regeneration of the charcoal is possible, it is not economically feasible when less than 225 kg spent charcoal/day are generated (Zanitsch and Stenzel, 1978). For this reason spent charcoal generated in small quantities is normally incinerated.

An alternative disposal treatment for spent charcoal may involve the degradation of sorbed pesticides by microorganisms. The degradation of organic pollutants in soil is frequently the result of microbial activity. However, the sorption of some organics by soil constituents has been found to reduce the availability of organic molecules to microorganisms and decrease the rate of degradation (Miller and Alexander, 1991). The typical diameters of activated charcoal micropores range from 10 to 1000 angstroms while most bacterial cell diameters range from 5000 to > 10,000 angstroms. Consequently, bacteria are physically excluded from the micropore structure of activated charcoal (Perrotti and Rodman, 1974). For this reason it is not clear that microbial degradation of pesticides sorbed to spent charcoal will be feasible. However, the successful degradation of pesticides sorbed to soil (Kilbane et al., 1983; Somich et al., 1990) and peat moss (Mullins et al., 1989) suggests that the microbial degradation of pesticides sorbed to charcoal deserves investigation.

Simple techniques for assessing the adsorptive capacity of activated charcoal are needed in order to optimize the filtration of pesticide wastes. Although a thin-layer chromatography method was developed to detect pesticides in filtered effluent (Dennis, 1988), this is likely impractical for use under farm conditions. Another approach may be to use dyes to indicate when activated charcoal no longer has the capacity to effectively adsorb pesticides from solution. The use of dyes to assess the adsorptive capacity of activated charcoal has proven to be helpful in many industrial situations (Hassler, 1974). To qualify for use, the dyes should have adsorptive characteristics similar to those of the chemicals being adsorbed.

PURPOSE AND OBJECTIVES

The overall goal of this research was to further the progress towards an economical and practical pesticide waste disposal technology. The specific goals were to: a). fabricate and field test a pesticide rinsate disposal unit based on activated charcoal filtration technology, b). determine the feasibility of microbially degrading pesticides sorbed to spent charcoal, and c). determine if visual assays could be used to assess the remaining adsorptive capacity of activated charcoal.

MATERIALS AND METHODS

Activated Charcoal Filtration Unit

A schematic diagram of the activated charcoal filtration unit (ACFU) is given in Figure 1. The system, like that described by Dennis (1988), was fabricated using readily available materials and was simple in design. The fiberglass tank was filled with 23 kg of Cullar-D granular activated charcoal (American Norit Co., Inc.; Jacksonville, FL 32205). A 1/2 hp electric

centrifugal pump produced a flow rate through the charcoal filter of 0.65 L/s. A 30 μ m paper pre-filter was placed before the charcoal filter to remove sediment and debris from the wastewater. By mounting the pump and cartridge filter housing onto a wagon and using a hand-truck for the fiberglass tank, the unit was easily transported to the pesticide mixing/loading site.

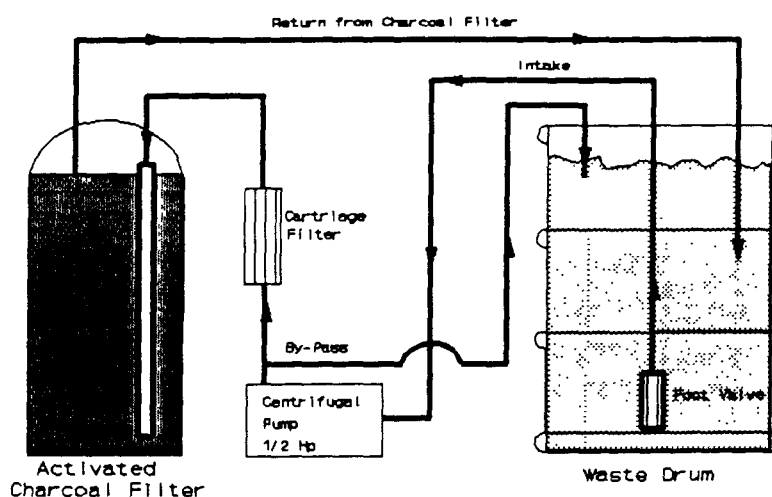


Figure 1. Schematic of the activated charcoal filtration unit used for rinsate disposal

Two modifications were made to the electric water pump. First, a low-pressure cutoff switch was added. This safety switch shut the system down when the water pressure dropped below 10 psi. Also, a manual reset button was installed which would not allow the pump to automatically restart after overheating without the assistance of the operator. These modifications increased the level of equipment protection and eliminated the need for constant supervision of the ACFU while in use. The retail cost of the ACFU, including modifications, was about \$1200.

Pesticide-laden wastewater generated during 1990 on the University of Arkansas Main Agricultural Experiment Station, Fayetteville (MAES) was stored in 208 L teflon-lined drums. The wastewater stemmed from two primary sources: leftover pesticide solutions and rinsates from cleaning spray equipment. Prior to filtration, the wastewater was mixed, solution pH and temperature measured, and a sample collected for time-zero analysis using either gas or high performance liquid chromatography. During filtration, effluent from the charcoal filter was circulated back into the containment drum. At various time intervals, more samples were collected from the bulk solution. As a general rule, filtration was continued until the wastewater was clear and odorless (ca. 3 to 5 h).

Microbial Degradation of Spent Charcoal

A system was designed to aid in determining the feasibility of microbial degradation of pesticides sorbed to spent charcoal. The system was similar to that reported by Wolf and Legg (1984) except that no CO₂ trapping was involved. The degradation of Lasso 4EC herbicide (alachlor, Monsanto Co., St. Louis, MO 63167) sorbed to activated charcoal was measured by using a gas chromatographic rather than a radioisotopic technique.

Alachlor-amended charcoal¹ was prepared to have a concentration of 24,820±1816 g alachlor/g GAC. Approximately 60 g (wet weight) of the amended charcoal was placed into a 125 mL erlenmeyer flask containing 25 mL of nutrient broth solution and 1 mL of a 10⁵ soil dilution. Six replications of the amended charcoal treatment were employed. Aeration was provided by bubbling room air through the samples. The samples were incubated at 33 ± 1 C in a water bath.

Two controls were included in the study. One was a charcoal control which contained similar amounts of charcoal, nutrient broth, and soil inoculant but had no alachlor added. A water control consisted of 30 mL of water containing 620 ± 89 ppm of alachlor with nutrient broth solution and soil inoculant but with no charcoal present. Five repetitions of these controls were incubated with the alachlor-amended charcoal samples.

Adsorptivity Assays for Used Charcoal

For the first series of tests Treflan herbicide and methylene blue dye (85%, Matheson Coleman & Bell, Norwood, OH) were used. To 1 g quantities of oven-dried charcoal dried (24 h at 105°C), various amounts of Treflan herbicide solution were added. Final concentrations of trifluralin ranged from 0 to 384 mg trifluralin/g charcoal. Three replications per concentration were used.

To the trifluralin-amended charcoal, 5 mL of a 0.021 M methylene blue dye solution (dissolved in a 0.22 M sodium phosphate monobasic buffer solution adjusted to pH 6.5) was added. The glass culture tubes were capped and shaken at 12 rpm for 15 min at room temperature. After measuring the absorbance of the dye remaining in solution, the dye concentration was estimated using a standard curve.

Similar studies were conducted using 0.021 M malachite green dye (99%, Eastman Kodak Co., Rochester, NY) and 0.022 M alizarin red dye (J.T. Baker Chemical Co., Phillipsburg, NJ). For the alizarin red study, the buffer concentration was reduced to 0.04 M to prevent precipitation of the dye.

RESULTS AND DISCUSSION

Field Evaluation of the ACFU

About 485 L of leftover pesticide solutions and 1768 L of rinsates were treated using the ACFU. These figures reveal that 79% of the wastewater treated stemmed from the cleaning of spray equipment. There were 3785 L of pesticide solutions mixed during the 1990 growing season. Of these, 485 L or 13% were

¹All studies used Cullar-D activated charcoal like that used in the ACFU.

returned unused to the waste drums. The average volume of the leftover solutions was 23 ± 23 L while that of the rinsates was 87 ± 34 L.

The ACFU effectively removed the commonly applied herbicides AAtrex Nine-O (atrazine, CIBA-GEIGY Corp., Greensboro, NC 27409), Bicep 4.5L (metolachlor, CIBA-GEIGY Corp., Greensboro, NC 27409), and Treflan EC (trifluralin, Elanco Products Co., Indianapolis, IN 46285) (Figure 2) and other pesticides including Benlate 50% WP fungicide (benomyl, DuPont Co. Inc., Wilmington, DE 19898), Sevin insecticide (carbaryl, Union Carbide Co. Inc., Res. Triangle Park, NC 27709), and Cotoran herbicide (fluometuron, CIBA-GEIGY Corp., Greensboro, NC 27409) (Figure 3). Typical initial pesticide concentrations were on the order of 300 to 1000 ppm while final concentrations after filtration were < 10 ppm.

An estimated 0.05 to 0.10 kg of pesticide active ingredient could be adsorbed by each kg of GAC. These values are based on the fact that after 1514 L of wastewater had been filtered, the 23 kg of GAC no longer effectively removed pesticides from solution. At this point the spent charcoal was replaced.

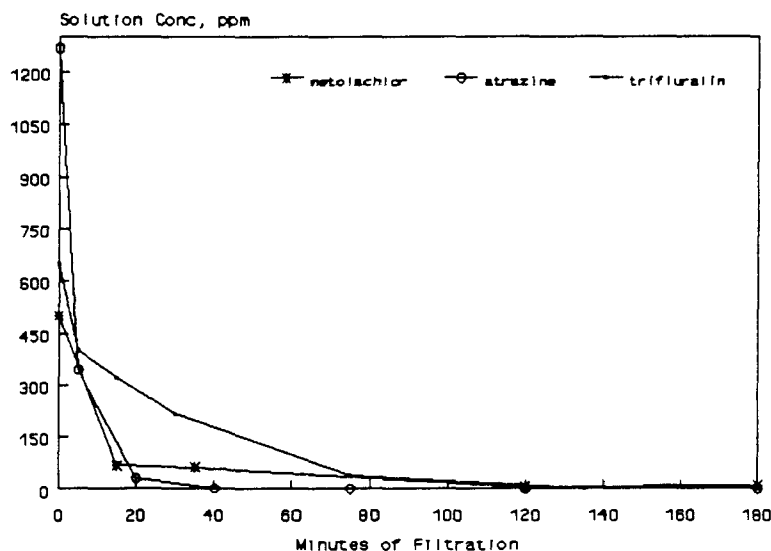


Figure 2. Removal of three herbicides using activated charcoal filtration.

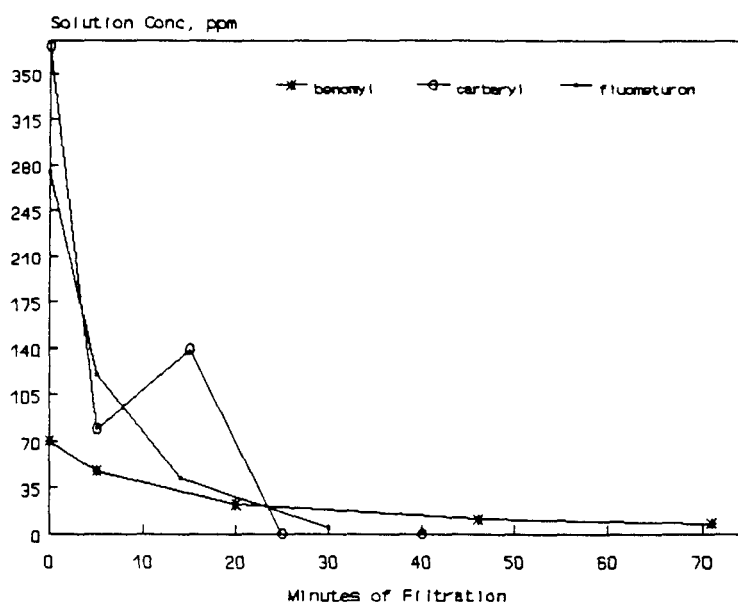


Figure 3. Removal of three pesticides using activated charcoal filtration.

Other than adsorption onto the charcoal, there were at least two other avenues of pesticide dissipation not explored in this study. First, some of the pesticides were trapped by the 30 m paper pre-filter. Solid-carrier pesticide formulations (e.g. AAtrex Nine-0) were trapped to some degree by the filter. Moreover, bright yellow stains formed on the paper filters, indicating that Treflan herbicide was being sorbed. Besides the spent charcoal, these contaminated filters are another source of contaminated material which will have to be properly disposed.

Volatilization from solution is a potential avenue of dissipation for some pesticides. Controlling factors of volatilization from water include the solubility, molecular weight, and vapor pressure of the pesticide and the nature of the air-water interface through which it must pass. The turbulence generated during the recirculation of the wastewater would likely enhance volatilization. Of the pesticides involved in this study, only trifluralin has a Henry's Law Constant great enough to suggest that volatilization from solution might be a significant problem (Jury et al., 1987).

Microbial Degradation of Spent Charcoal

Figure 4 presents data generated from incubating alachlor amended charcoal under conditions which should favor microbial growth. The degradation of alachlor on charcoal occurred at a slow, steady rate. After 21 d of incubation slightly less than 70% of the originally applied alachlor still remained on the charcoal. Thirty-nine days of incubation resulted in a 52% retention of the alachlor initially applied to the charcoal while the water control retained approximately 46%. After 59 d the amended charcoal retained 43% while the water control retained 33% of the initial alachlor. These data suggest a half-life of about 50 d for the alachlor sorbed to charcoal.

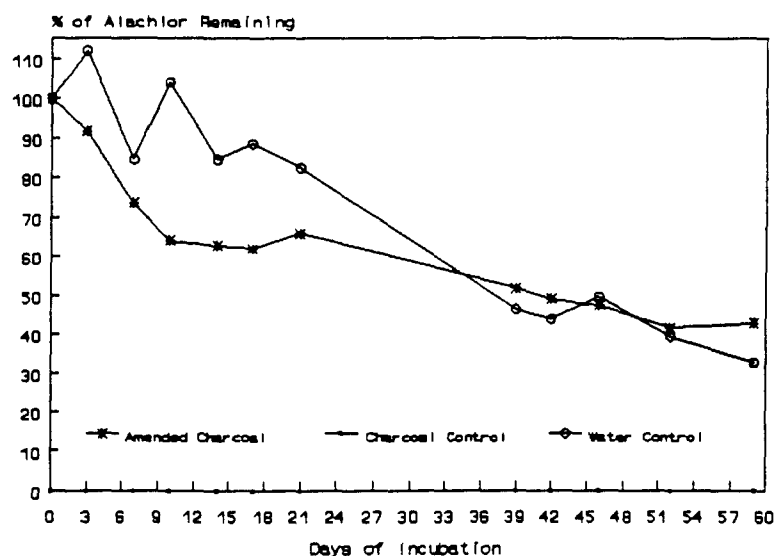


Figure 4. Degradation of alachlor sorbed to activated charcoal.

While these data are preliminary, results suggest that the degradation of alachlor sorbed to charcoal via microbial action can occur. Alachlor is degraded in soil primarily by microorganisms and its losses due to volatility are low (Humburg, 1989). This study did not address the possibility that degradation may have occurred through chemical reactions.

Until the feasibility of microbially degrading spent charcoal is fully determined, spent charcoal can be incinerated. For this reason, an estimated cost of disposing the spent charcoal via incineration at the Environmental Systems Company (ENSCO) El Dorado, AR plant was calculated. According to an ENSCO representative, charcoal containing pesticides can be incinerated for \$2.10/kg. Transportation costs normally run \$25/208-L drum with a \$50 stop-fee. An analytical determination of the drum contents is also required (\$300/sample).

About 23 kg of spent charcoal was generated by filtering 1514 L of wastewater. Given an apparent density of 470 kg/m^3 , a 208 L drum of charcoal would weigh about 97 kg. At \$2.10/kg disposal fee, this would cost about \$210, plus \$75 for shipping and \$300 for analytical costs. Since there is a minimum invoice of \$1000, at least 2 drums would be required for economical reasons. Two drums would contain 200 kg of charcoal, resulting in a total cost of \$1120 to dispose of charcoal (including transportation and analytical costs). Excluding the cost of charcoal, this amount of charcoal could treat about 13000 L of wastewater at a cost of about \$0.09/L.

Adsorptivity Assays for Used Charcoal

Figure 5 gives the results of the dye test studies. All three dyes experienced reduced adsorption with increasing trifluralin concentration on the charcoal. Compared to methylene blue and alizarin red dyes, malachite green dye adsorption was not as affected by increasing amounts of trifluralin. For trifluralin concentrations less than 200 mg/g, there was little difference in the amount of dye adsorbed compared to the control. Trifluralin concentrations greater than 200 mg/g resulted in greatly diminished adsorption of the dyes.

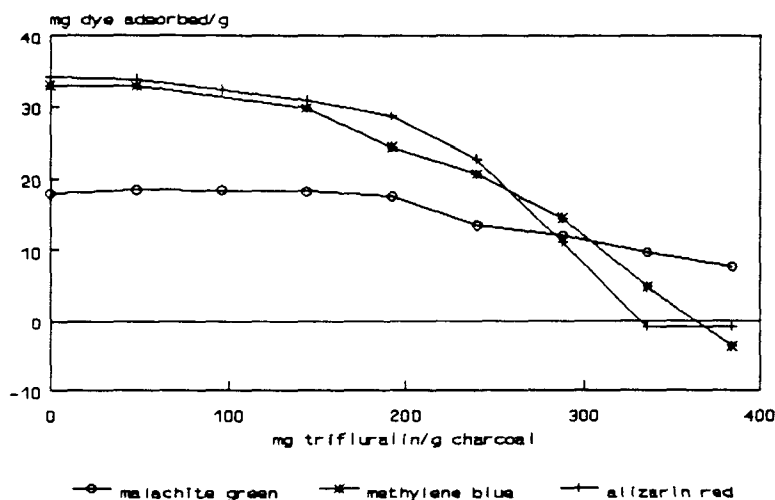


Figure 5. Adsorption of three dyes onto trifluralin-amended charcoal.

These results suggest that it might be feasible to use methylene blue or alizarin red dye to assess the remaining pesticide capacity of charcoal. A possible scenario might have a pesticide user needing to filter 300 to 500 gallons of wastewater. Filtration of this waste could take a considerable amount of time (18 to 24 h). To test the remaining adsorptive capacity of used, but not

necessarily spent charcoal, the pesticide user would take a sample of charcoal and add a known amount of dye dissolved in buffer solution. If any color remains in solution after shaking the dye and charcoal together, the charcoal may not have the capacity to remove pesticides from pesticide-laden wastewater. In this case, the charcoal would be replaced, saving the operator valuable time by not using charcoal with a diminished capacity to remove pesticides.

CONCLUSIONS

An activated charcoal filtration unit, fabricated using readily available components, effectively removed the pesticides atrazine, benomyl, carbaryl, fluometuron, metolachlor, and trifluralin from leftover pesticide solutions and rinsates. Approximately 1500 L of wastewater could be effectively treated using 23 kg of Cullar-D activated charcoal before replacement was necessary. The disposal of spent charcoal via microbial degradation is still under investigation. Results from an alachlor incubation study suggest that this may represent an alternative to incineration but more research is required to fully determine the treatment's potential. The ability of methylene blue and alizarin red dye to reflect differing amounts of adsorbed trifluralin on charcoal suggests that these dyes could potentially be used as a rapid test to indicate when the capacity of activated charcoal is exhausted and, therefore, when it is necessary to replace the charcoal filter.

ACKNOWLEDGEMENTS

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Preliminary Studies of Batch Chemical Oxidation of
Wastewaters Containing Agrichemicals

By

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ABSTRACT

The increased use of containment in the agribusiness industry has resulted in improved control of contaminated wastewater but has also resulted in an accumulation of wastewater that contains agrichemicals and cannot be easily recycled or reused. TVA is currently investigating chemical oxidation methods to decontaminate this wastewater. The major objective of the investigations have been to develop procedures that can be carried out onsite using existing process equipment. One approach tested was the use of strong acids and air sparging. This resulted in air stripping of the volatile compounds and little oxidation. A second approach has been to use hydrogen peroxide in the presence of a catalyst. This method has resulted in a high level of destruction of the original agrichemical but only about 80 percent destruction of the total organic carbon (TOC) present. Future test work will be directed toward identification of the remaining TOC and developing procedures to oxidize it.

TVA's National Fertilizer & Environmental Research Center (NFERC) is actively engaged in environmental research work as part of its ongoing mission, especially as it relates to environmental issues and problems which have an impact on fertilizer manufacturers, dealers, and users. One such problem faces more than 3,000 small dealers who custom mix fertilizers and pesticides for sale to local farmers. After a dealer prepares a custom mix and transfers it to the farmer, he often rinses his storage and mixing equipment so as to avoid contamination of the next mix. This results in a volume of rinse water (rinsate) containing a low-level pesticide contamination. Additional contaminated water results from external equipment wash down and spills during transfer or storage. In the past, dealers generally disposed of the contaminated water on his own site, and this resulted in localized soil or ground water contamination from repeated disposal. Currently, the main alternatives open for a dealer are to field apply the contaminated water, reuse it in formulations of similar blends, or in the worst case, to pay a waste disposal company to remove and treat the waste rinsate.

NFERC initiated an applied research project with a narrow focus to determine if a simplified, cost-effective method of destroying (or removing) pesticides in rinsate solutions could be developed. A major objective was to make the method simple enough that it could be carried out using process equipment commonly available to the mix dealers. A secondary objective was to tailor the decontamination process in such a way that the decontaminated solution could be recycled, thus allowing the dealers to avoid the problems (and costs) associated with effluent monitoring and reporting.

The work was done in two main phases, the first being to test the use of strong acids/heat/air to oxidize the pesticides. This work was followed by a study of the use of chemicals and heat to oxidize the materials.

Strong Acids/Heat/Air Oxidation

The initial research test work focused on the possibility of using strong acids, such as phosphoric, sulfuric, or nitric, to catalyze the oxidation of pesticides by air in a batch system. This idea was appealing because of the unique operating and marketing position of the fertilizer dealers. A dealer would be able to take the process by-product solution, which now contains acid from the decontamination process, and convert it to a usable fertilizer product by ammoniation. In this way, the dealer could substantially recover the cost of the acid. Potentially, the ammoniated acid solution could be used for blending with other solutions or, if adjusted to a standard grade, sold directly to the customer.

The test work was performed using synthetic waste rinsates containing one of four commonly used herbicides: trifluralin, alachlor, metolachlor, and 2,4D amine. All synthetic rinsates used in the testing were produced by adding a commercial-grade herbicide solution directly to tap water. The concentration of the active ingredient was standardized to a level of 1,500 parts per million, a level that is considered to be at the upper end of the range for dealer rinsates. Since all of the commercial herbicides that were tested, except 2,4D amine, contained an organic solvent, the concentration of total organic matter in the synthetic rinsates varied among the different test pesticides.

Tests were made using each of the three strong acids (phosphoric, sulfuric, and nitric) added directly to the synthetic rinsates. Combinations of these acids were also tested. The test equipment was arranged so that the acid-dosed rinsate could be pumped to a venturi mixer and returned to the batch holder. Air was injected into the venturi to produce a turbulent contact between the two streams. Most of the oxidation was expected to come from the oxygen in the air, rather than donation of oxygen from the acid. Test solutions were heated to accelerate the rate of oxidation. Test temperatures ranged from a low of 140°F up to a high of about 190°F. Also included as part of the test work was the addition of soluble trace metals, as suggested by the literature, to act as catalysts. The catalytic metals were generally limited to those metals that are innocuous in fertilizer solutions or are micronutrients, such as copper or iron.

The results of these tests were generally disappointing. In most cases, the test herbicides were simply removed by air stripping in the venturi. The least volatile herbicide, 2,4D amine, was essentially unaffected in these tests. Some attempts were made to set up new equipment arrangements that would utilize fixed-bed catalysts, instead of soluble catalysts. However, it was soon realized that any such scheme would violate a core objective of the project--simplicity. These efforts did, however, lead to the generation of an idea involving three-phase batch oxidation.

Chemical/Heat Oxidation

The second phase of the bench-scale work involved the use of chemicals and heat to oxidize pesticide contaminants. Two separate approaches were tested, the first utilized a phosphoric acid, MnO₂, and the second, Fenton's reagent (ferrous ions in presence of peroxide). Results of these tests were encouraging.

Phosphoric Acid - MnO₂ Slurry: With this method, a solid, relatively insoluble catalyst, manganese dioxide, was slurried by an agitator in a 2,4D amine rinsate solution to which phosphoric acid had been added. The key to the system was to operate the agitator at a sufficiently high rotational speed that a deep vortex was produced. This created an intense three-phase mixing zone for the air, manganese dioxide, and rinsate solution to come in contact with each other. This method was able to effectively oxidize all of the test pesticide, 2,4D amine, within detection limits (about 10 ppm). However, about a quarter of the original organic matter remained, as measured by a standard laboratory test, total organic carbon (TOC). Since the 2,4D amine herbicide solution contains only water as a solvent, it is assumed that the remaining organic matter existed as fragments of the original herbicide. No attempt has been made to identify the fragment compounds to date. However, it is clear from the total quantity of oxidation that took place, that the molecular bonds in the chlorinated aromatic rings of 2,4D amine were broken. This was considered a major hurdle in the oxidation chemistry since these bonds are considered to be particularly oxidation resistant.

A major drawback of this method is the potential energy cost. During the lab experiments, nearly all of the water in the solution is evaporated due to the large volume of air pulled into the solution by the agitator. This is also due, in part, to the high operating temperature, 230°F, needed for oxidation to proceed. (Note: The presence of phosphoric acid elevates the boiling point of the solution to well above 230°F.) A second drawback to this method is that those pesticides which are relatively volatile are likely to be evaporated before oxidation can take place. This would probably mean that the off-gas from the process would have to be treated in some manner, perhaps by incineration or activated carbon recovery. Both of these methods would complicate the process beyond the desired objective.

Fenton's Reagent: A method of liquid phase oxidation that is commonly used in laboratory analytical chemistry is Fenton's reagent. This reagent, discovered during the late 19th century, is a mixture of ferrous ions and hydrogen peroxide that was observed to have enhanced ability to oxidize organic compounds. The basis for this property is the initial reaction of peroxide with ferrous ions to form ferric ions and hydroxyl radicals. The hydroxyl radicals react readily with organic hydrogen by attacking carbon-hydrogen bonds. This attack in turn facilitates direct oxidation of the organic compound by reaction with free hydrogen peroxide.

Potentially, an adaptation of Fenton's reagent could meet all the project objectives. It is simple enough to be applied in a single tank batch. The oxidant, hydrogen peroxide, is relatively inexpensive compared with other chemical oxidants. Furthermore, if the decontaminated solution is used in the preparation of fertilizer mixes, then the catalyst, ferrous ion, becomes a fertilizer micronutrient. Additionally, commercial sources of ferrous ion are available in which the associated cationic species is also a nutrient (e.g., ferrous sulfate). Finally, since the literature suggests that Fenton's reagent is more active under conditions of acidic pH, strong acids, such as phosphoric, can be used that add nutrient value to the solution.

Test work was initiated to determine the parameter effects and the overall effectiveness of Fenton's reagent when applied to synthetic rinsate solutions. The herbicide 2,4D amine was again selected for the initial series of tests. All test work was done using synthetic rinsates containing about 1,500 ppm by weight

2,4D amine. Ferrous sulfate heptahydrate was chosen as the source of ferrous ions. Phosphoric acid was used to adjust the pH of the test solutions in the acid range, and potassium hydroxide was used for the basic range. Tests were made using mild agitation and temperatures ranging from 120 to 180°F. Laboratory grade 30% hydrogen peroxide solution was used in all tests.

Early tests focused on determining the overall effectiveness of the Fenton's reagent method. Tests in which a large quantity of peroxide was used (about 16 times the stoichiometric quantity needed to oxidize all of the organic matter) and with a high temperature (180°F) produced very good results. As much as 86% of the organic matter was oxidized in one of the tests. None of the original 2,4D amine pesticide, within detectable limits, remained after oxidation. In these early tests, ferrous ion content and pH were studied to determine parameter effects. Both parameters exhibited plateau-shaped curves. Organic destruction increased with increasing ferrous sulfate heptahydrate addition up to a level of about 7 grams per liter, above which no further benefit was found. Similarly, organic destruction increased with increasing pH up to a level of around pH of 4, above which the effect was generally flat, even into the basic range. This seemed to be somewhat contradictory to literature sources, which suggested that acidic conditions were beneficial, and that a maximum effect in most cases might be expected near a pH of 3.5. However, based on the test results, pH adjustment was eliminated in subsequent testing. (Since ferrous sulfate is slightly acidic, the unadjusted test solutions have an initial pH of about 5.)

The follow-up test work with the Fenton's reagent has focused on two related objectives: (1) increasing the percentage of total organic matter that is oxidized during the process, and (2) reducing the quantity of hydrogen peroxide required by the process. The first objective, increasing oxidation percentage, has not been achieved in subsequent tests. It appears that a destruction level of 85 to 88% was a barrier for Fenton's reagent when applied to 2,4D amine. Longer retention times, and even repeated applications of Fenton's reagent to the same solution, were unable to increase the quantity of organic matter destroyed. It appears that in future tests of 2,4D amine and all other pesticides which exhibit similar oxidation resistance, the organic compounds which remain after oxidation must be identified by qualitative analysis. If these compounds are innocuous, then the decontaminated solution may be reuseable as make-up water for fresh fertilizer/pesticide mixes. If not, then clearly, additional treatment steps will be required. At this point in the research work, this is a major problem to be identified.

Modest improvements were made during the study of the second objective, reducing hydrogen peroxide usage. By adding a small amount of copper (II) sulfate to the solution as a supplemental catalyst, the hydrogen peroxide usage was cut in half, from 16 times stoichiometric to 8 times stoichiometric, while still maintaining the maximum organic destruction level of 85 to 88%. In terms of commercial scale volumes, the quantity of 30% hydrogen peroxide solution was lowered from 23 gallons per 100 gallons of rinsate to 11.5 gallons.

A further reduction of hydrogen peroxide is desirable. In a commercial process, the cost of hydrogen peroxide will be the major operating cost. At the minimum peroxide requirement stated above, the peroxide cost will be approximately \$32 per 100 gallons of rinsate.

Conclusions from Preliminary Test Work

The results of this preliminary test work has shown the use for a simplified approach to the onsite treatment of contaminated rinsewater is feasible. Depending on the composition of some of the residual degradation compounds, the proposed process based on Fenton's reagent appears to be the most promising approach tested to date. Other treatment schemes will be considered in future work and the most attractive process will be carried to pilot and/or demonstration scale.

[illegible]

1. The first step is to identify the problem or question that needs to be answered. This involves understanding the context and the specific information required.

2. Next, gather relevant data and information. This can be done through research, interviews, or direct observation. It is important to ensure the data is accurate and reliable.

3. Once the data is collected, analyze it to identify patterns, trends, and relationships. This step often involves statistical analysis or qualitative interpretation.

4. Based on the analysis, develop a hypothesis or a proposed solution. This should be grounded in the evidence gathered and logical reasoning.

5. Finally, test the hypothesis or solution. This may involve conducting experiments, further research, or a pilot program to see if the proposed solution works in practice.

[illegible]

ABSTRACT

by varying the temperature and/or the pressure such that the density of the fluid can approach that of typical liquid solvents. For example, at 50°C and 68 bar (1000 psi) CO₂ has a density of 0.2 g/mL, at 120 bar (1760 psi) the density is 0.6 g/mL, and at 214 bar (3150 psi) the density is 0.8 g/mL. If a constant temperature is maintained and the pressure is increased sufficiently the density will approach the liquid density. The density of liquid CO₂ is 1.101 at -37°C (1). At its critical point (T_c = 31°C, P_c = 73 bar) CO₂ has a density of 0.46 g/mL (3).

The unique characteristic of supercritical fluid extraction (SCFE) is that an SCF remains in a gaseous state and as such can penetrate the interstitial spaces of solid materials much more readily than liquids. This allows the SCF to make intimate contact with any substance that is sorbed to the solid material and facilitates the removal of contaminating materials. Figure 2 shows the self-diffusivity of CO₂ over a wide temperature-pressure range and, for comparative purposes, the range of diffusivities for solutes in organic liquids ((average of about 10⁻⁵ cm²/sec (4)). With changes in temperature and pressure an SCF can be tailored to extract substances that are difficult, if not impossible, to separate by other means. Supercritical CO₂ is a nonpolar solvent, and a good rule of thumb is that most compounds that are soluble in hexane will also be soluble in supercritical CO₂. However, the extraction characteristics may be changed to make the extraction fluid more polar by adding enhancers such as methanol or acetone to the system.

Another interesting characteristic of SCFs is that shown in Figure 3 (5). The figure shows the solubility of naphthalene (wt. %) in supercritical CO₂ with varying temperature and constant pressures. The diagram shows that at lower pressures the solubility increases with increasing temperature but at some point the solubility begins to decrease with an increase in temperature. However, at about 150 atmospheres and higher, the solubility continues to increase with an increase in temperature. If the temperature is increased sufficiently, the solubility will probably again begin to decrease. This is because the SCF becomes more like a gas than a liquid and, as such, has much less solvating power. The dashed line represents the solubility of naphthalene in liquid CO₂. Figure 4 (6) shows similar behavior for the solubility of SiO₂ in water, and it is suspected that this behavior will exist for all solutes in SCFs.

The following equation of state was taken from an English translation of the Russian text Thermophysical Properties of Carbon Dioxide (7).

The expanded form of the equation of state for gaseous CO₂ may be written as:

$$PV/RT = 1 + (Bd + Cd^2 + Dd^3 + Ed^4 + Fd^6 + Gd^8) \text{ where}$$

$$B = 0.486590(1+97/96+\tau) - [(1.90843+5.351e^a)/\tau] - (0.079526/\tau^8)$$

$$C = 2.39169 - [(6.9619-12.1824e^a)/\tau] + (6.86903/\tau^2) - (3.34265/\tau^3)$$

$$D = -1.69007 + [(10.2469-6.38963e^a)/\tau] - (14.7337/\tau^2) + (7.32711/\tau^3)$$

$$E_1 = 8.69339 - (16.9642/\tau) + (8.92312/\tau^3)$$

$$E_2 = -2.40368 + (6.61817/\tau) + (9.92898/\tau^2) - (36.4789/\tau^3) + (22.0167/\tau^4)$$

$$F_1 = -37.3064 + (102.476/\tau - 6737594/\tau^2)$$

	<u>Atrazine</u>	<u>Alachlor</u>	<u>Bentazon</u>	<u>Permethrin</u>
Wt. % in soil	3.6	8.9	11.9	10.2
Wt. % in soil after ext.	0.06	0.18	0.59	0.21
Wt. % removed	98.3	97.9	95.0	97.9

The use of SCFE in remediating sites contaminated with various organic compounds is currently under consideration by EPA's Superfund Innovative Technology Evaluation (SITE) program. Other laboratories (outside TVA) have indicated that supercritical CO₂ readily extracts compounds such as PCBs, DDT, and toxaphene from contaminated soils. Initial work by Brady et al. (9) demonstrated CO₂ extraction efficiencies of 70-90% for these compounds and found that no difference in overall extractability existed between contaminant removal from dry soil and wet soil.

CONCLUSIONS

SCFE should be applicable to remediation of contaminated soil. There are both advantages and disadvantages to using supercritical CO₂. The advantages include: 1) CO₂ is non-polluting, 2) CO₂ is relatively inexpensive, 3) material can be recycled if enough is extracted, and 4) it should be possible to build a portable unit that can be moved from site to site without problems associated with interstate regulations because no hazardous materials are transported. Disadvantages include: 1) relatively high pressures needed, 2) all contaminants may not be extracted with one set of conditions, and 3) the contaminants are not destroyed. However, because the volume of contaminated material is reduced considerably, a small secondary treatment unit such as incineration, ultraviolet ozonation, or chemical reduction could be added to the system. Incineration may be the most readily adaptable, if local regulations do not prohibit it.

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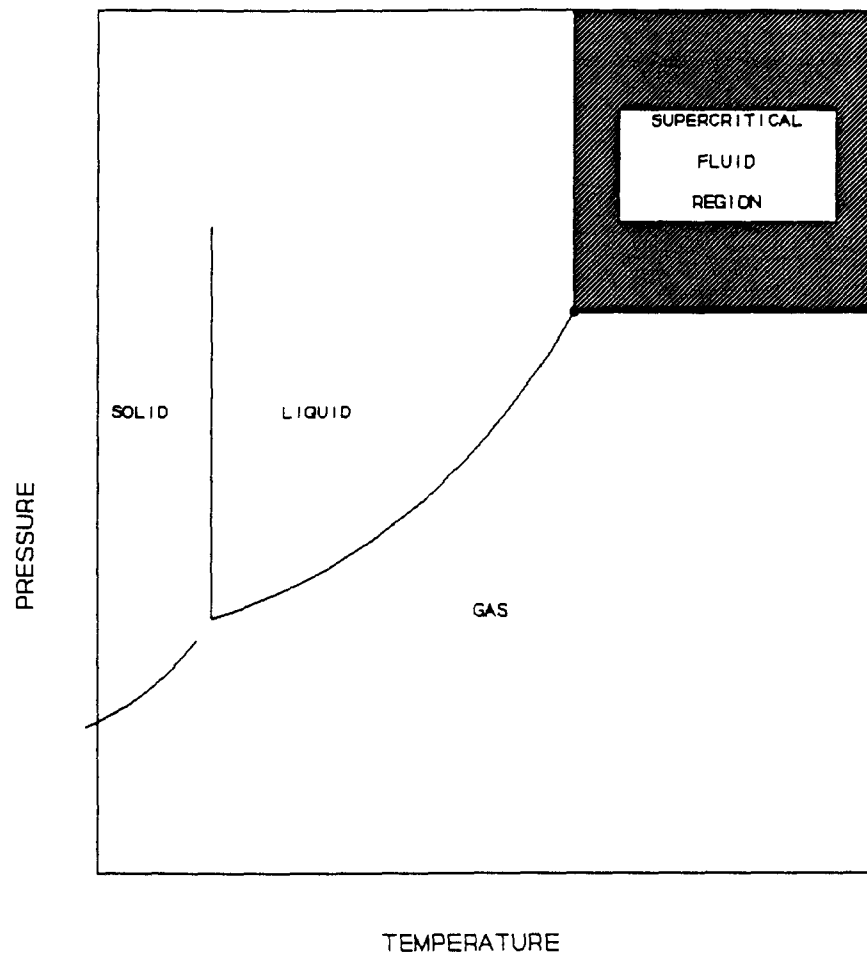


Figure 1 Pressure-temperature diagram for a pure component

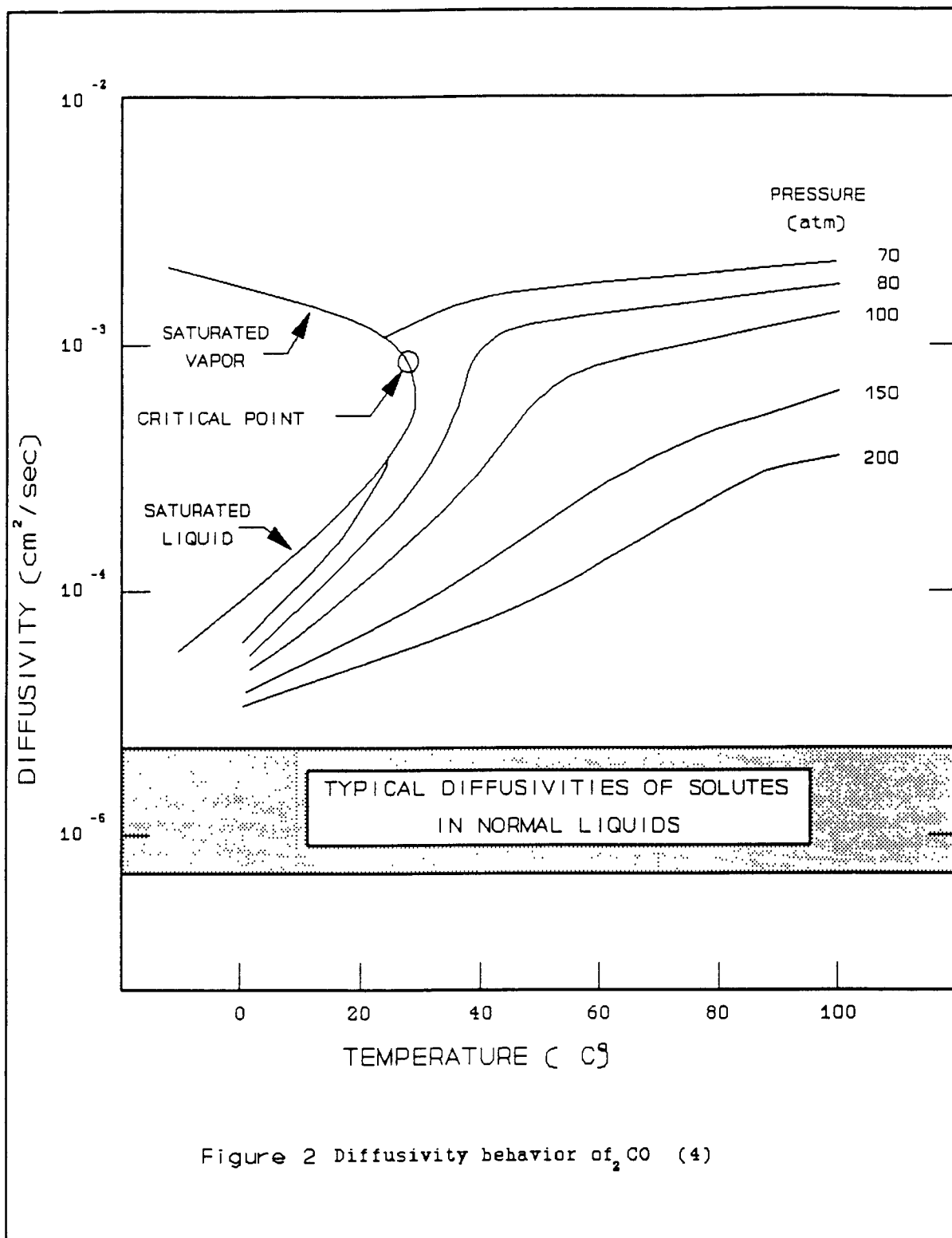


Figure 2 Diffusivity behavior of CO_2 (4)

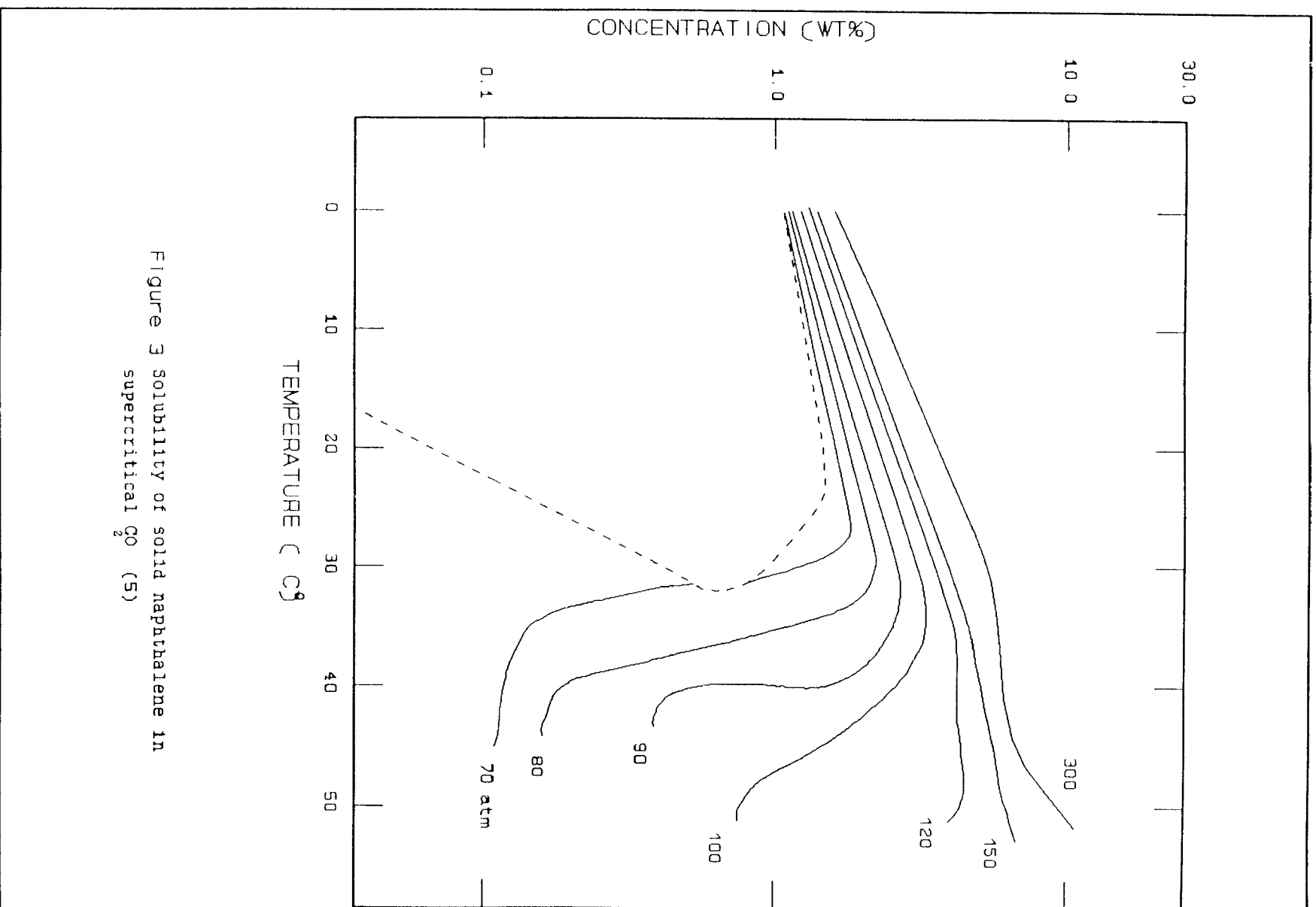


Figure 3 Solubility of solid naphthalene in supercritical CO₂ (5)

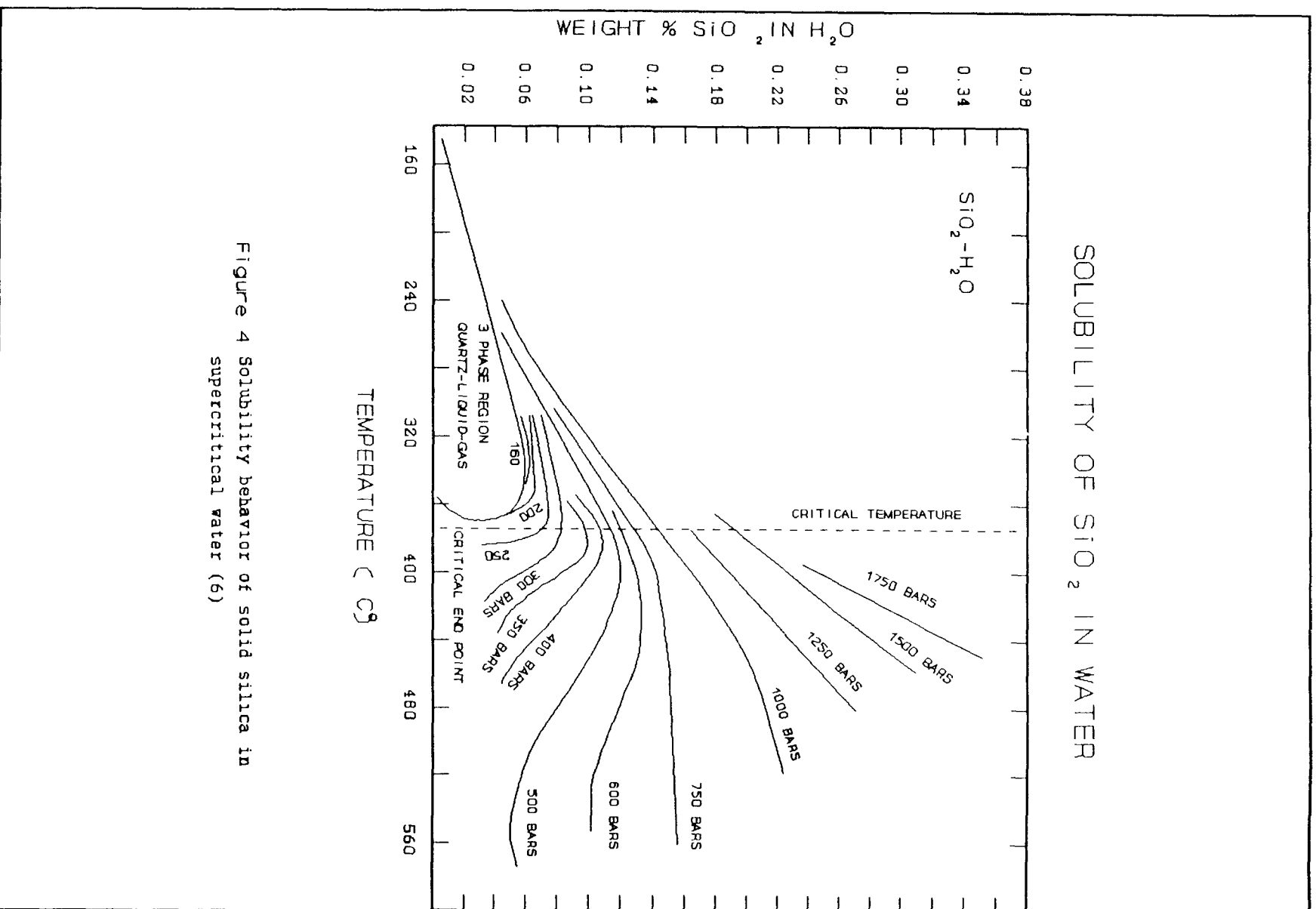


Figure 4 Solubility behavior of solid silica in supercritical water (6)

details in multiple sizes. Kammel and O'Neil (1990) reported on a farm sized concrete loading pad that meets many small facility needs.

STANDARDIZED MODULAR CONCRETE PAD DESIGN

Modular concrete mixing/loading/storage containment pad designs are needed to fit individual operator requirements. Standardized pad designs can be used by aerial and ground pesticide applicators using 1,100 to 1,900 liter (300-500 gallon) rinsate tanks, pesticide mini-bulk or small volume returnable (SVR) containers, non-returnable containers, and a range of pesticide or liquid fertilizer bulk tank sizes.

DESIGN OBJECTIVES

Modular design objectives are to:

1. Develop a simple, modular concrete pad design suitable for mixing/loading and rinsing aerial or ground pesticide and liquid fertilizer sprayers.
2. Develop watertight reinforced concrete specifications to resist ground and weather stress, and chemical or mechanical damage.
3. Design shallow watertight sumps that can resist ground and weather stress cracks, and can be easily cleaned.
4. Provide secondary containment for pesticide and liquid fertilizer leaks and spills.
5. Incorporate areas for pesticide and liquid fertilizer and rinsate storage, handling, mixing, transfer, recovery, and disposal.

FUNCTIONAL PAD LAYOUT AND USE

Agrichemical facility management functions should be the first item addressed in planning new or remodeled facilities areas and functions should include the following:

- | | | |
|----------------------|-----------------------|-----------------------------|
| • Chemical Storage | • Mixing/Loading | • Secondary Containment |
| • Loading Pad | • Worker Safety | • Rinsate/Waste Disposal |
| • Pesticide Security | • Storm Water Control | • Tanking Mounting/Plumbing |

Chemical Storage

Pesticides should be stored in a building for protection from theft, vandalism, temperature extremes and unauthorized personnel. It should be used only for pesticides and be isolated from other buildings. Warning signs indicating dangerous toxic materials must be posted outside by all building or fence entrances. Buildings should be ventilated to prevent an accumulation of toxic fumes. Figure 1 shows the arrangement of functional areas in a farm or small business-sized pesticide facility. Figures 2 and 3 illustrate plan and cross section details of this same facility. Specifications for a small storage

Rinsate/Waste Disposal

Rinsate is segregated by crop or pesticide and reused on the target crop, eliminating disposal as hazardous waste. If the loading pad is not roofed, rainwater falling on the pad is collected and stored for future use, if there has been a spill. If the pad is clean, rainwater may be pumped off the pad. To eliminate contaminated solids disposal problems, exterior washing of ground applicators should be done at the application site immediately after each operation.

Pesticide Security

Chemical and rinsate storage containment areas should be secured by heavy chain-link fencing (Figure 4) or be inside a locked building. Fencing mounted flush with the outer containment wall should be at least 1.8 meters (6 feet) of combined height. Fencing not flush wall mounted (with a concrete ledge) should extend 1.8 meters (6 feet) above concrete walls. Containment section widths (Figures 4 and 8) can be sized for the installation of pesticide storage buildings, such as the OSU (1983) pesticide building, Midwest Plans Service (1979) storage building or other suitable structures.

Empty disposable containers should be stored on a covered, curbed area to prevent rain entry into containers or leaks from containers contaminating the soil. Empty minibulk or Small Volume Returnable (SVR) containers should also be stored in this area.

Storm Water Control

Divider walls separating loading from containment areas, Figures 5, 6, and 7, have no openings. Spills, leakage, or stored rinsate can not be discharged into surface water channels without pumping. Sumps should be formed using coned bottom cylindrical stainless steel sump liners cast in-place with the liner used as the inside concrete form for ease of cleanout.

Tank Mounting and Plumbing

Rinsate tanks should be elevated at least 8-15 centimeters (3-6 inches) above concrete floors for quick leak identification. Tanks must be anchored to prevent overturning and plumbed with flexible hoses between tanks to avoid pipe ruptures from floatation of partially filled, improperly anchored tanks during major leakage events or rain storms. Transfer hoses should be marked by crop or chemical for positive I.D. of tank and product to eliminate cross-contamination.

LIQUID FERTILIZER CONTAINMENT

The major problem in designing containment sections is determining the best combination of containment area and wall height (CVD + liquid freeboard) to provide the 125% of volume of the largest tank. The area displaced by all tanks, including the area of the largest tank, plus any equipment in the containment area must be added to the net fluid volume that can be released by the largest tank when the liquid level stabilizes. The volume of fluid remaining in the largest tank at the liquid level equilibrium height must be subtracted from the total tank volume in the computation, Equation 1.

The containment holding volume should be designed to provide a minimum of "125% of largest tank" for pesticide, rinsate, or liquid fertilizer tank containment to provide inches of liquid level freeboard. Rinsate tank management systems normally are operated with 3 to 6 tanks ranging from 300 to 500 gallons each. If small to moderate sized liquid fertilizer tanks, ranging from 5,000 to 25,000 gallons are planned for use with this pad design, containment section widths and sidewall heights need to be sized to accommodate the required 125% volume of largest tank. Some states use 110% of largest tank plus a 6" rain as their containment volume regulation design.

The use of very large liquid tanks (50,000 - 1,000,000 gallons) is outside the scope of this paper. These tanks require development of special containment pads and foundations due to their size. They may be incorporated into the main concrete pad containment, or be designed as individual structures with their own containment areas separate from the wash pad and pesticide tank containment area. Design guidance by Midwest Plan Service (1983) for circular concrete tanks may be helpful for large tank foundation designs.

Some state laws allow non-concrete containment designs for large liquid fertilizer tank installations. One design uses flexible liners, either a 36 or 45 mil thickness DuPont Hypalon, laid on a sand sub-base with 6 inches of clean smooth washed river run gravel as ballast. Liners are placed over soil berms, concrete outer walls (padded on the inside), or special composite plastic structural walls. Some states allow compacted clay or other impervious soil lined containment; the risk of having to dispose of contaminated soil after a leak or spill makes this option a high risk.

NOTE: The total containment volume must be reduced by the volumes displaced by tanks and equipment that take up containment space. Pesticide rinsate should not be stored in the same containment section with fertilizers. Fertilizers must not be stored in the same containment section with full strength pesticides. BY LAW!

DESIGN LAYOUT CONSIDERATIONS

NOTE! It is extremely important to do scale drawing layout of the area with the tanks drawn to scale in position, as the 125% of largest tank provides minimum area when depths of 3 ft. or more are used.

Functional Layout Questions:

- (1) Is there adequate space for present and future tanks plus mixing and transfer equipment in the proposed containment area?
- (2) Will the area be adequate for potential growth and can small existing tanks be replaced by larger tanks in the future?
- (3) From a safety standpoint, can workers move between tanks with hoses and move over containment walls without undue risk or hazards?
- (4) Will safety steps and handrails be required to move over walls, and if so, will this be a continual problem for workers, especially in icy weather?
- (5) Can all outside surfaces of all tanks be visually inspected for corrosion, damage and potential leaks?
- (6) Are tanks securely anchored individually or braced together to prevent floatation, tipping over, and damage to other tanks.

- (7) Are tanks plumbed individually or with flexible plumbing connections to avoid plumbing damage and multiple leaks from tank floatation (No rigid pipe manifolds connecting tanks).

These questions should all be answered "YES" when the layout design is checked for tank fit and completed and the wash/containment layout plan is submitted to the appropriate state regulatory agency.

In general, a 30 to 36 inch containment section depth (27-33 inch CVD + 3 inch freeboard) appears to be the most practical, although it may be slightly more expensive than a deeper section. If a deeper section is selected, wide steps on both sides of the wall at security fence gate openings must be provided for personnel safety, comfort, and convenience.

Table 5 gives volume data tank sizes from 5 ft. to 15 ft. diameter for heights to 20 ft. Volume for additional heights can be computed by selecting the volume at the additional incremental depths used for heights above maximum table values and adding the two values together. Tank base areas are needed in computing the total tank area displaced.

CONTAINMENT VOLUME SIZING

Containment volume and liquid freeboard must provide at least 125% of volume of the largest tank. The area displaced by other tanks, plus any equipment in the containment area must be added to the net secondary fluid containment volume (SCV) that can be released by the largest tank when the liquid level stabilizes.

The secondary containment volume can be computed for 125% of the largest tank by using Equation 1:

EQUATION 1.

$$SCV = \frac{LTV \times 1.25 + TBV}{1000} \quad (\text{METRIC}) \quad \text{or} \quad SCV = \frac{LTV \times 1.25 + TBV}{7.5} \quad (\text{ENGLISH})$$

EQUATION 2:

$$CFA = SCV/CVD$$

Where:

SCV	=	Secondary Containment Volume, Cubic Meters. [Cubic Feet]
LTV	=	Largest Tank Volume, Liters [Gallons]
CFA	=	Total Containment Floor Area, Square Meters. [Square Feet]
CVD	=	Containment Volume Depth, meters [Ft.] (Total Average Liquid Depth Plus Freeboard Depth)
1.25	=	125% of Largest Tank Leakage (Provides Freeboard)
1000	=	Liters of Liquid per Cubic meter
[7.5]	=	[Gallons of Liquid per Cubic foot]
TBV	=	Sum of Tank Base Volumes, Cubic Meters [Cubic Feet] (Does not Include Largest Tank as Some Liquid Remains in the Tank.)

NOTE: The volume of fluid remaining in the largest tank at the liquid level equilibrium height must be subtracted from the total tank volume in the computation. The total containment volume must include the volumes displaced by tanks and equipment that take up containment space. Once the approximate wall height or depth of the containment section is selected, and the secondary containment volume (SCV) is determined, the floor area can be calculated. The total containment floor area (CFA) is computed from Equation 2.

For states that use 100% of largest tank plus a 24 hour 25-year storm instead of 125% of the largest tank, use 1.00 (100%) in place of 1.25 (125%) and add the predicted volume of water that falls on the containment area. REMEMBER: All tank bases displace water, so a 6 inch rainfall may raise containment level by 9-12 inches, if 25% to 50% of the volume is taken up by tanks.

EXAMPLE: A liquid fertilizer dealer has 2 - 12 ft. x 20 ft., 3 - 10 ft. x 15 ft., and 2 - 9 ft. x 15 ft. vertical storage tanks that must be contained. He is concerned with building an economical containment section as part of his new applicator load pad and his bulk truck unloading safety pad. He is trying to decide between a 3 ft. 3 in. and a 4 ft. 3 in. containment depth. These depths will provide a 3 inch freeboard depth plus average containment volume depth (CVD).

He first needs to calculate the Net Containment Volume, NCV for each of the two containment section depths, Table 7.

$$\begin{aligned}\text{For 3 ft., NCV} &= \frac{(\text{LTV} - \text{GPF} \times \text{CVD})}{7.5} \times 1.25 = \frac{(16,690 - 848 \times 3)}{7.5} \times 1.25 = \\ &= \frac{(16,960 - 2,544)}{7.5} \times 1.25 = 2,402 \text{ cu. ft.}\end{aligned}$$

At 3 ft. depth, the floor area covered by the leaking liquid = $2,402/3 = 801 \text{ sq. ft.}$

For 4 ft.,

$$\text{NCV} = \frac{(16,960 - 848 \times 4)}{7.5} \times 1.25 = \frac{(16,960 - 3,392)}{7.5} \times 1.25 = 2,261 \text{ cu. ft.}$$

At 4 ft. depth, the floor area covered by = $2,261/4 = 565 \text{ sq. ft.}$

Equipment area or displacement volume of transfer pumps is usually insignificant and will be ignored in this example. If large mixing tanks and transfer tanks or pesticide rinsate containment tanks are to be placed in the containment area, their displacement area and volume must be included.

The floor area displaced by all tanks, including the "leaking" tank is 2×113.1 (12 ft. tanks) + 3×78.5 (10 ft. tanks) + 2×63.6 (9 ft. tanks) = $226.2 + 235.5 + 127.2 = 588.9$ or 589 sq. ft. The total containment section floor area for a 3 ft. depth = total liquid displacement area + total tank and equipment area = $801 + 589 = 1,390 \text{ sq. ft.}$ For the 4 ft. depth, the total area = $565 + 589 = 1,154 \text{ sq. ft.}$ A 23 ft. x 60 ft. or 28 ft. x 50 ft area would

Competition causes significant price differences, even within a 30 to 50 mile radius. For example, in central Oklahoma a 6 or 7 bag Type IIA concrete mix will cost about \$45-50 per cubic yard. In central Indiana in an area with little or no competition, prices run \$55-60 per cu. yd. Type II cement normally costs \$2-5 per cubic yard more than Type I cement. A 45' x 70' pad of this design installed at an aerial applicator site in North Eastern Idaho in November, 1989, had delivered concrete costs of \$46.00/cu. yd. Today, this cost would run about \$50-52/cu. yd.

Table 4 lists estimated prices for components and services needed to construct the modular concrete pad designs shown in Figures 4-6 and Table 1, for 6.0 and 7.0 bag mixes. From Table 2, the cement volume required is basically a function of the maximum aggregate size selected. With 1.0 inch to 1.5 inch aggregate, a 5.5 or 6.0 bag/cubic yard mix should provide equivalent strength to a 7.0 bag mix using 1/2 inch aggregate for approximately 4,000-4,500 psi compressive strength concrete.

Forming labor and finishing labor usually quoted on a cost/sq. ft. basis. Some concrete contractors combine forming and finishing quotes at slightly lower costs. Typical forming costs range from \$.20 to .30/sq. ft.; finish costs range from \$.25 to .35/sq. ft. Total forming placement and finishing costs range from \$.45 to .65/sq. ft. These costs may increase by 30-50% in some high labor cost areas. The differences in total cost for 6.0 bag versus 7.0 bag mixes amounts to about \$5.00-\$7.00/cu. yd. finished, or about 5% added cost for a 7.0 bag mix.

NOTE: The cost estimates in Table 4 are based on constructing new concrete pads on bare undisturbed earth within the base zone of the concrete plant, when no unusual construction problems are encountered. No security fences and gates, rinsate tanks, pumps, plumbing, electrical wiring, buildings, or approach ramps are included.

Concrete pad costs vary significantly with geographic location, availability and competitive costs of concrete and concrete readimix plant location from the construction site. Total pad costs as a ratio of delivered concrete costs typically range from about 2.5 to 3.0 X (where ground is level and clear -- minimum earthwork). If substantial earthwork or reconstruction is required, costs may run 3.5 to 4.5 X delivered concrete costs. At a ratio of 3.0 for \$50/cu. yd. concrete, total finished cost would be 3.0 X \$50/cu. yd. = \$150 cu. yd. At that rate, a 50' x 65', 68 cu. yd. pad would cost \$10,200. With substantial site preparation or removal of an existing structure was involved at a remote site, the cost for this size pad may be \$13,000 to \$15,000.

FUTURE DESIGN ASSISTANCE

Standardized concrete wash and containment pad designs for aerial and ground agricultural chemical applicators in the U.S. are now being developed by the authors of MWPS-37, "Fertilizer and Pesticide Facilities Handbook" for Midwest Plan Service, Ames, IA and Tennessee Valley Authority (TVA) for Summer 1991 publication. More construction cost, structural design and tank volumes vs. containment pad size and shape detail on the commercial pads can be obtained by requesting the technical paper by Noyes and Kamme1 (1989), and on the farm pads by contacting Kamme1 and O'Neil (1990).

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Table 1. CONCRETE PAD DIMENSIONS

<u>Dimension</u> ^{***}	<u>Pad Size</u> m x m (ft x ft)					
	6.1x9.1 (20x30)	9.1x12.2 (30x40)	12.2x16.8 (40x55)	15.2x21.3 (50x70)	18.3x24.4 (60x80)	24.4x33.5 (80x110)
A	6.10 m (20'-0")	9.14 m (30'-0")	12.19 m (40'-0")	15.24 m (50'-0")	18.29 m(60'-0")	24.38 m (80'-0")
B	3.05 m (10'-0")	3.05 m (10'-0")	4.57 m (15'-0")	6.10 m (20'-0")	6.10 m(20'-0")	9.15 m (30'-0")
C	9.14 m (30'-0")	12.19 m (40'-0")	16.76 m (55'-0")	21.3 m (70'-0")	24.38 m(80'-0")	33.53 m (110'-0")
D	6.10 m (20'-0")	9.14 m (30'-0")	12.19 m (40'-0")	15.24 m (50'-0")	18.29 m(60'-0")	24.38 m (80'-0")
E	3.05 m (10'-0")	4.57 m (15'-0")	6.10 m (20'-0")	7.62 m (25'-0")	9.14 m(30'-0")	12.19 m (40'-0")
F	35.56 cm (14")	43.18 cm (17")	45.72 cm (18")	45.72 cm (18")	45.72 cm (18")	60.96 cm (24")
G	35.56 cm (14")	43.18 cm (17")	45.72 cm (18")	53.34 cm (21")	60.96 cm (24")	76.20 cm (30")
H	41.91 cm (16.5")	53.34 cm (21")	58.42 cm (23")	68.58 cm (27")	78.74 cm (31")	96.52 cm (38")
I	0 cm (0")	0 cm (0")	0 cm (0")	0 cm(0")	0 cm (0")	0 cm (0")
J	20.32 cm (8")	27.94 cm (11")	30.48 cm (12")	38.10 cm (15")	45.72 cm (18")	60.96 cm (24")
K	13.97 cm (5.5")	17.78 cm (7")	17.78 cm (7")	22.86 cm (9")	27.94 cm (11")	40.64 cm (16")
L	20.32 cm (8")	27.94 cm (11")	30.48 cm (12")	38.10 cm (15")	45.72 cm (18")	60.96 cm (24")
M	30.48 cm (12")	45.72 cm (18")	45.72 cm (18")	45.72 cm (18")	45.72 cm (18")	45.72 cm (18")
N	45.72 cm (18")	76.20 cm (30")	76.20 cm (30")	76.20 cm (30")	76.20 cm (30")	76.20 cm (30")
O	5.08 cm (2")	5.08 cm (2")	5.08 cm (2")	5.08 cm (2")	76.20 cm (30")	76.20 cm (30")
P	11.43 cm (4.5")	12.70 cm (5.0")	12.70 cm (5.0")	13.97 cm (5.5")	13.97cm (5.5")	15.24 cm (6.0")
Q	3.5%	3.0%	2.5%	2.5%	2.5%	2.5%
R	0.95 cm (3/8")	0.95 cm (3/8")	0.95 cm (3/8")	1.27 cm (1/2")	1.27 cm (1/2")	1.27 cm (1/2")
S	3.05 m (10')	3.05 m (10')	3.96 m (13')	3.96 m (13')	4.57 m (15')	3.96 m (13')
T	2.13 m (7')	3.05 m (10')	3.96 m(13')	3.96 m (13')	4.57 m (15')	3.96 m (13')
U	2839 L (750 Gal.)	5678 L (1500 Gal.)	12924 L (3415 Gal.)	27303 L (7215 Gal.)	39612 L(10465 Gal.)	110230 L(29125 Gal.)
V	54.61 cm (21 1/2")	85.09 cm (33 1/2")	85.09 cm (33 1/2")	85.09 cm (33 1/2")	85.09cm (33 1/2")	85.09 cm(33 1/2")
W	49.53 cm (19 1/2")	80.01 cm (31 1/2")	80.01 cm (31 1/2")	80.10 cm (31 1/2")	80.01cm (31 1/2")	80.01 cm(31 1/2")
X ₁	60.96 cm (24")	91.44 cm (36")	91.44 cm (36")	91.44 cm (36")	91.44 cm (36")	91.44 cm (36")
X ₂	50.48 cm (19 7/8")	80.96 cm (31 7/8")	80.96 cm (31 7/8")	80.96 cm (31 7/8")	80.96cm (31 7/8")	80.96 cm (31 7/8")
Y ₁	66.04 cm (26")	96.52 cm (38")	96.52 cm (38")	96.52 cm (38")	96.52 cm (38")	96.52 cm (38")
Y ₂	55.56 cm (21 7/8")	86.04 cm (33 7/8")	86.04 cm (33 7/8")	86.04 cm (33 7/8")	86.04cm (33 7/8")	86.04 cm(33 7/8")

NOTES:

* "I" can be increased to provide Increased containment volume; If "I" is changed, add the new "I" value to "G","H","J" and "K" dimensions.

** "U"= Total Containment Section Volume, Gallons; Displacement Volume of tanks, and equipment must be subtracted to determine Net Usable Volume to meet EPA requirements.

*** See Figures 2-8 for letter designation

Table 2. WATERTIGHT CONCRETE MIX DESIGNS - APPROXIMATE VALUES

Max. Coarse
Aggregate Size

cm / (Inches)	Kg(L)/m ³		Lbs (Gals) /yd ³		% By Volume	Kg/m ³ (bags/m ³)	lb/yd ³ (bags/yd ³)	Kg/m ³ (lbs/yd ³)	Kg/m ³ (lbs/yd ³)	Kg/m ³ (Lbs/yd ³)	
	0.40 ⁽¹⁾	0.45 ⁽¹⁾	0.40 ⁽¹⁾	0.45 ⁽¹⁾						0.40 ⁽¹⁾	0.45 ⁽¹⁾
1 3/4 (1 1/2)	119(119)	134(134)	200(24)	225(27)	7.0	384(9.6)	650(6.5)	783(1520)	914(1540)	2200(3710)	2215(3735)
1 9/16 (3/4)	109(109)	124(124)	183(22)	208(25)	6.0	362(8.5)	510(6.5)	731(1215)	1026(1730)	2236(3764)	2251(3793)
1 5/16 (1)	99(99)	114(114)	167(20)	192(23)	5.0	345(8.1)	503(6.2)	703(1200)	1103(1860)	2250(3795)	2265(3820)
1 1/2 (1 1/2)	94(94)	104(104)	158(19)	175(21)	5.5	320(7.7)	435(5.7)	691(1105)	1169(19.0)	2274(3828)	2284(3845)

Note

- (1) Available surface water in coarse aggregate estimated @ 1.5% K₁. Available surface water in fine aggregate estimated @ 3.5% K₂. Gravel w/ some crushed aggregate may require less water required by (1) 9 Kg/m³ (20 lb/yd³)
- (2) Type III or IA or Type II or I portland cement with air-entrainment additive
- (3) Fine Aggregate (sand) and Coarse Aggregate (crushed rock or gravel) should have a fineness modulus of approximately 2.50
- (4) Water/Cement Ratio of 0.40 or 0.45

Table 3. CONCRETE AND STEEL COMPONENT ESTIMATES

Pad Size		Concrete (1)			Reinforcing Steel(2)			
W x L	Total Volume	Pad Thickness	Reinf. Steel Size		Steel Pattern Spacing (3)			
			Containment	Wash	Length	Weight	Pad & Walls	Sum
m x m (Ft x Ft)	cu. m (Cu. Yds.)	cm (in)	Centimeters (in)	Dia. cm (in)	m (Ft.)	kg (lb.)	cm (in)	cm (in)
6.1x9.1 (20x30)	9.2 (12)	15.2 (6.0)	11.4 (4.5)	0.95 (3/8)	610 (2,000)	340 (750)	30.5x30.5 (12x12)	15.2x15.2 (6x6)
9.1x12.2 (30x40)	18.3 (24)	15.2 (6.0)	12.7 (5.0)	0.95 (3/8)	1,158 (3,800)	649 (1,430)	30.5x30.5 (12x12)	15.2x15.2 (6x6)
12.2x16.7 (40x55)	33.6 (44)	15.2 (6.0)	12.7 (5.0)	0.95 (3/8)	2,000 (6,560)	1,120 (2,465)	30.5x30.5 (12x12)	15.2x15.2 (6x6)
15.2x21.7 (50x70)	52.0 (68)	15.2 (6.0)	12.7 (5.0)	1.27 (1/2)	2,778 (9,120)	2,770 (6,110)	30.5x30.5 (12x12)	15.2x15.2 (6x6)
18.3x24.4 (60x80)	78.7 (103)	15.2 (6.0)	12.7 (5.0)	1.27 (1/2)	3,955 (12,975)	3,945 (8,695)	30.5x30.5 (12x12)	15.2x15.2 (6x6)
21.3x29.0 (70x95)	108.6 (142)	15.2 (6.0)	12.7 (5.0)	1.27 (1/2)	5,300 (17,390)	5,285 (11,650)	30.5x30.5 (12x12)	15.2x15.2 (6x6)
24.4x33.5 (80x110)	149.1 (195)	15.2 (6.0)	12.7 (5.0)	1.27 (1/2)	6,875 (22,560)	6,855 (15,115)	30.5x30.5 (12x12)	15.2x15.2 (6x6)

Note:

- (1) Concrete volumes computed at 10% discount for below grade.
 (2) Steel includes 5% joint overlap allowance; overlap at steel joints - 20 diameters or 12" minimum.
 (3) Sump area steel at 6" x 6" spacing in steel channel steel base with an 18" extension into the concrete pad.

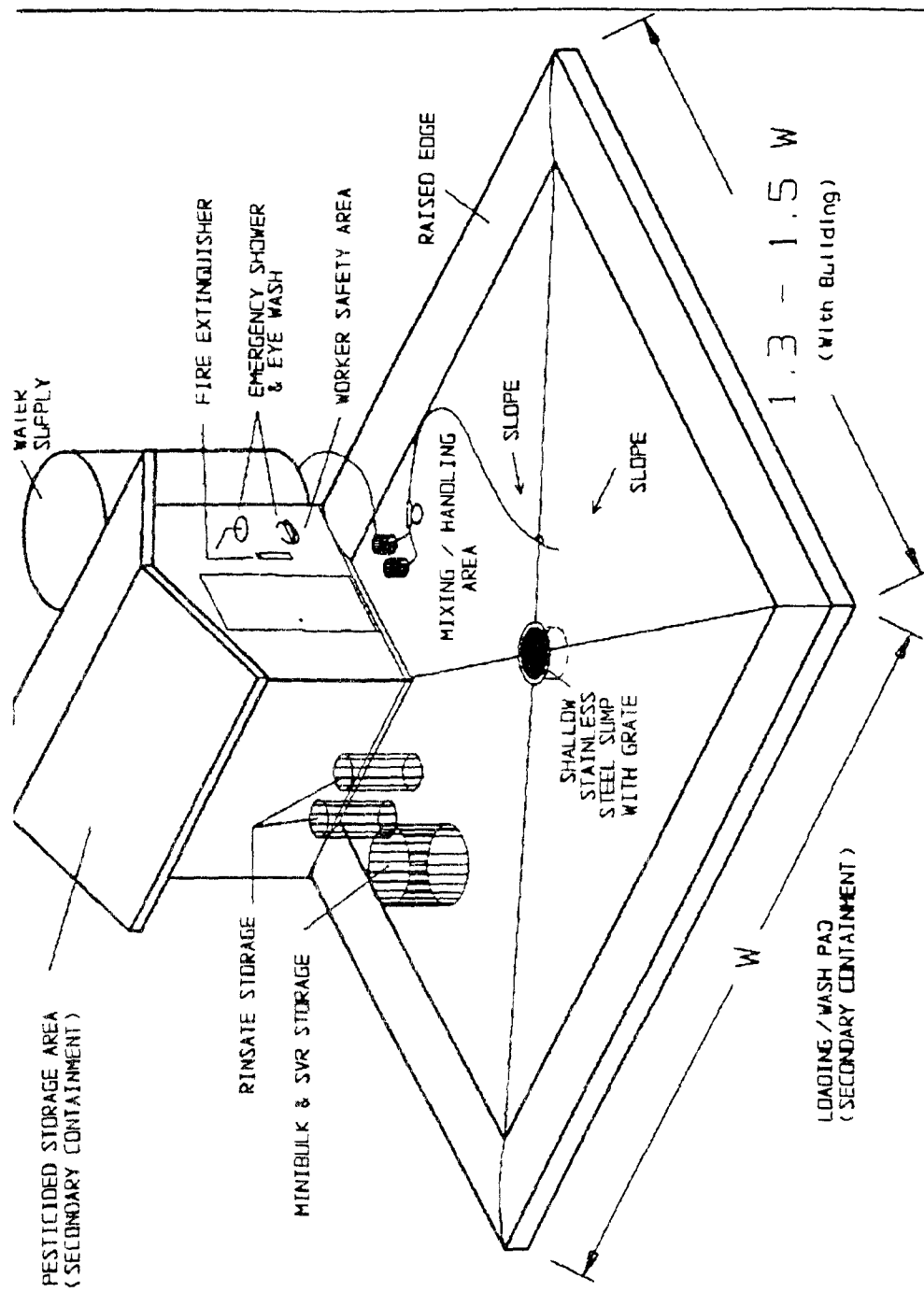


Figure 1.

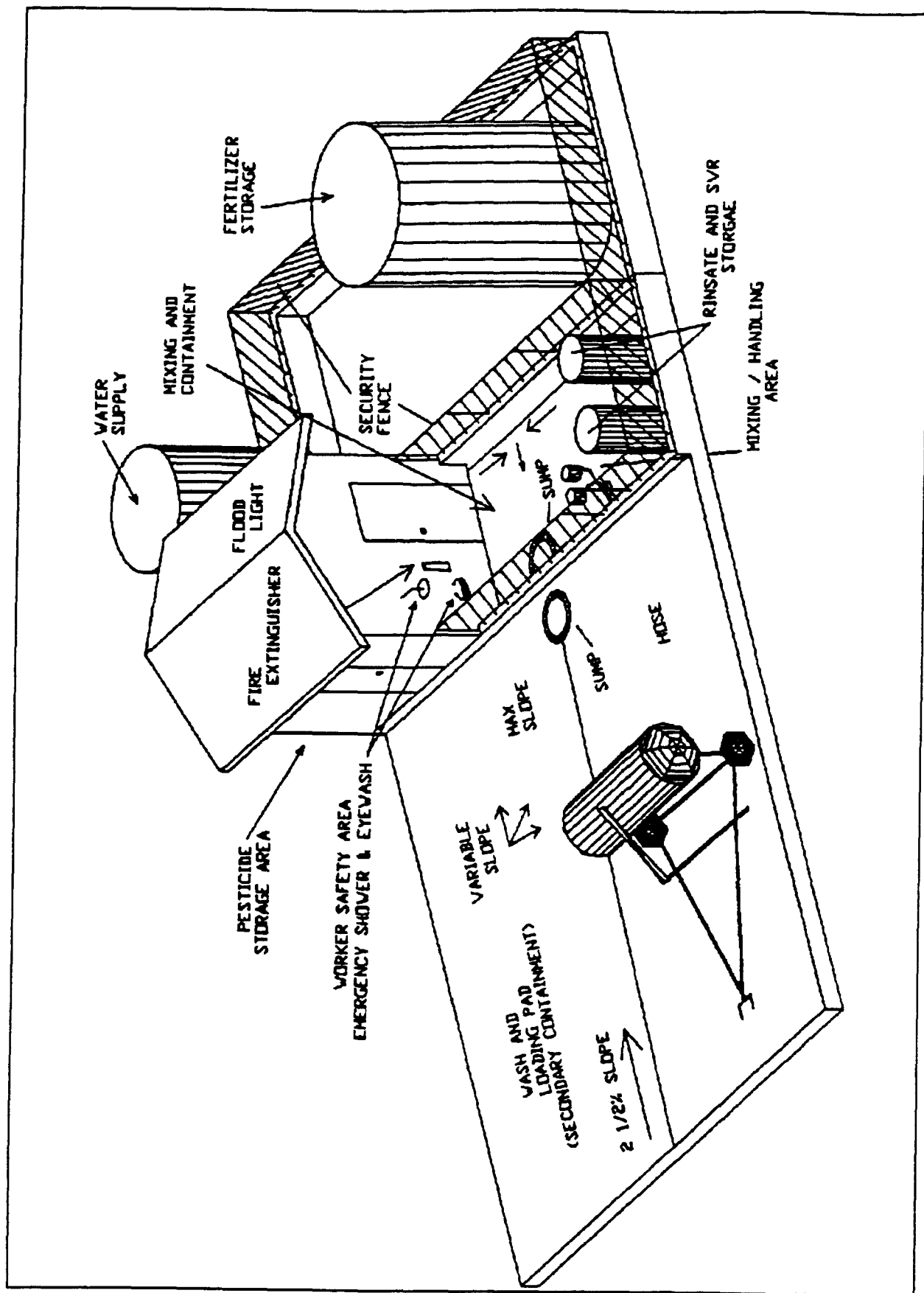


Figure 4.

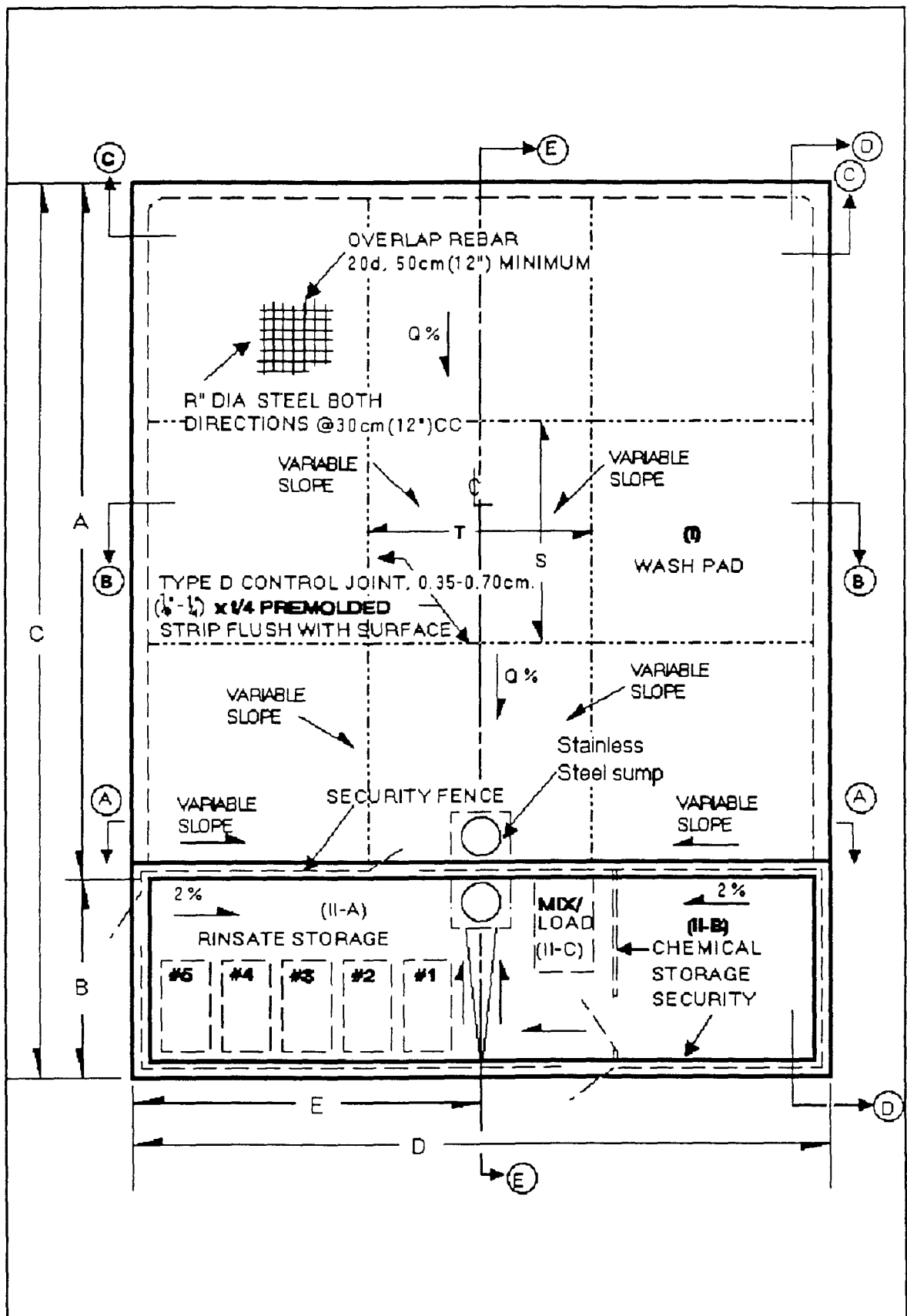
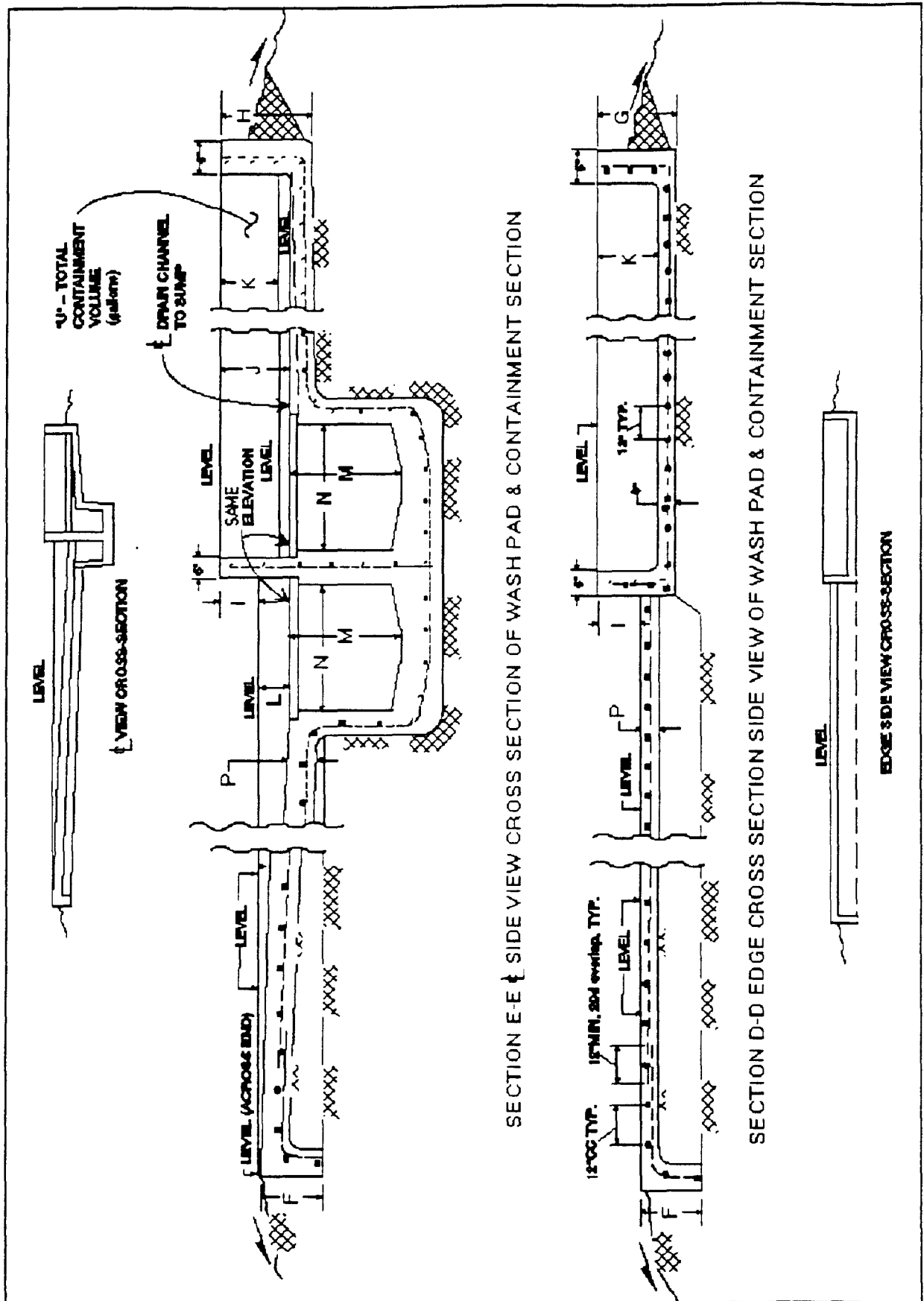


Figure 5.



SECTION E-E SIDE VIEW CROSS SECTION OF WASH PAD & CONTAINMENT SECTION

SECTION D-D EDGE CROSS SECTION SIDE VIEW OF WASH PAD & CONTAINMENT SECTION

Figure 6.

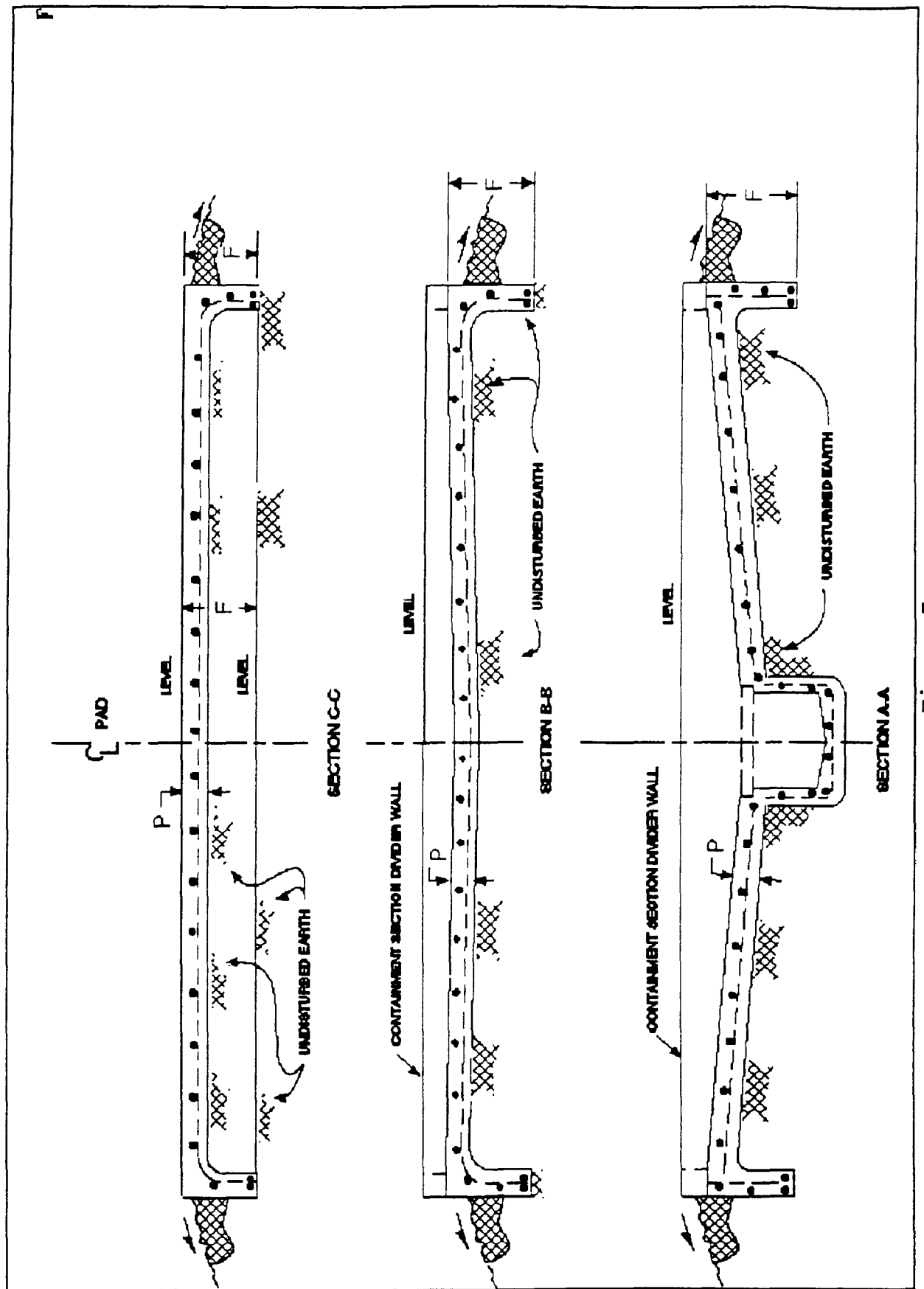


Figure 7.

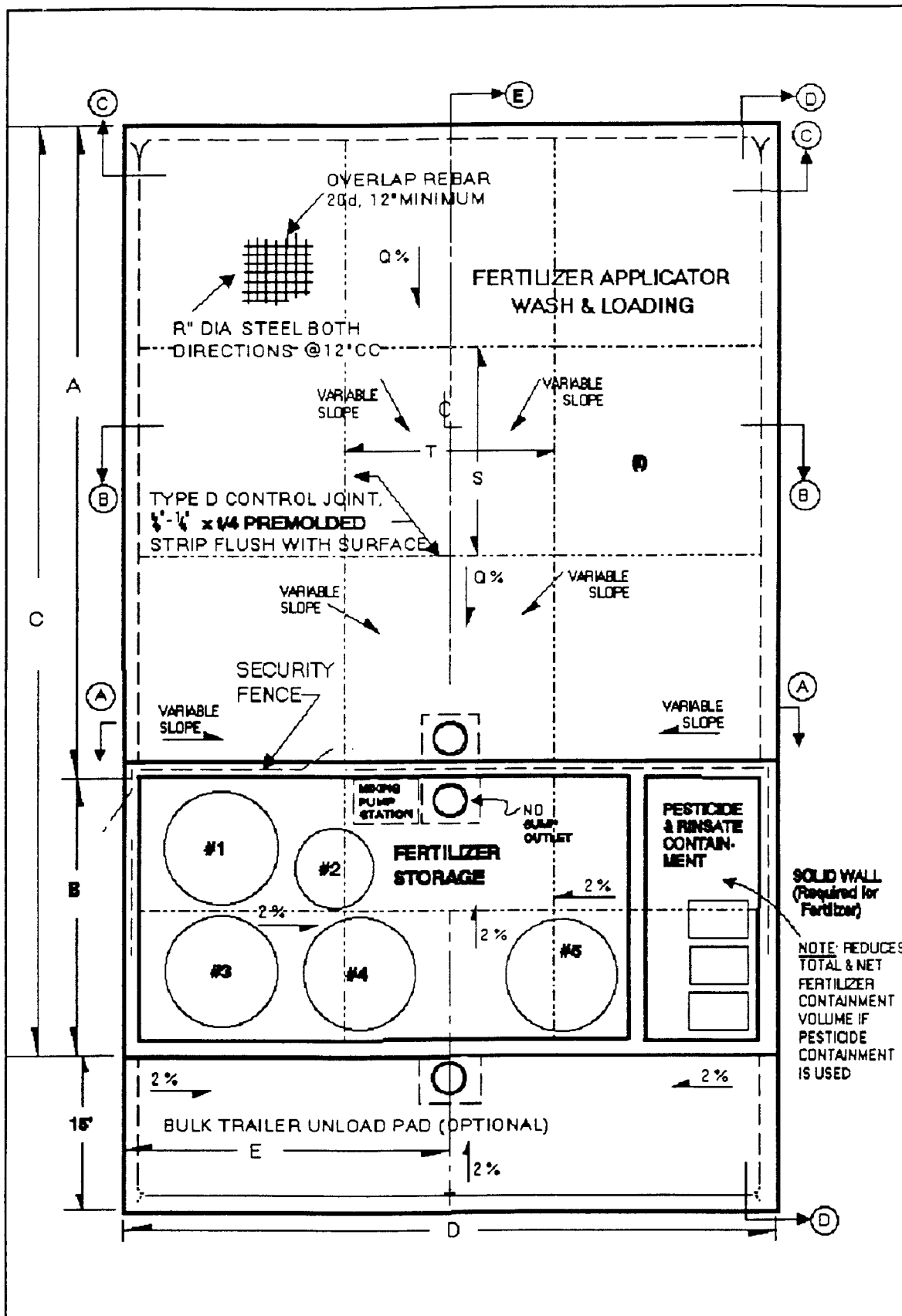


Figure 8.

Waste Minimization for
Non-Agricultural Pesticide Applicators:
EPA's Pollution Prevention Guide

by

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INTRODUCTION

U.S. EPA's Office of Research and Development is preparing a guide to be published later this year for non-agricultural pesticide applicators which will provide specific information about waste minimization for pesticide users in industries such as commercial lawn care, structural pest control, greenhouse operations, and forestry. The guide is being published under the authority and responsibility given to EPA under the 1984 Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act (RCRA). As the federal agency responsible for writing regulations under RCRA, the U.S. Environmental Protection Agency (EPA) has an interest in insuring that new methods and approaches are developed for minimizing hazardous and other wastes and that such information is made available to the industries that generate waste. The guide being developed for non-agricultural pesticide applicators is one in a series of industry-specific pollution prevention guides that will assist companies from selected industries in minimizing wastes generated within their operations.

EPA has defined waste minimization to consist of source reduction and recycling. In EPA's four tiered waste management hierarchy, which presents the Agency's ordered strategy for addressing waste generation and management, source reduction and recycling are the top two tiers:

- source reduction
- recycling
- treatment
- disposal

Of the two waste minimization approaches, source reduction -not creating waste in the first place - is considered environmentally preferable to recycling. The recently passed "Pollution Prevention Act" of 1990 further emphasizes the preference for source reduction in that Congress requires EPA to carry out a number of activities related to researching and promoting source reduction. The treatment and disposal of wastes, long the focus of EPA's research and regulatory attentions, are considered neither waste minimization nor pollution prevention.

EPA'S WASTE MINIMIZATION OPPORTUNITY ASSESSMENT MANUAL

Before EPA began work on developing industry specific guidance manuals for waste minimization, EPA's Office of Research and Development (ORD) published a general manual for waste minimization which can be used by companies within all industrial and commercial sectors, including non-agricultural pesticide users.

The Waste Minimization Opportunity Assessment Manual (USEPA 1988) describes how to conduct a waste minimization assessment and develop options for reducing waste generation. It explains the management strategies needed to incorporate waste minimization into company policies and structure, and discusses how to establish a company-wide waste minimization program, conduct assessments, implement options, and make the program an on-going one.

The systematic procedure outlined in the manual for carrying out a waste minimization opportunity assessment (WMOA) has four phases. They are: 1) planning and organization, 2) assessment, 3) feasibility analysis, and 4) implementation. In the planning and organization phase, essential elements are: getting management commitment, setting waste minimization goals, and organizing an assessment task force. The next phase, the assessment itself, involves the following steps:

1. Collect waste generation data
2. Prioritize and select assessment targets
3. Select assessment team
4. Review data and inspect site
5. Generate options for reducing waste
6. Screen and select options for feasibility study.

Options that pass the assessment screening are carried into the third phase, the feasibility analysis, in which a technical evaluation and an economic evaluation are performed. The technical evaluation determines whether a proposed option will work in the specific application that is envisioned at the company. During the feasibility phase, an economic evaluation is carried out to analyze the cost ramifications of implementing an option using standard measures of profitability, such as payback period, return on investment, and net present value.

Finally, in the fourth phase, implementation, the options that pass technical and economic feasibility reviews should be executed. It is then up to the assessment team, with management support, to continue the process of tracking wastes and identifying opportunities for waste minimization by performing periodic reassessments.

INDUSTRY SPECIFIC POLLUTION PREVENTION GUIDES

While the WMOA manual has been very popular and has proven successful in providing generic guidance to industry for establishing waste reduction programs, EPA's Office of Research and Development wanted to build on this achievement by offering recommendations for waste reduction techniques and technologies that were industry specific. And so in 1989, ORD's Pollution Prevention Research Branch began developing a series of industry specific pollution prevention guidance manuals.

The manuals are based on existing waste reduction reports already developed for targeted industries by the State of California Department of Health Services (DHS). California's DHS performed waste reduction assessments for several businesses within an industrial category and compiled them in a report for the industry. What EPA is doing is modifying and augmenting the California reports so that they are comprehensive, nationally applicable guidance documents. The EPA manuals describe wastes and waste generating processes within the subject

industry followed by specific suggestions for reducing these wastes through source reduction and recycling. Also provided are industry-specific worksheets to assist companies and environmental professionals in methodically conducting waste minimization assessments for facilities within the subject industry.

In 1990, EPA published seven industry-specific pollution prevention guides, and plans another 12 for 1991. One of the manuals already published, Guides to Pollution Prevention: The Pesticide Formulating Industry, EPA/625/7-90/004, and the manual to be published later this year for non-agricultural pesticide applicators should be of special interest to this audience. It is this second manual that is the subject of the present paper. Below, a summary will be provided of the major recommendations for reducing waste generation within companies and operations that use pesticides for non-agricultural purposes.

NON-AGRICULTURAL PESTICIDE APPLICATOR INDUSTRY PROFILE

The non-agricultural pesticide application industry consists of the following types of firms: landscape maintenance firms, commercial nurseries, and structural pest control firms, as well as government agencies that run these kinds of operations. The SIC codes which apply to the industry are lawn and garden services (SIC 0782), tree spraying (SIC 0783), ornamental floriculture and nursery products (SIC 0181), food crops grown under cover (SIC 0182), forest pest control (SIC 0851), mosquito eradication (SIC 4959), and disinfecting and pest control services for dwellings and buildings (SIC 7342).

This group represents a sizable portion of the demand for and use of pesticides. A 1980 study, which presented the results of a survey of pesticide users classified into three categories: agriculture, industry and government, and home and garden, attributed 21% of pesticides use to the industry and government sector, roughly equivalent to the non-agricultural pesticide applicators group. Of the remainder of pesticide used, agriculture accounts for 72% and only 7% is due to home and garden use (Aspelin and Ballard, 1980).

WASTE GENERATION

Operational activities within the industry that have the potential for generating wastes include: pesticide storage and distribution; pesticide mixing and formulation; application of pesticides; cleaning of storage, mixing, and application equipment; and waste management. Major waste streams within this industry are: used protective clothing; empty pesticide containers; rinsate from pesticide containers and applicators; and surplus inventory. In a broader, but still very legitimate sense, pesticide wastes also include those pesticides unnecessarily or over-applied to targeted areas and pesticides mistakenly or inadvertently applied to non-targeted areas.

SOURCE REDUCTION

Source reduction as mentioned above is the preferred method of waste minimization. It can be defined as any activity that reduces or eliminates the generation of waste at the source, usually by substituting non- or less toxic or hazardous chemicals for more highly toxic or hazardous chemicals, changing operations and maintenance procedures to reduce waste, and technology innovations

that improve efficiency of raw material usage.

Integrated Pest Management

Clearly, one of the best ways of minimizing pesticide waste is to minimize pesticide use. By utilizing a whole range of approaches, including cultural, biological and chemical methods, for controlling pests to acceptable levels, integrated pest management (IPM) significantly reduces pesticide use. The amount of reported reduction in pesticide use upon implementation of an IPM program commonly ranges from 50% to 90% and above. Instead of relying on pesticide application frequencies that are predetermined and calendar based, IPM strategies only resort to chemical pesticide applications when other methods have failed and plant or habitat monitoring indicates that chemical pesticide applications are needed to prevent pest damage from exceeding economic or aesthetic thresholds. An added advantage of IPM is that with decreased exposure to chemical pesticides because alternatives are employed, pests are less likely to become resistant. When chemical pesticides must be used they are likely to be more effective.

Much has been written about various IPM programs within the non-agricultural sector, including descriptions of programs used for controlling pests in forests and parks (Daar, 1987; Widin, 1987; and Nielsen, David, 1989; Ticehurst et al., 1988; Collman, 1990) greenhouses (Helyer and Payne, 1986), commercial lawn care (Leslie et al., 1989), and mosquito abatement. The citations provided are only a partial listing; the literature describing IPM is extensive for non-agricultural, as well as agricultural sectors. Because of the success of IPM and the large reductions in pesticide use and pesticide waste that can be achieved, an investigation of IPM alternatives should be a fundamental part of any waste minimization program for the pesticides application industry.

Inventory Control

Within the pesticide applicator industry, as with any industry that uses raw materials which in themselves are hazardous or toxic, proper inventory management can prevent chemicals from becoming waste when shelf life has been exceeded or improper storage has resulted in spills or spoilage. To avoid this kind of waste generation, tight controls should be placed on ordering pesticides, and only those needed for the current season should be purchased and stored on-site. This reduces the chance that pesticide will become out-of-date or useless due to bans on its use. Larger operations may want to go to a computerized inventory control system. In the event that pesticide expiration dates are exceeded, the prudent purchase of pesticides from suppliers who have policies for accepting the timely return of full, unopened containers will avoid this material from becoming waste.

Good storage and spill control provisions help reduce pesticides waste resulting from spoilage and spills. Precautions should be in place to secure pesticide storage locations and to prevent entry and mishandling by unauthorized personnel. Only a limited number of trained personnel should have access to storage areas. To reduce the possibility of spoilage, pesticides should be stored in areas that are protected from moisture, sunlight, and extremes in temperature. Most pesticides have a longer shelf life if stored in cool, dry areas out of direct sunlight (Ware, 1983). To reduce the possibility of spills, exposure to high activity areas, floor traffic and machinery should be avoided. Pesticides should be stored on pallets or shelves that allow for easy, periodic inspection for signs of damage or leakage. To isolate and properly handle those

spills that may occur, storage areas should have secondary containment or drainage control (California DHS, 1991).

Product Substitution

Pesticide wastes may be reduced by replacing or substituting a toxic pesticide with one that is less toxic. Examples include using biodegradable or short-lived herbicides instead of those that are very persistent; using relatively non-toxic insecticidal soaps instead of toxic insecticides; using pesticide formulations that rely on less toxic "inerts" for active ingredient carriers, such as water instead of solvent; and using non-chemical or mechanical pest control devices such as traps instead of chemical pesticides (California DHS, 1991).

Choice of formulation can minimize loss of pesticide to the non-targeted environment as well as reduce worker exposure. Solid formulations for popular sprayable products, which must be dispersed in water before spraying, may be sold as wettable powders, dry flowables, or water dispersible granules. While the powders have significant dust making potential, especially when conditions are windy, dry flowables and water dispersible granules have the advantage of being dust free if they are well designed. Liquid formulations that carry especially toxic actives, can be microencapsulated to improve their safety and reduce release to the non-targeted environment (Hudson and Tarwater, 1988).

Containers and Packaging

Containers that are triple rinsed are not regulated as hazardous waste, but they remain a source of solid waste if disposed of and not recycled. (The recycling of rinsate and containers will be covered below). Businesses should take a critical look at their container wastes. Product should be purchased in the size container needed for one season's usage and, to minimize waste containers, the procurement of multiple small containers should be avoided. The use of refillable containers could be explored by purchasers and suppliers. For example, pesticide applicators could purchase and dispense product from refillable containers. Fifteen-gallon small volume returnable containers are available for some termiticide products.

The purchase and use of pesticide in premeasured water soluble packages can eliminate packaging as a source of waste because the packaging dissolves and becomes part of the application mixture. Cleanup of measuring and mixing equipment is also avoided. Certain pesticides that are marketed as wettable powders can now be purchased in water-soluble, polyvinyl alcohol film packets that are added directly to application equipment. Water-soluble packaging is also being investigated for liquid pesticides sold as emulsifiable liquid concentrates. (Hudson and Tarwater, 1988)

Improved Mixing and Application Technology

Wastes from mixing and application processes can be minimized by a combination of good standard operating procedures and improved mixing and application technology. By mixing only enough pesticide for the job at hand, using premeasured water soluble packages if available, and using closed mixing systems, wastes can be kept to a minimum. (Marer et al., 1988). In addition, computerized mixing and application systems are now available that reduce cleaning requirements and have the added advantage of accurately controlling the

quantity of pesticide applied. In these systems pesticide and water are independently pumped to spray nozzles by computer controlled metering pumps and mixed directly in the nozzle, thus eliminating the need for a large volume container for holding ready-to-apply diluted pesticide. (California DHS, 1991)

The correct application equipment for the job should be selected because most application equipment used by the non-agricultural applicators group is suited only to a limited number of situations (Marer et al., 1988). Equipment too large for the job is likely to release pesticide to the non-targeted environment as well as increase the amount of rinsate generated during equipment cleanup.

With the advent of controlled droplet technology, the size of droplets emitted from pesticide spraying equipment can be tightly controlled and standardized so that exactly the right droplet size is generated by the spray equipment, maximizing the amount of pesticide hitting its target. Historically used high volume spray equipment reliant on hydraulic nozzles produces a wide range of droplet sizes, from 100 to 1000 microns in diameter, some of which is wasted: too large droplets may fail to meet their target, fall to the ground and end up as run off, and droplets that are too small are prone to wind or drift loss. Other waste minimizing technological improvements to the controlled droplet sprayer are the ultra low volume sprayer and electrodyne spray technology. (Sastry, 1987).

Application Sequencing and Application Timing

Cleaning requirements for application equipment can be minimized by proper sequencing of pesticide applications. By applying all pre-emergent products in sequence followed by all post-emergents, applicator cleanings between different product types can be avoided. As an alternative, dedicated application equipment for each type of pesticide would result in similar reductions (California DHS, 1991). By properly timing the application of pesticides, additional applications can be avoided. For example, by applying pre-emergents at the correct time, future applications of post-emergents may not be needed.

Weather conditions should be taken into account when planning pesticide applications so that pesticide effectively meeting targeted plants or insects is maximized. Application efficiency will be compromised on windy days and applications should be rescheduled if windy conditions prevail. Depending on the type pesticide applied, rain in small to moderate amounts can be a help or a hindrance to pesticide application efficiency.

RECYCLING AND REUSE

According to EPA's waste management hierarchy, if wastes cannot be eliminated via source reduction practices, recycling and reuse are the next best solution to managing them. For non-agricultural pesticide applicators, opportunities exist for recycling rinsate and product containers. Rinsewaters generated by cleaning product containers, application equipment, and vehicles can be recycled by using them as make-up water in new formulations that are compatible with the specific rinsate. Plastic containers of the size used by this industry are not widely recycled; however, several states have test programs to investigate the feasibility of recycling the plastic containers used for packaging agricultural pesticides.

SUMMARY

The above provides a brief summary of the options for minimizing waste that will be included in EPA's upcoming guide for non-agricultural pesticide applicators. In addition to the presentation of options, the manual will include a more detailed description of the industry than is presented here and will include worksheets to assist companies in examining wastes generated as well as opportunities for reducing them. Comments are invited from non-agricultural pesticide applicators and the companies and/or universities that are researching and promoting waste reducing techniques and technologies of interest to this industry.

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Pesticide Container Management in the United States

by

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ABSTRACT

The disposal of containers is a very visible problem in the agricultural pesticide industry. EPA's role in pesticide container management increased drastically with the 1988 amendments to the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Section 19 of FIFRA requires EPA to address pesticide containers in three ways: to promulgate container design regulations, to promulgate residue removal regulations, and to conduct a study of pesticide containers and report the results to Congress. In fulfilling these tasks, EPA has gathered a great deal of information on pesticide containers including use, refill, residue removal, and disposal. The two most common disposal methods for nonrefillable containers are landfilling and open burning, although there are problems associated with both of these options. Recycling is becoming an increasingly viable pesticide container management option. As a result of the container study, EPA has developed a container management strategy, including a hierarchy of desirable containers. The hierarchy is designed to reduce the number of containers requiring disposal. To accomplish this, EPA would like to encourage the use of refillable containers and water soluble packaging as well as increasing the number of containers being recycled.

INTRODUCTION

The disposal of containers is a very visible problem in the agricultural pesticide industry. Accordingly, pesticide containers have received a significant amount of attention beginning with a National Conference on Pesticide Containers in 1972. At the 1985 National Workshop on Pesticide Waste Disposal, container disposal was a focus of the keynote address. Additionally, another speaker at the 1985 workshop discussed the three feasible options for managing empty containers:

- Return for reuse or refilling;
- Recycling to the scrap stream or use for energy recovery; and
- Disposal by burial or burning in approved facilities. (Trask, 1985).

These are still the three main options available for pesticide container management, although all of the options have changed since 1985.

EPA's role in pesticide container management increased drastically with the 1988 amendments to the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Section 19 of FIFRA requires EPA to address pesticide containers in three ways:

- To promulgate container design regulations;
- To promulgate residue removal regulations; and
- To conduct a study of pesticide containers and report the results to Congress.

Specifically, the study is required to develop options to encourage or require:

- The return, refill, and reuse of containers;
- The development and use of formulations that facilitate residue removal; and
- The use of bulk storage facilities to reduce the number of containers requiring disposal.

In the past two years, EPA has worked with many of the people involved with pesticide containers, including industry trade organizations, State agencies, equipment and container manufacturers, packaging experts, and many individuals such as distributors, dealers, commercial applicators, and farmers to gather as much data on pesticide containers as possible. This information is compiled in the report to Congress and is being used to develop the regulations.

The container design and residue removal regulations are intended to apply to containers in all segments of the pesticide industry including agricultural, institutional, industrial, household, and specialty markets. EPA has data that show there are approximately three times as many aerosol pesticide containers (used almost exclusively in the household and institutional markets) produced each year than agricultural pesticide containers. Despite the wide range of pesticides intended to be included in the regulations, this paper will focus on the agricultural segment of the pesticide industry.

A great deal of progress has been made in the past five years in terms of pesticide container disposal and waste minimization, although there are still problems. This paper will briefly present the common types of containers in the agricultural pesticide industry, discuss the disposal options for nonrefillable containers, and describe the EPA container management strategy.

CONTAINER TYPES

EPA has divided pesticide containers into two major types: nonrefillable and refillable. Nonrefillable containers are considered one-way or "throw-away" packages. Generally, nonrefillable containers are relatively small, although there is no maximum size limit. Nonrefillable containers include 1- and 2.5-gallon jugs, 5-gallon cans and pails, bags, bag-in-a-box designs, aerosol cans, and water soluble bags. One major change in nonrefillable containers in the 1980's was the nearly universal adoption of plastic as the major packaging type. Plastic containers were introduced to the pesticide market in the late 1970's and, with the exception of aerosol products, have become the dominant container type for liquids. Most recently, with the advent of dry pesticide products that require smaller amounts of active ingredient per unit area, more of these products are being packaged in plastic jugs.

Refillable containers are designed and intended to be refilled with pesticide for further sale or distribution. The construction materials and design specifications are generally selected to maintain the structural integrity of the container under adverse storage, shipping, and use conditions over the course of multiple fill and use cycles. Some of the containers that fall into this category are bulk storage tanks, minibulks, small volume returnable containers, and refillable bags.

MANAGEMENT OF NONREFILLABLE CONTAINERS

As discussed in the introduction, the relative use of the container management and disposal options available in 1985 have changed. This section addresses the methods currently used to dispose of nonrefillable containers and recycling; reuse and refilling are discussed in greater detail in the next section.

Many states have done surveys to determine the container disposal methods used by farmers and dealers. Table 1 contains the results of a survey done by the Minnesota Department of Agriculture in 1988, which is representative of the various surveys.

Table 1
Methods of Container Disposal (Minnesota, 1988)

Percent of Respondents Who Use Method ¹ (%)		
<u>Disposal Method</u>	<u>Farmers</u>	<u>Dealers</u>
Burn	65.0	30.1
Rinse/take to landfill	23.7	56.1
Rinse/bury	27.5	8.3
Return to dealer	17.8	7.8
Store on site	11.8	7.4
Salvage	3.6	11.5
Can't dispose	2.8	3.2
Out-of-state hazardous waste landfill	1.3	0.7
Other	14.2	7.6

¹ The columns total to greater than 100 percent because respondents could list more than one disposal option.

By far, the two most common disposal methods for nonrefillable containers are landfilling and open burning. Also, in some states, a significant number of farmers bury containers on their own property.

However, there are problems with these disposal methods. An increasing number of farmers, commercial applicators, and dealers are having their containers rejected by landfill operators for several reasons:

- Existing landfill space is diminishing and siting new landfills is difficult;
- Concern for ground water contamination from earlier disposal practices is increasing;
- States are adopting solid waste management strategies that rank landfilling as the least desirable disposal option; and
- Potential liability for future releases of hazardous substances exists.

Open burning is restricted or prohibited by a number of Federal and State regulations. The open burning of pesticide containers is a good example of the interjurisdictional nature of pesticide disposal issues and involves regulations on air, solid waste, and pesticides. Additionally, burying containers presents a certain risk of contaminating soil, ground water, and surface water.

Because of the difficulty and problems associated with the disposal of nonrefillable containers, a number of container collection and recycling programs have begun. EPA is aware of such programs in Mississippi, Oregon, Iowa, Florida, Illinois, North Carolina, Missouri, and Washington. Currently, most of these programs are in the pilot project stage, although many are expanding. Also, Maine has a deposit and return program, although it does not involve recycling.

The existing collection and recycling programs are all different. For example, some are run by the State and others by industry. Additionally, some of the programs collect only plastic containers, while some accept both plastic and metal. However, there are two common features of the collection and recycling programs:

- Properly rinsed containers are essential for a successful program; and
- Inspection of the containers is necessary to ensure proper rinsing.

EPA believes that these are two crucial aspects of establishing successful container collection and recycling programs.

EPA CONTAINER MANAGEMENT STRATEGY

Several general conclusions relating to the development of a pesticide container management strategy emerged from EPA's study and report to Congress. Part of this strategy includes promulgating the container design and residue removal regulations. Additionally, the pesticide container management strategy includes long-term goals, which can be divided into several main categories.

Formulation and Container as a Unit

The first long-term goal is to have the pesticide industry consider the pesticide formulation and its container as a single entity. This would require a significant change in philosophy. Generally, formulating and packaging a pesticide are separate projects done by different groups within a company or by different companies altogether. The change in perception from considering a container simply as a vessel to transport a pesticide to seeing the container as an important part of the pesticide itself is an integral step in the long-term

improvement of containers. The relationship between the container and the pesticide is important in all stages of the pesticide/container life cycle, including use of the container (transportation, storage, transferring pesticide from the container, etc.), residue removal, and disposal of the container.

Provide Leadership

The second long-term container management goal is to provide leadership in the area of pesticide containers. The container study involved a great deal of cooperation between EPA, other Federal agencies, State agencies, industry groups, environmental organizations, and many individuals involved with pesticide containers. EPA would like to continue this dialogue and cooperation in the future.

Move Toward Environmentally Preferable Containers

Another part of EPA's leadership role is to monitor and affect the trends of pesticide containers. In conducting the study, EPA determined that there are several desirable classes of containers. EPA has identified a hierarchy of environmentally sound container classes. This hierarchy is based on information collected on the use of containers, residue removal, and disposal, as well as pollution prevention and reducing solid waste. The Agency would like to encourage the development and use of the most desirable container classes. These container classes are described in the following hierarchy.

This hierarchy is based on the characteristics that EPA has identified for optimal pesticide containers. Any efforts, both public and private, to address pesticide containers should strive for:

- Protection of the integrity of the pesticide product and the environment through which the container passes;
- The safe and easy transfer of pesticide from the container to the application equipment;
- Minimization of the amount of unused pesticide residue remaining in the container after the pesticide has been transferred; and
- Minimization of the number of pesticide containers requiring disposal.

Preferred Pesticide Container Hierarchy

The hierarchy of preferred pesticide container classes is given in Table 2. The most desirable container classes are on top and the least desirable are on the bottom. For the purposes of this paper, a container is considered recyclable if the technology exists to recycle the material from which the container is constructed.

Table 2
EPA Pesticide Container Hierarchy

Refillable containers and water soluble packaging

Nonrefillable, recyclable containers that are currently being recycled

Nonrefillable, recyclable containers that are not currently being recycled

Nonrefillable, nonrecyclable containers

The first two characteristics of optimal containers -- protection of the pesticide product and the environment, and the safe and easy transfer of pesticide -- are functions of the container design. Therefore, these two characteristics are generally independent of the position within the hierarchy, although they vary within each class. Improperly designed or handled containers in the most desirable category may be potentially more harmful than the best designed or handled containers in the least desirable category.

Refillable containers and water soluble packaging are the most desirable container class because they:

- Reduce or eliminate the need for residue removal; and
- Reduce the number of containers requiring disposal.

The next category -- nonrefillable, recyclable containers currently being recycled -- is attractive because it reduces the number of containers requiring disposal as waste.

The third category, nonrefillable, recyclable containers not currently being recycled, includes most nonrefillable steel and plastic containers. Also, the steel industry maintains that aerosol cans are recyclable, although EPA believes additional study is necessary in this area. With the proper infrastructure and market, the containers in this category could move up the hierarchy to reduce the number of containers requiring disposal.

The least desirable category, as determined through the study, are nonrefillable, nonrecyclable containers. Because multiwall paper shipping sacks are usually constructed of more than one material (e.g., kraft paper and a barrier layer), they are not recyclable.

In summary, EPA is addressing pesticide containers in several ways. EPA would like to reduce the number of containers requiring disposal by encouraging the use of refillable containers and water soluble packaging. Also, EPA would like to increase the number of pesticide containers that are being recycled. At the same time, EPA is addressing pesticide container issues on a broader scale than just disposal. The container design and residue removal regulations that are being drafted are intended to increase safety during use, refill, residue removal, and disposal of containers.

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PESTICIDE DISPOSAL IN GUINEA-BISSAU: A CASE HISTORY

by

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ABSTRACT

Guinea-Bissau is a small, underdeveloped country on the southwestern coast of Africa. In June 1990, the Guinea-Bissau Crop Protection Service (CPS) requested USEPA assistance with disposal of surplus pesticides. This paper describes the problems encountered, and outlines several practical disposal options which were presented to the CPS. These low-cost, low-technology approaches can provide developing countries such as Guinea-Bissau with viable methods of pesticide disposal.

INTRODUCTION

Although the chemical approach to pest problems can significantly improve crop yields and reduce the incidence of insect-borne diseases, without careful handling, pesticides also can pose a serious threat to human health and the environment. One unfortunate consequence of chemically-intensive pest control programs is their tendency to generate potentially toxic wastes. The problem of disposal of obsolete or unwanted stocks of pesticides is of vital concern, particularly in developing countries which may lack the technical expertise or financial resources necessary to accomplish sophisticated disposal solutions.

Disposal of unwanted pesticides is of special concern in Africa, where severe tropical climates cause chemicals and their containers to deteriorate more rapidly and where poor storage practices are common. (Jensen, 1983; Jensen, 1987a; Jensen, 1987b; Jensen, 1990; Krueger, 1989) Aging pesticide drums are frequently encountered being stored in the open sun, with leaking chemicals posing a direct threat to human health and surface or groundwater quality.

In the countries in and near the Sahara desert, thousands of tons of obsolete pesticides stocks require disposal. (GIFAP, 1991; World Environment Center, 1987) Many of these stocks were purchased in the late 1960's to control pests such as migratory locusts, tsetse flies and other insects, Quelea birds and weeds.

Government officials in these countries are acutely aware of the potential problems posed by these obsolete stocks, but are unaware of feasible, low-cost options for implementing their safe disposal.

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This paper provides a case study of surplus pesticide problems in the developing African country of Guinea-Bissau and describes several practical, low cost disposal options which the USEPA identified for the Guinea-Bissau authorities.

BACKGROUND INFORMATION

Guinea-Bissau is a small, underdeveloped country, located on the southwestern coast of Africa. The capital city of this predominantly agrarian nation is Bissau. Table 1 provides limited economic statistics for this country.

TABLE 1

Economic statistics for Guinea-Bissau

- \$160 per capita income
- 36,125 square miles
- 900,000 population
- 90% rural population
- 20% adult literacy
- 134/1000 infant mortality
- 90% employed in agriculture

Self-sufficiency in staple food production is a national priority in Guinea-Bissau. To assist in achieving this goal, in 1978 the U.S. Agency for International Development (USAID) initiated a \$4.25 million dollar crop protection. (USAID, 1988) The purpose of the project was to strengthen the capacity of the National Crop Protection Service (CPS) so that it could develop, direct and implement its own crop protection program. The USAID project ended in September 1990.

The USAID program developed integrated pest management (IPM) as the crop protection strategy of choice, with the use of pesticides as a key element of the IPM program. CPS concerns regarding the importation, storage, handling, and disposal of pesticides as well as the management of pesticide containers resulted in formal requests to the USEPA for technical assistance before the end of the project. This assistance was provided by the author in June 1990. Although assistance was provided in all of these areas, only the disposal portion of the assistance will be addressed in this paper.

DISPOSAL OF "OLD" PESTICIDE STOCKS

As an initial step, the CPS conducted an inventory of all pesticide stocks in country, including pesticides potentially requiring disposal. (Castleton, 1990; CPS, 1990) Generally, these pesticides had been stored under unsatisfactory conditions for many years, and the Service was uncertain of the quality of the products and the integrity of their containers. No quality testing laboratory was available in Guinea-Bissau to assist in this evaluation. The pesticides ultimately identified for disposal, primarily on the basis of their age and the condition of their containers, are listed in Table 2.

TABLE 2
Pesticides for Disposal in Guinea-Bissau

Pesticide	Chemical Type	Quantity	Warehouse Location
carbaryl (Sevin*)	c	6,400l	Bissau
dichlorvos (DDVP*)	op	350l	Contuboe1
dicofol (Kelthane*)	oc	600l	Bissau
edifenphos (Hinosan*)	op	600l	Sonoco
fenitrothion (Agrothion*)	op	78l	Bafata/Contuboe1
fenthion (Baytex*)	op	100l	Bafata
phoxim (Volaton*)	op	1,000l	Contuboe1
triadimefon (Bayleton*)		75kg	Bafata
pesticide with no label		200l	Bafata

c = carbamate
op = organophosphate
oc = organochlorine
* = trade name

The next step was to develop practical, low cost options for the disposal of these relatively small quantities of over-age pesticides. Carbaryl, the only pesticide present in significant quantities, was considered separately.

CARBARYL DISPOSAL

The Carbaryl Story

Carbaryl (6,400 liters) was imported into Guinea-Bissau in 1988 for the locust campaign being carried out by donor organizations in West Africa. The carbaryl formulation purchased was Seven 4-Oil, chosen primarily because it could be aerially applied and because it contained sticking agents which enhanced its persistence on foliage.

Because the oil-based formulation was a thick suspension, an agitation pump was needed for application. However, the outbreak of a more severe locust infestation in neighboring Senegal caused a realignment of priorities, and the spray plane and agitating pump destined for Guinea-Bissau never arrived. Consequently, none of the carbaryl was used.

All of the carbaryl drums were stored in one warehouse near the capital city and were in good condition. However, because the drums had never been agitated or rolled as recommended on the label, the carbaryl settled in the containers and resuspension efforts by the CPS proved futile. This eliminated the possibility for using the carbaryl for other locust control methods such as coating grains to make baits, or for application with available ground equipment.

Return To Sender

One disposal option identified for these carbaryl stocks was to return them to the US manufacturer for reformulation and resale, with the manufacturer paying for transportation costs. This course of action was being pursued for remaining carbaryl stocks in neighboring Senegal and was strongly recommended to the CPS. The CPS was advised to decide quickly, as shelf-life considerations for carbaryl limited the time for which this option was viable. The manufacturer could reformulate and resell the carbaryl, but not if its effective date had expired.

In-country Disposal

This was a less desirable option. There was no high temperature incinerator or dedicated hazardous waste landfill in Guinea-Bissau. Co-firing pesticides as fuel in a cement kiln is being considered in several African countries and this method of disposal may be appropriate when there are large amounts (>50 metric tons) of pesticides to be discarded. (World Environment Center, 1987; Krueger, 1989) Although it can be a practical and efficient method of disposal, cement kiln incineration of wastes typically invites a variety of technical and political complications. (Jensen, 1987b)

Land burial of the carbaryl was not recommended. Because of a high water table and routine flooding in most areas in Guinea-Bissau, there is a real potential for groundwater contamination or for run-off into receiving waters, streams, drinking water or other pathways that affect the environment.

OTHER PESTICIDES FOR DISPOSAL

For the pesticides in Table 2 other than carbaryl, practical, low cost options were recommended for the disposal of these relatively small quantities of over-age pesticides.

Find Safe Alternative Uses

In a country like Guinea-Bissau with extremely limited financial resources, taking advantage of the economic benefit of the pesticide product is always the preferred method of disposal. Finding safe alternative uses for pesticides of questionable integrity was recommended.

A strategy for obtaining additional information on alternative uses and methods for safe disposal for the pesticides in Table 2 was worked out with the CPS. A first step in the strategy was to test the products for quality. Six of the nine pesticides in Table 2 are products of Bayer Chemical Company. The USEPA consultant recommended that the CPS request that Bayer -- at no charge to the CPS, which has no foreign exchange to pay for the analysis -- analyze samples of their products in Guinea-Bissau for quality. It was possible that this request would be granted, considering the enhanced product stewardship programs now in place with the large chemical companies. Bayer would advise the CPS how to safely collect and ship the samples for analysis.

Many of the pesticides in Table 2 potentially can be used to control pests where the exact dosage rate is not critical. (Farm Chemicals Handbook, 1990; Asian Development Bank, 1986) For example, dichlorvos could be sprayed on the inside of the walls and ceiling of mud grain storage bins to limit

pest infestation. Phoxim is also registered for controlling stored product pests in granaries and for armyworm control. The dicofol could be used successfully against the cassava green spider mite, which was identified in 1990 as a major pest problem in Guinea-Bissau.

To summarize, it is preferable to use these chemicals as they were designed to be used, rather than dispose of them. All possible effort should be made to avoid disposal.

In-country Disposal

Chemical degradation was considered as a possible disposal option, given that: 1) relatively small quantities were involved, and 2) most of the pesticides in Table 2 are carbamates or organophosphates, which decompose when treated with alkaline (basic) chemicals, such as lye or lime. (Lawless, et. al. 1975) Lime is readily available in Guinea-Bissau. (Chemical degradation was not considered as a realistic option for the large stocks of carbaryl on hand.) A "cook book" chemical treatment procedure using lime was provided to the CPS.

If the chemical degradation option is selected, the procedure is best done in the middle of the dry season (January), not during the rainy season, when water contamination would be of greater concern.

No Action

This option was not recommended. Other than the carbaryl stocks, the containers for the pesticides in Table 2 are not in good condition. Some are leaking and the released material has contaminated the porous concrete floors of the storage areas and may have passed through to the ground. The fumes could pose a risk of worker exposure by inhalation, and increase the risk of fires. Most of the storage facilities are located in populated areas.

CONCLUSION

The purpose of the technical assistance to the Crop Protection Service was to provide guidance on practical, low cost options for the disposal of relatively small quantities of over-age pesticides. The intent of the Service was to carefully consider these options, and start the implementation phase in the near future.

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DOWNSTREAM INJECTION EQUIPMENT FOR SPRAYERS AND FERTILIZER SPREADERS

by

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INTRODUCTION

Agway Inc., a regional agricultural cooperative, owned by 91,000 farmer-members provides truck mounted custom application spraying and spreading services on farms in twelve Northeastern states. Motor Transportation Services (MTS), is a division on Agway Inc. It is responsible for manufacturing and/or assembling the truck mounted equipment that service 287 Agway owned stores, 350 certified representatives, 54 fertilizer plants and contract operators for Agway. A total of 213 liquid applicators and 219 lime and fertilizer spreaders at 80 locations cover from 2,000 to 15,000 acres each per year with 90% of the liquid units applying some kind of agricultural chemicals.

BACKGROUND

Because of Agway's total involvement with agriculture and the application of crop protectants, fertilizer, and lime to improve crop production, Agway has made major efforts to improve facilities, spraying and spreading equipment.

In 1975, a major research effort was initiated resulting in a new design for spraying equipment which produced constant application rates regardless of ground speed. This design in turn was reflected in less driver error and more exact control of the amount of material applied per acre. These improvements became standard on all new Agway spray trucks and were made available to retrofit older spray units.

In 1977-78, Agway introduced impregnation (usually of herbicides) of dry fertilizers in their fertilizer blend plants. This allowed spreading by all available spreading equipment but caused some problems with cleanup in order to prevent contamination of blend plant and spreading equipment. Also, segregating and storing impregnated leftover material from field miscalculations of acreages was a problem. Washing units after use and waste water disposal was a strong concern during this time period. Agway studies showed that from seventeen to twenty gallons of water were required to internally and externally wash down a 650 gallon sprayer unit and its booms.

In 1983, a dilute pesticide management facility was constructed at the Agway Farm Research Center (AFRC) at Tully, New York. This consisted of an underground, roof covered storage system with an adjacent, interconnected building with concrete washdown pad and an ag chemical storage room. This facility was based on the design of the Iowa State units that had been functioning successfully for several years. The idea was to construct and monitor a unit that would serve as a model for possible future facilities at Agway sprayer and spreader locations. Monitoring began in 1984 and continues to the present in cooperation with New York State Department of Environmental Conservation (NYSDEC). The facility has been operating continuously since it was installed.

During the early 1980's, Agway cutbacks in people and research funding delayed research work on experimental and/or prototype units but work continued on studying the problems and travel to witness demonstrations of some equipment made by other manufacturers. It was recognized that rinse pads and storage structures were not only expensive but that the time required for sprayer units to come in from the field to be cleaned and reloaded before going back to the field was not cost effective. Studies were initiated on the concept of chemical injection systems using positive displacement pumps as well as pump-tube units during this period but funding to build a unit was unavailable and we could find no one in the industry to cooperate with Agway in putting such a unit together for field testing.

In 1986, some research funding became available and hydraulic boom controls were designed allowing variable boom height adjustment and folding and unfolding the booms--all done by a touch of the controls by the driver in the cab. This innovation provided ease of changing from short to tall crops, hastened entering and exiting fields and cut down on driver fatigue.

Also in 1986, a spray truck tank rinse and wash-down system was developed that allowed the inside of the spray tank to be rinsed with clean water and then sprayed off in the field. A hose and hand gun nozzle were a part of this system so that after inside tank rinsing, the outside of the truck unit could be rinsed with clean water before leaving the field and traveling down the road. An eye wash system was also made a part of this cleanup system.

During this time period, a second look was taken of the direct injection project and information was assembled from various resources. From this assembled information, specifications for a system were established. The number of modules, rate controllers and interfacing were specified to adapt to Agway sprayer systems in the field. Agway selected a three module system with fifteen gallon tanks, positive displacement pumps and range capabilities of 5 to 200 ounces per minute for each module. The Agway concept was to inject liquid ag chemicals directly into the boom on a spray truck so that it could go to the field with clean water in the tank and have as many as three separate crop protectants and/or liquid fertilizers directly injected into the boom where they would mix before being sprayed through the spray nozzles. Since each crop protectant is carried in its own special container, at the end of the field the container valves can be shut off, fresh water from the spray tank flushed through the boom, and a clean machine is ready to leave the field and go to the next customer with a clean rig and a clean tank of water (no rinsate or leftover spray mixes for disposal). Such a system added from \$8,000 to \$10,000 to each sprayer unit and no store location could be found willing to pay this additional cost for a unit.

In September 1989, Agway top management made the decision that at least one of these injection units would be placed at strategic locations within the Agway territory so that experience with operators, managers and customers could be obtained. The plan was to place each unit at a site having an experienced, well-trained driver and a diversified spray business that was well established.

With this mandate, nine downstream injection sprayer units were built and eight of them were placed at strategic locations in the field during the Spring and Summer of 1990. The ninth unit was kept at MTS for testing and research work with chemical companies with new products. During the Spring of 1990, newly formulated liquid and dry flowable ag chemicals from Monsanto and DuPont were tested through the MTS unit.

In the early 1980's, pneumatic spreaders were new, were investigated, and found to be inferior in spread pattern performance when compared with Agway's dry spreader trucks. As time passed and more manufacturers entered the field, the air spreaders showed improved performance. After six years of evaluation, attending demonstrations, and testing different brands and models it was found that the Tyler pneumatic spreader was the unit that could be recommended for use by Agway.

In the Spring of 1989, a Tyler unit was purchased and put into service at one of Agway's western New York locations. It had the capability for on-board impregnation (both liquid and dry), which is a method of one-pass, in-field mixing and application of herbicides and fertilizer. The key to this concept is that it takes mixing away from the blend plant and puts it in the field where the product is being applied. Only the amount of herbicide and/or fertilizer required is applied and there is no mixed product to go back to the plant. It also saves time and allows the fertilizer rate to be varied on-the-go.

DISCUSSION AND RESULTS

The Tyler air spreader successfully operated in the field for 6,200 acres in 1989 and 8,200 acres in 1990. A new improved liquid injection system was installed and replaced the old liquid system on the unit after the 1989 season. Although this spreader unit has the capability of both dry and liquid fertilizer impregnation, the operation manager and driver feel that the liquid system is superior and used it exclusively during the 1990 season.

Each injection sprayer unit operated in the field covered from 2,500 to 14,000 acres for the 1990 season. A questionnaire was sent to each location and filled out by the store manager and equipment operator. Follow-up personal interviews were also conducted with some store managers and operators. From the questionnaires and interviews Agway learned that some equipment modifications will be forthcoming on all 1991 models that will retrofit the 1990 models. Results of the first year of testing and interviews with farmers and Agway Crop Center managers clearly indicate that application accuracy and protection of the environment were both achieved with this type of equipment. Injection equipment had the following advantages over conventional spraying equipment:

- Main spray tank contamination eliminated -- no unused product in the main supply tank.
- Ground orientation was the most accurate system ever used.

- Rate and chemical changes can now be made in the field.
- Costly run-outs and mix times are reduced or eliminated.
- Exact usage of chemicals.
- Unused chemicals can be easily transferred from 15 gal. module tanks to containers.
- Reduced cost for wash down and containment areas.
- Environmental threats minimized.
- Ability to go to isolated, distant field locations and spray all day.

Acceptance of the injection sprayers by customers has been outstanding. Most demand that their fields be sprayed with the new injection sprayers. However, when asked, most are not willing to pay any more for the service than for conventional, less accurate equipment. The dilemma faced by Agway is that in high competition areas, spraying or spreading rates are determined by the lowest bidder and expensive equipment will not pay for itself unless a higher, more realistic fee is charged. Also, Agway is forced to charge the same price per acre for the more expensive equipment as they charge for their own conventional equipment.

Because of mandated state and federal licensing requirements for applying and storing crop protectants, many farmers and small custom applicator operations have made the decision to get out of the application business. This puts the burden of providing equipment, chemicals and the storage of chemicals directly on those who have chosen to remain in the custom application business. Agway is especially concerned with handling and accuracy in applying ag chemicals and fertilizers. One of the primary challenges for Agway is handling of ag chemicals that must be returned from the farm (such as sprayer rinsate) to an Agway farm center location. Ag chemical storage and containment structures can be very expensive.

State and federal laws and mandated requirements continue to change so that those trying to comply to the best of their ability are always shooting at a moving target. A good example of this is Agway's dilute pesticide management facility. It has been monitored continuously and functioned successfully as designed since 1983. If a similar unit of the same capacity was to be built today, the cost would be from two to three times the cost of the original facility because of new mandated structural requirements. Inflation over the eight year period would, of course, add even more to the cost. Agway originally planned to build these management facilities at many locations, but now cannot afford to do so. When rules are different from state to state it becomes very difficult to meet competition. Agway feels that all its facilities and all its equipment must meet the requirements of all states.

For 1991, six new injection spray units are expected to be built and located at strategic Agway locations.

Agway Inc. is not in the equipment selling business. All equipment is designed and specified in-house and built to Agway specifications by others, and used at Agway locations to serve farmers.

Evolution of the Pesticide Container
Disposal Program in Alberta
(speech)

by

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Alberta Environment

I would like to outline our present comprehensive system in Alberta. We do have a complete system which is up and running.

In this discussion, I will indicate how we got there as well as pointing out things that did not work. Finally, I will describe some of our still outstanding problems, some of which I hope will be solve though information exchange at these types of meetings.

The present system in Alberta, handles each year about 700,000 containers made up of about 500,000 plastics and 200,000 metal containers or a million lb of plastic and metal.

Our system started in 1980 when one of our staff members collected loose containers in the coulees of Southern Alberta and piled them in a snow fenced enclosure. Within a short time farmers had started to use the site as a drop off place for the container. During the years, 1980 to 1986, Alberta Environment started to provide funding to the local level of government to build these sites and periodically contracted for their clean out. There was no planned program as the program grew incrementally. But by 1986, Alberta Environment realized that it should not be involved and wanted to turn the program over to industry.

The present system consists of 106 sites classed as permanent. These sites received funding of up to \$10,000 per site from Alberta Environment. We published construction standards and guidelines to ensure that the sites were well constructed. In the design, we followed three principles namely security ie fenced: containment, ie berms and clay or plastic liner and water control. The province has a dry southern half where we recommended evaporation areas to remove the projected rainfall while in the northern parts with high rainfall we recommended roofs on the sites. At this time more than 2/3 of the sites have been upgraded although a very small number of local levels of government ran into siting problems. The word NIMBY describes the problem. The local level of government can set up any number of their own temporary sites but the system allows for clean out only from the permanent improved sites.

The sites are operated by the local level of government, either a municipal district, a county or in some cases a regional Landfill Authority. The sites therefor are a local responsibility and is legislated under the Public Health Act which make the local level of government responsible for wastes generated within their jurisdiction. The system thus operates as part of the waste stream without any extra costs or facilities. The 106 sites are operated by 64 of these local levels of government. The most any local government has is four sites and the average would be one or two sites. A great deal depends on the shape of the local unit. In cases where the farmer may have to drive greater distances we have provided for another site.

In our system, the farmer is responsible for triple rinsing and bringing the empty containers to the sites. Our agriculture consists of wheat barley and canola with an average farm size of one to two sections. We do not have a large percentage of custom application. This means that we have to train the individual farmer to triple rinse.

The Alberta Environment Minister has appointed the Alberta Special Waste Management Corporation to act as program manager. The Corporation is also the part owner of the Swan Hill Waste Treatment facility. The Corporation puts out a tender to the private sector for the clean out of all the sites. The clean out involves the shredding of the plastic and metal, transport to a storage location, processing and washing the material and finally recycling.

We have one processing plant in operation operated by Wearmouth Waste Services in Medicine Hat, Alberta. The plant is based on water washing with carbon absorption of the pesticide material, all in one closed loop with no discharge allowed. Another plant is on the drawing board by Newalta at Ryley, Alberta.

The washed and processed metal is sold as #2 scrap to an Alberta scrap dealer. They in turn will ship the material to one of two Alberta steel mills. The steel mills have indicated that they will accept the metal as long as it meets our 100 ppm standard and there is no odor or liquids which can be identified as pesticides.

However the recycling of plastic material is another matter. We funded an early study which clearly indicated that even over prolonged extraction more and more pesticide could be removed from the plastic. It meant that pesticides can migrate into the plastic and that we would never be able to remove all the contaminants from the plastic.

On the recycling of plastic, the joint industry and government consensus in Canada is that we have three options: either into new cans, into other plastic products or incinerations. As government policy, we are not in favour of the incineration options for various reason. The first option of closing the loop into new containers will require a number of years of lead time which leaves the middle option. We have done some trails on fence posts and curb stops with the Superwood process. We would consider geomembrane liner or other uses as long as we could get some comfort as to the final use of the end product.

In summery, it is hard to predict how we will finally recycle the plastic material. We recognize that some of these concepts belong in the private sector although we are interested in ensuring that the material is handled properly in recognition that they do contain residues.

I indicated that in the early days of the program, it was Alberta Environment that operated the program. However that changed with the establishment of the "the polluter must pay" and "industries being responsible for its own wastes" concept. The Canadian industry took the position that it was a shared responsibility. Consequently we had a two year time period where the containers piled up on our sites. Industry did take a major step by collecting a \$1.00 surcharge per container shipped into Alberta. That meant that there was money on the table to set up a program.

In Canada, we have the Crop Protection Institute of Canada to represent the chemical producers. CPIC would be your equivalent to NACA.

Starting in November 1988, CPIC collected the \$1.00 per container and places the money into a Trust Fund. I understand that the operation of the trust fund by CPIC involves no extra staff or other costs. The money collected is to be used to cover the operational disposal costs as well as such agreed to costs as farmer education and research.

We recognized very early on that we needed toxicology support in areas such as occupational health and recycling. I have been on container sites in the middle of an Alberta summer day and there is a smell of pesticide there. Our strategy was to bring together a number of Universities resources and set up our toxicology support system. That system is now made up of staff from the Universities of Guelph, Alberta and Saskatchewan. We thus have available independent expert advice to ensure that we are operating a safe system.

A major study is currently underway by this toxicology network. We have a \$250,000 project, all paid out of the CPIC funds, made up of four components. The first component looks at the occupation health aspect of the crews that clean out the sites. We expect to get the first result in May. The second components looks at the occupation health aspects of the washing and processing plants. Thirdly we will look at the recyclers either the steel mill operators or in the recycling plastic plants, all for occupational health. Finally, we will investigate a number of plastic products as suitable end products for the pesticide contaminated material.

In the program we always run up against the rhetorical question "How clean is clean" or "What level of contamination will you accept?" Again we turned to our toxicology support group and they have set an arbitrary standard of 100 ppm of total pesticide. We use a standard screen of the seven most common chemicals in Alberta including trifluralin, triallate, bromoxynil, 2-4-D, M.C.P.A., picloram and diclofop-methyl. We use this standard as a requirement for the final wash processing step. The figure itself is based on WMIS standards and a safety factor of 10. The guideline is useful in that it provides for a quality controllable endpoint and a level at which we will class the material as recyclable.

I have talked mainly about the Alberta program. However, I should stress that we are part of a three provinces block where we share the same agriculture and disposal problems. While each province, has its own infrastructure, we freely exchange information and coordinate our programs. Looking at the three provinces, our market now comes to nearly 2.5 million containers in total. It is a hope that eventually we will rationalize the system so that it becomes as efficient as possible.

In the programs early stages, we took the strategy of identifying all the stakeholder in the program and bringing them around one table to share information and ideas. The committee of stakeholder is made up of interested and affected parties. It has no formal power at this stage.

The stakeholder we have around the table are:

- two farmer end user
- an Alberta Environment member involved in regulations and monitoring
- one representative of the local municipal governments who operates the waste streams and sites
- one CPIC member
- one representative of the Boards of Health who are active in the public safety aspect

one member of the recycling industry
one member of the regional landfill association who operate the sites
one representative of the operational agricultural staff involved in
rural agriculture.

The committee meets about every three months. It has served as an excellent sounding board for new ideas and approaches to operational problems. The individual members serve as informational links to their respective organizations who continue to support the program.

Each of the above stakeholders has an important part to play in our program. Many aspects of our system are unique to our province. But I believe that the concept to identify your stakeholders and work them into the decision making process makes the program work better.

Alberta Environment role is in the monitoring and regulatory areas. I have indicated that we provided site design specifications. We also soil sample off and on sites. We have established water wells to monitor for any off site movement. We inspect sites three to four times a year and can take regulatory action if sites are not operated correctly.

I would now like to touch on some problems we have faced.

We are not happy with the amount of "other than pesticide containers" waste streams on the sites. The sites are not under our control and we are addressing the problem through various education and training program. The presence of any of the other wastes on the sites, increases the program costs.

Our sites grew up around the various landfills. The containers have become associated with wastes and being just another waste stream. As a consequence, people have taken to dropping off other wastes stream including household wastes, industrial wastes and hazardous wastes on sites which were not planned for this purpose. We are vigorously pursuing proper site maintenance and operation as per our own guidelines. If sites are not operated properly we will not clean them out and we have the legal power to take other actions to remove other wastes streams from the sites. What I want to suggest is that you consider locating site outside of the general waste stream.

We are still not happy with the triple rinsing done at the farm level. We believe that the solution to our problems starts with the farmer triple rinsing. We estimate that about 70% of can are washed. The problem has to be addressed through education and I suppose we must be patient. Both industry, through CPIC, and various government agencies are getting the message out. We still have a long way to go on farmer education keeping in mind that we are dealing with more than 50,000 farmers

We have had contractor problems. Many did not know what business they were getting into. The first contracts were not specific and open ended as to what was required. We both learned on the fly. Some contractor quickly left the business but a few have survived. In the future, we will both be getting more efficient leading to decreased costs.

In the early stages there was a lack of funding. This was solved by the \$1.00 per container surcharge.

It took nearly three years to resolve the government vs industry responsibility. Right now, government is still too heavily involved in the program. We agree that all parties must have an active and supporting role in getting the system operational. We want to help and be around the table but we do not see our role working on the operational aspects of the program.

We have a major question mark in regards to the washing and processing steps. We believe that washing or processing is necessary. However the current water washing and carbon filtration may not do the job. It is old technology which has some questions in regards to costs, efficiently and through put.

The final end products of the recycled plastic material is still not clear. I outlined the three options. The future may be a combination of the three. We may also take the attitude that this is an industry problem and our program will voluntary or involuntary give it back to industry.

Perhaps this next one deserves a separate heading. It has to do with the total costs of the program. As noted, the funds collected under the program is currently \$1.00 per container. However, it is clear now that this will not be enough. We wont get an accurate figure until we have been in operation for two or so years. We may be able to rationalize the system and optimize it between provinces and thus be able to cut down costs. We need to finally close the loop by getting rid of all the material. So we have a number of uncertainties impact my estimated cost figures.

My best guess is that the final figure will probably be around the \$1.50 per container in Canadian dollars. This is a best estimate based on some practical experience and some future assumptions. Not all costs for example those from CIPC or government are attributed back to the actual program. The local levels of government do not in Alberta at present receive any funding for their work. Also Alberta Environment has funded the site construction for an estimate of \$1.5m Can.

That brings me to the last point. The provincial government has largely carried out the program even though we believe in the "cradle to grave environmental principle." We are able to turn over a functioning system at this time to industry. Industry can and should be able to operate the system much more efficiently and effectively and be in a better position to control the costs which in our program seem to be rising steadily.

The program has been voluntary up to the present time for all parties whether farmer or industry. With the current legislative review in Alberta, Alberta Environment will be gaining broad new powers in the recycling and waste minimization areas. We are prepared to legislate the recycling of pesticide container by all parties if that becomes necessary. We hope that industry will take over the program in keeping with the cradle to grave environmental approach.

Retail Fertilizer Dealer Product Containment

by

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INTRODUCTION

Environmental protection is one aspect of the retail fertilizer industry that has become as important as the products and services the retail fertilizer dealer supplies. This emphasis on environmental protection at the dealer level has largely been in response to regulations being written by some States to protect groundwater. States were given the predominant role in developing their own groundwater protection strategies when the U.S. Congress passed amendments to the Clean Water Act in 1987. To keep abreast of regulations being developed and to maintain public trust in the fertilizer and agrichemical industry, fertilizer dealers have been called upon to take an active role in promoting the protection of groundwater. This paper describes several containment systems for fertilizer and pesticides at dealer locations, and is intended to help dealers decide how to best modify their plants to protect groundwater.

SOURCES OF GROUNDWATER CONTAMINATION

By understanding the sources of groundwater contamination one can begin to design an environmentally sound fertilizer dealership. Sources of groundwater contamination can be grouped under three headings: water supplies, transfer areas, and storage areas.

A poorly designed wellhead or one with a faulty casing can allow contaminants to move directly into ground water. Connections to public water supplies must be designed to prevent material from back siphoning into the water system.

Transfer areas (where fertilizer is loaded, unloaded, or transferred to and from the mixer) are sites of accidental spills that find their way to groundwater if not properly contained. Some dry materials, not protected from rainfall runoff, are as likely to reach the groundwater as are liquids. Nitrate's mobility in water make it susceptible to leaching from any nitrogen fertilizers in contact with rainfall. Nitrate contamination of ground water has been linked to spillage of dry nitrogen fertilizer at dealer locations.

Storage areas are potential sources of groundwater contamination. Tanks or piping attached to tanks can rupture causing a massive spill that can pollute surface water and eventually ground water, if not contained in a dike. Even dry fertilizer stored under roof can enter surface water during storms if the storage is in a low area prone to flooding. New sites are not likely to be built in areas that flood, however, many existing sites are located in areas that are less than ideal from an environmental standpoint.

SITE SELECTION

When choosing a site for a new location or rearranging an existing facility the environmental suitability of the site should be assessed. An ideal site should be located a safe distance from private wells or surface water supplies. Sites in a flood plain or with shallow groundwater depth should be avoided. Soil bearing capacity should be sufficient to support the loads of buildings, storage areas, and vehicle traffic. Existing drainage patterns and topography should be studied to determine how the site is affected by surface water movement on and off the site. A loading pad, for example, should not be located in the path of runoff. Likewise, a well should not be located down grade from fertilizer or pesticide handling areas. A dealership handling materials that can become airborne should be located upwind of populated areas. Due to the liability associated with vehicle transport of fertilizer and pesticides, a dealership should not be located in urban areas where traffic problems exist.

A problem facing many dealers is their close proximity to urban areas. This is common in the East where towns have grown around dealer sites that were built in rural areas. In these situations, serious consideration should be given to relocating to a more remote area before investing in a major environmental upgrade of a facility.

When relocating an entire facility or part of a facility it is important to determine the level or presence of contamination from past practices. Those considering covering up storage tanks in a concrete structure should consider the long term solubility of the site. Contaminated soil should be tested to determine if remediation (clean up) needs to be done. If the contaminants are a type that will break down in a reasonable time, a structure that prevents further downward movement of water can be desirable. Contaminants which do not readily break down should not be buried under a structure. The future clean-up costs could be insurmountable. Some environmental remediation of contaminated soil should be consulted when dealing with such contamination.

CONTAINMENT

A common perception is that once the dikes used as secondary containment around liquid fertilizer and pesticide tanks. Dealers in states where groundwater protection laws are in effect have learned that containment involves more than merely having a backup tank. Gasoline tank failure. Tank failures are rare compared to the number of spills during while loading and unloading product. In some cases, faulty tank and hose and water connections are the main cause of ground water contamination.

Wellhead Protection

The first step in making a dealership environmentally secure is to inspect the water source. Dealers using an onsite well should thoroughly inspect the wellhead. The concrete pad or curb full around the well should be elevated above the surrounding area to ensure that runoff is carried away from the well. Runoff allowed to pond around the well head or near the wellhead can find its way to groundwater by seeping around the well casing or through a crack in the casing. The risk associated with well head groundwater contamination is such that regulations in some states require that all fertilizer and pesticide handling facilities within 100 feet of a water well (Illinois Department of Agriculture, 1989; South Dakota Department of Agriculture, 1989).

Frost pits are not allowed on new well installations in most states. Dealers with a wellhead in a pit should consider extending the casing above the surrounding soil surface. The minimum recommendation is to ensure that the pit is water tight and that no contaminants can enter the pit. Local officials should be contacted concerning requirements for private wells.

Abandoned wells or wells that are rarely used are common at dealer sites. These should be retired and sealed. Generally a permit is required to close down a well. The Cooperative Extension Service or local Public Health Office should be contacted for details regarding well closures.

Water System Protection

All connections to the process water supply system should be inspected to ensure that fertilizers and pesticides can not enter the water system by back siphoning. Areas where this can occur are through the water inlet to the mix tank or where vehicles are filled through a bottom connection. Even hoses which have their discharge end submerged in a pool of liquid can allow material to back siphon when there is a loss of pressure in the system. The two standard methods for preventing back siphoning are an air break tank and a reduced pressure principle zone (RPZ) valve.

An air break tank is merely a water supply tank which receives water from a well or public water system through a pipe having an air space between the pipe discharge and highest water level attainable in the top of the supply tank. Generally, the distance between the pipe and maximum water level is two pipe diameters. The supply tank generally provides water for the entire facility and a pump can be used to boost pressure if the static pressure in the supply tank is inadequate.

An RPZ valve is a special device that has two independently acting check valves and a pressure differential relief valve located between the two check valves. When there is a loss of pressure in the water supply the two check valves close to prevent the flow of water from reversing and siphoning process material into the water supply. One undesirable feature of RPZ valves is that they may reduce line pressure by as much as 10 psi. These valves may have to be regulated by State or local agencies and will, thus, require approval for installation and be periodically tested and inspected.

Transfer Operation Containment

Transfer operations include loading, unloading, and other operations involving the movement of pesticides and fertilizers. Before emphasis was placed on groundwater protection, there was little concern over the small quantity of material spilled when spreaders or nurse trucks were overfilled. Likewise, leaks from valves, pump seals, and dry fertilizer conveyors were not thought to have a detrimental effect on water supplies. At some dealer locations the accumulation of these types of spills have not only contaminated soil but also the groundwater. Consequently, containment for loading and mixing areas are receiving the highest priority in many state regulations (Iowa Department of Agriculture, 1988; South Dakota Department of Agriculture; Illinois Department of Agriculture, 1989).

Loading areas (load pads) are generally concrete pads designed to collect spills occurring while loading tenders, spreaders, nurse equipment, and sprayers. The main design features are; liquid holding capacity, pad length, pad width, slope, sump location, and sump design. No single load pad design will satisfy everyone's needs. Many pads are used for equipment washing. Pads used to wash dirt and residues from field equipment should be large enough to catch all liquid sprayed while washing and should have a good sediment removal system, particularly if rinse water is intended for use in solution (clear liquid) fertilizers. The following discussion applies to both loading pad design and equipment wash pad design. At most locations a single pad serves both purposes.

Liquid Holding Capacity--

The liquid holding capacity of load pads should be based on the volume of the largest tank loaded on the pad. For example, a pad used for loading large transports should be designed to hold the entire contents of the transport, typically 4,000 gallons (Illinois Department of Agriculture, 1989; South Dakota Department of Agriculture, 1990). One state requires that loading pads for fluid fertilizer have a capacity of at least 1500 gallons (Wisconsin Department of Agriculture, 1988). Some states do not require a pad for unloading raw materials at the site: other states require load-in pads but with volumes as small as 25 gallons (South Dakota Department of Agriculture, 1990; Illinois Department of Agriculture, 1989). Consequently, a single pad used for loading out as well as unloading raw materials should be sized to satisfy the requirement for load-out pads. Since incidental spills at raw material unloading sites are common, some containment should be provided for recovering spills.

The entire contents of the tank on a large transport vehicle can be difficult to contain on a pad designed to accommodate one vehicle. For example, a pad 12-feet wide and 60-feet long designed to hold 4,000 gallons of liquid, will be 2.2 feet lower at the sump if the four edges are at the same elevation and all slope to the sump (see figure 1). If the pad has a 12-foot long trough in the center, the top edge of the trough would be 1.5 feet below the height of the edges (figure 2). The steep slope of both pads would make vehicle access difficult.

Increasing the area of the pad permits a shallower pad for a given volume. However, a larger pad will be more likely to overflow with rainfall accumulation. The pad in figure 1 can hold 9 inches of rain. A pad with the same volume but twice as wide will be half as deep and will hold only 4.5 inches of rainfall. Rainfall can only be discharged if the pad is clean before rain begins. Otherwise, it must be handled as a dilute fertilizer or pesticide mixture. For this reason, many dealers are building roofs over loading pads. This should be considered in high rainfall areas.

One practical way to increase the volume of a pad is to form a roll-over curb on the perimeter. The addition of such a curb, 4 inches high, on the pad in figure 1 increases its volume 45 percent (see calculations under figure 1).

In some state regulations the volume requirement for the load pad can be met using an automatic sump pump connected to a storage tank inside a secondary containment basin (Illinois Department of Agriculture, 1989; Wisconsin Department of Agriculture, 1988). A more reliable method for increasing the volume of a load pad is to provide an overflow to another basin. This can be done by elevating the load pad above a secondary containment dike. Buried tanks or pits should not be used to store liquid from loading pads. Some states allow

temporary storage of liquid from load pads (Department of Agriculture - Illinois, 1989; South Dakota, 1989; Wisconsin, 1988). Long term storage of fertilizer or pesticides in pits or wet wells is prohibited without an approved ground water monitoring system (Wisconsin Department of Agriculture, 1988). Dealers using pits or buried tanks should remove them or retire them by thoroughly cleaning them, sealing all inlets, and filling them with sand or clay.

Pad Length and Width--

The pad dimensions should be based on the area required for work done on the pad. A pad used for equipment washing should be a minimum of 20 feet wide. If the pad will be used for both loading and unloading, it should be wide or long enough to accommodate two vehicles. Dealers handling liquid fertilizer and pesticides may need extra space for loading or unloading mini-bulk containers. Some dealers may require space on the load pad for tanks used to store spillage or rinsates. Experience has shown that load pads are never too large. Load pads 40 feet by 60 feet are not uncommon for fluid fertilizer/pesticide dealers.

Pads for loading dry fertilizer must be sized to collect material which spills over the sides of spreaders or tenders. Experience has shown that the pad should extend about 10 feet beyond each side of vehicles being loaded with the elevation of the edges of the pad being about 4 inches above the center. Pads for dry materials have no volume requirement. A gravity drain with a lockable shut-off valve can be installed to discharge snow melt or rain free of fertilizer and pesticide residues. As in liquid operations, rainfall accumulation contaminated with fertilizer must be handled as a dilute fertilizer/pesticide mixture. Most problems associated with rainfall and snow can be eliminated by building a roof over the load pad.

Spills occurring while filling dry fertilizer bins should also be collected and kept away from rainfall. Some dealers place the boot of portable augers inside a large tray to collect spillage. The most common type of containment around these areas is a concrete pad that facilitates the manual collection of spilled material. Railcar unloading areas are a problem to keep clean. The best way to keep the area between the tracks clean is to pave the area and slope the pavement away from the conveyor. A water tight lid should be placed over the conveyor to keep rain water out of the conveyor. This is critical if the bottom of the conveyor is not sealed to prevent water from leaking out, carrying fertilizer nutrients downward.

Liquid railcar unloading sites have been contained by paving the area between the tracks and sloping the pavement to a point where a tie can be removed permitting liquid to flow under one rail and into a basin where it can either be used as make-up water or, if free of contaminants, discharged. There are prefabricated pans made of fiberglass reinforced plastic that can be installed between and on both sides of the rails for collecting liquid spills. These prefabricated pans are sloped to built-in sumps which facilitate the recovery of spilled material. Portable pans can be used to collect small spills at rail sidings, however, catastrophic spills are difficult to contain.

One method for containing large spills at liquid railcar loading areas is to install a synthetic liner in the gravel beneath the tracks. The liner can be extended away from the tracks and sloped to a sump for recovering liquid.

Few dealers have installed spill containment systems for railcar loading and unloading areas and state regulations have not addressed this problem. As containment technology and regulations progress, more methods for containing spills at rail sidings should be developed.

Pad Slope--

The slope of loading pads should be a minimum of 2 percent. Concrete surfaces which come in frequent contact with fertilizers or pesticides should be sloped 2 percent to minimize the corrosive effect of these materials and to facilitate the washing down of the pad (Noyes, 1989). This slope is preferred over shallower slopes because it reduces the chance for errors in finishing that will cause liquid to puddle on the pad after being drained.

Sump Location--

The location of the sump depends on how it is used and how vehicles travel on the pad. If the pad is to be accessible from all four sides, then the sump should be near the center of the pad. A sump located in the center of the pad can interfere with the movement of product if the sump has to be cleaned out or manually pumped out while product is being loaded. For this reason sumps are often located on one side of the pad. This still permits vehicle access from three sides. Some dealers have a sump in the middle of the pad and a deeper sump on the side. The two are connected by a trough or a pipe that runs beneath the pad. The sump in the middle of the pad traps solids while liquid is pumped from the second sump.

Sump Design--

Sump designs vary considerably in terms of how they are used to handle solids. Suspension dealers who can handle solids in their products have simple sumps and pump all the sediment directly into applicators. A screen either over the sump or the pump inlet is used to remove rocks, cigarette butts and other debris. Other dealers go to great length to separate all solids from liquid being recycled. These dealers either use an extra sump for solids removal or use a sediment trap around their sump. Figure 3 shows a typical concrete sump with a perimeter sediment trap. Some dealers slope the sediment trap to one side to decrease the area where solids settle. Sediment traps must be cleaned periodically to keep sediment from overflowing into the main sump from where liquid is pumped. Figure 4 shows a pad with two sumps. A pan can be fabricated to fit beneath the discharge of the higher sump. Solids can then be removed by dumping the pan. Dealers not equipped to handle sediment in sumps should realize that this material may be too contaminated to discard as dirt. Experience has shown that, where pesticides are handled, sediment collected in sumps can destroy vegetation. The two approaches for handling these solids is to slurry them into a liquid mix or dry them and add them to dry fertilizer, being careful to apply the material on crops not subject to injury from the contaminants and at rates at or below that specified on product labels.

The labor associated with forming and pouring a concrete sump can be avoided using prefabricated sumps. Stainless steel sumps are usually double walled with ports on top to permit leak detection between the walls. Stainless steel sumps can be fabricated in any size, however, most have a capacity of about 30 gallons.

Precast-concrete sumps can be custom built in a range of sizes and with fittings to accept piping connected to other load-pads and operational areas. At large facilities recycling of rinsates can be simplified by collecting

material in a common sump. Pipe inlets should be above the bottom of the sump so that liquid can be pumped to a level below the inlets. This reduces the chance for liquid to leak into the ground around pipe inlets. Concrete sumps usually have a capacity of about 100 gallons. Some dealers prefer a large sump and sediment collection system to increase the time between clean-out. If pesticides are rinsed or handled on the pad, a large sump is undesirable because of the problems associated with contamination. For example, if a dealer switches from corn to soybean herbicides, he has to completely clean the sump to avoid contaminating his soybean make-up water with corn herbicide residues. The simplest way to avoid contamination of herbicides is to use a small sump that is cleaned daily or more often if needed to purge the system. Sumps in areas not protected from rainfall should be kept clean to permit the unrestricted use or discharge of collected rain water.

There are alternatives for segregating rinsates other than cleaning out the pad and sump. One is to divide the load pad into two or more areas by sloping sections of the pad to different sumps. Another alternative is to slope the pad to a wall where multiple drains with valves are used to direct spills and rinsate into a particular sump. Each sump has a dedicated pump and rinsate storage tank. This system is ideal for locations where rinsate segregation is important.

A trend in the industry is to add pesticides to fertilizer products in the applicator in the field and rinse the applicator in the field. This practically eliminates the need to segregate rinsates because they will normally not contain pesticides. This management practice permits the use of one rinsate tank. Other management practices which enhance the environmental security of a dealership will be discussed later.

Mixing Area Containment

Mixing areas are the site of incidental spills that require containment. A variety of materials are handled in the mixing area. Spills occur when materials are manually added to the mixer. Piping systems and conveyors for dry materials often leak. Consequently, mixing areas are as important as loading areas with regard to containment.

Liquid Mixing Areas--

Containment for the liquid mixing area usually involves installing a curb along the inside wall of the mix house. The containment volume should be equal to the volume of the mix tank. At several locations the mixing area has been contained by allowing the area to drain onto the loading pad and installing a curb on the inside of the other three walls of the mix house. Figure 5 illustrates how a curb can be built on an existing slab. At some sites the mixer has been moved to one corner of the load pad. Combining the mixing containment and load pad is common because they are usually adjacent and both receive all the products handled at the facility.

Since it is desirable to keep fertilizer containment areas free of pesticides, areas where pesticides are mixed should not be allowed to drain into the fertilizer containment. Mixing area containment should be large enough to accommodate mini-bulk containers and other portable pesticide containers that are not located in a secondary containment dike. When combining containment areas it is sometimes desirable to segregate different areas inside smaller dikes to keep incidental spills isolated. For example, a pump that leaks or a place where hose connections are frequently made, can be contained in a pan or inside a

separate curb. Confining frequent spills to a small area can reduce the amount of rainfall that becomes contaminated and must be handled as dilute product.

Piping from storage tanks to the mixer and to the load pad should also be contained. At most facilities, these areas are connected and the piping is always above a contained area or over the load pad. Piping used to transfer full strength materials should not be buried underground without being placed inside a larger pipe. The larger pipe can be sloped so that leaks in the inside pipe will flow to one end of the piping system where leaks can be contained and detected. Buried pipes are acceptable for transferring rinsate or material collected in sumps to a larger sump or to a rinsate holding tank.

Dry Mixing Areas--

Dry fertilizer mixing areas are best contained under roof. Several dealers have extended the roof of their dry fertilizer storage building to include their blender and load-out conveyor. Others have kept their blender inside the storage building and have built a concrete pad to collect material which falls beneath the conveyor as well as material spilling over the side of spreaders and tenders. The latter approach has been taken in the Great Plains where annual rainfall amounts are below 20 inches.

Blending towers, blending systems having a cluster hopper, weigh hopper, and blender stacked vertically in a tower, should be enclosed and have a roof over the loading area. If the tower is not enclosed, the pad beneath the tower should be large enough to catch leaks in the blending system as well as material spilling over the sides of spreaders and tenders.

Facilities where dry fertilizers are impregnated with herbicides must have containment for confining pesticide spills in a manner to prevent contamination of fertilizer raw materials. The impregnation operation and load-out should be under roof, otherwise, rainfall coming in contact with pesticide residues in the blender or conveying system must be collected and handled as a dilute pesticide/fertilizer mixture. Spilled material and product cleaned out of the blender should be stored inside and added in small proportions to blends. Pesticide concentrations may be too high in this material to permit it to be directly applied. If water is used to clean the blender, it must be treated as a dilute pesticide. Dealers without liquid application equipment may not want to use water to decontaminate their blender. Limestone or potash can be used to purge the system of pesticides. This fertilizer-pesticide mixture should then be applied on crops in accordance with the labels of the pesticides contained in the mixture.

Storage Area Containment

When dealing with liquid products, storage area containment involves secondary containment, a dike or basin which holds the material if the primary containment (storage tank) fails. The major difference in secondary containment for fertilizers and pesticides is the construction material. Earthen dikes are allowed for fertilizer secondary containment and are not permitted for pesticides (Illinois Department of Agriculture, 1989). When dealing with dry fertilizer, containment involves storing material in a building that has a roof, walls, and floor that prevents fertilizer from coming in contact with precipitation and surface water.

Liquid Fertilizer Storage Containment--

Secondary containment for liquid fertilizer consists of a basin with a floor and walls that are essentially impervious to liquids. The basin is usually sloped to a sump where liquid can be pumped to a holding tank or discharged is not contaminated. The volume of the secondary containment, excluding the space taken up by tanks, must be at least 110 or 125 percent of the volume of largest tank in the containment (Departments of Agriculture - Iowa, 1988; South Dakota, 1989; Wisconsin, 1988; Minnesota, 1989). The percentage varies by state and one state requires that the secondary containment hold 6 inches of rain in addition to the volume of the largest tank (Illinois Department of Agriculture, 1989). The following discussion deals with secondary containment for tanks, not in-ground pits with flexible liners. In-ground pits are not permitted for primary containment of fertilizers or pesticides in most states. If allowed, pits will be regulated as underground storage tanks and must be double-lined and have a means to check leaks in the primary liner. In-ground systems are well suited for secondary containment. This application will be discussed later. Local regulatory officials should be contacted by dealers considering pits for primary storage.

In secondary containment systems, piping runs should be over and not through the containment wall. If piping must pass through a containment wall, care should be taken to get a good seal between the pipe and wall. The structural integrity of the wall should not be compromised nor should the liquid holding capacity.

Rain accumulation should be pumped out with a manually controlled pump. Drains should only be used with a lockable valve that is strictly managed to prevent the inadvertent release of contaminated water or fertilizer (South Dakota Department of Agriculture, 1989). In some states, drains are prohibited (Department of Agriculture - Iowa, 1988; Illinois, 1989).

Sight gages used to monitor liquid levels in tanks are a source of liability because they are easily damaged or broken, releasing the contents of the tank. Sight gages should only be used if a stainless steel valve which is normally closed is installed between the bottom of the sight gage and the tank.

The most difficult aspect of retrofitting secondary containment at a facility is selecting dimensions that will conserve space without impeding vehicle and employee access to the tanks. A typical facility has tanks grouped in one or more clusters. If possible, tanks should be consolidated in one cluster. This usually minimizes the required wall height since the volume of the containment is based on the largest single tank. Providing adequate space between tanks will also decrease wall height. Spacing tanks close together will minimize floor area, but will increase wall height. In general, 36 inches is the highest practical height for secondary containment walls, even though higher walls can result in a less expensive design due to the reduction in floor area. Higher walls impede employee access, increase problems associated with tanks floating, and expose employees to more risk while inside the wall.

The first step in sizing a secondary containment is to determine the required volume. Then a scaled drawing of the plan view of the tanks and containment should be made. The net containment area should be determined by subtracting the area of all but the largest tank from the total containment area. The height of the containment wall is determined by dividing the required volume by the net containment area. If the containment wall is higher than desired the

containment area should be enlarged. For example:

Assume a containment for four 25,000-gallon tanks is desired. All tanks are 12 feet in diameter, have flat bottoms, and are 29 feet high. The containment floor dimensions are 20 feet by 60 feet. Containment volume must be 110 percent of the largest tank.

Required volume (RV) in cubic feet

$$RV = LTV \times FF / 7.5$$

Where,

LTV = Largest tank volume in gallons

FF = Freeboard Factor, 1.1 for 110% or 1.25 for 125%

7.5 = gallons per cubic feet

For this example,

$$RV = 25,000 \text{ gal} \times 1.10 / 7.5 \text{ gal/cubic ft}$$

$$RV = 3,667 \text{ cubic ft}$$

Net containment area (NCA) in square feet

NCA = Total area - tank area

$$NCA = (20 \times 60) - (3 \times 113)$$

$$NCA = 1200 - 339 \text{ sq ft}$$

$$NCA = 861 \text{ sq ft}$$

Note: The area of only 3 tanks was subtracted since the spilled liquid will occupy space in the leaking tank.

Wall height (WH) in feet

$$WH = RV/NCA = 4.3 \text{ ft}$$

The required wall height for this design is 4.3 feet or 52 inches. The floor area should probably be increased to decrease the wall height.

Tanks should be anchored to prevent them from floating when empty. The concern is that other tanks in the containment can lose product from damaged plumbing or can rupture from collisions with the floating tank. The simplest way to anchor tanks is to weld three or more brackets to the tank where the sides meet the floor. Each bracket is then bolted to the concrete with anchoring bolts. Chains and tie-down cables can be used with brackets welded above the tank bottom. In clay-lined earthen dikes, weights can be added to the tanks or cables can be used to secure the tank to anchors outside the dike. Anchors in the soil beneath the liner or cables connected to concrete deadmen can be used if the area where the liner is penetrated is properly sealed. Anchoring of tanks is a practice often neglected when tanks are placed in secondary containments. The following example should illustrate the importance of anchoring tanks.

A typical carbon steel tank, 12-feet in diameter and 29 feet high, holds 25,000 gallons of liquid and weighs about 13,000 pounds when empty. An inch of ammonium polyphosphate solution in the tank weighs 825 pounds. Sixteen inches of material in the tank weighs about 13,000 pounds. Exceeding this same level of solution outside the tank will cause the tank to float when empty. If a 36-inch-high containment were full of solution the buoyancy force pushing upward on the empty tank would be the same as 20 inches of solution in the tank or 16,500 pounds. Shorter tanks of the

same diameter weigh less and would float in a shallower depth of liquid. Stainless steel tanks weigh slightly less than carbon steel tanks of the same size and fiberglass and some polyolifin tanks are considerably lighter.

Another design consideration of secondary containment is the method for leveling tanks on a sloped containment floor. Containment floors should be sloped to minimize the corrosive effects of fertilizer on the floor and to ensure proper drainage. Concrete floors should be sloped a minimum of 2 percent. The simplest way to level the tanks is to place them in a metal ring filled with coarse, washed gravel. In addition to providing a level surface for the tank, the gravel provides a space for detecting leaks and keeps moisture away from the tank bottom, thus prolonging the tank life by reducing corrosion. The objection some dealers have with gravel is the difficulty in cleaning the gravel after a spill. The quality of rain water could be adversely affected long after a spill has been recovered.

An alternate method for leveling tanks is to pour raised concrete pads beneath each tank. This is most easily done by pouring the tank foundations first and making a second pour for the space between tanks. This is not the preferred method of construction because of the sealing required around tank foundations. The best method is to make the sloped and level surfaces in one pour. The second best approach is to pour the entire bottom of the pad and use dowels to attach the tank foundations made in a second pour. Many dealers have had success with level secondary containment floors with tanks setting directly on the floor. The key to their success is attributed to keeping the floor dry and free of fertilizer.

The most common construction material for secondary containment is reinforced concrete. The major considerations are that the walls and floor be strong enough to support the gravity loads of the tank and the hydrostatic loads of a massive spill with a minimum amount of cracking. It is also important to provide a watertight seal between the floor and wall connection. Figure 6 shows a typical concrete containment floor and wall construction. Figure 7 shows a containment wall on a floating slab. Floating slabs are common in colder areas where frost depths are such that deep footings are required. A typical secondary containment showing tank foundations and anchors (Kammel et al. 1990) is shown in figure 8.

Dealers not experienced in water-tight concrete construction should secure the services of a qualified contractor. A brief summary of recommended concrete specifications is given in a another section.

Concrete block can be used for secondary containment walls. To withstand the hydrostatic forces of liquids, block walls must be reinforced with steel and filled with concrete. Some type of sealer should also be used since concrete blocks are not watertight.

Large Tank Containment--

Designing secondary containment for tanks with capacities over 100,000 gallons presents some engineering challenges. These tanks are usually built on sand, providing no barrier to downward movement of leaking material. They cannot be raised with a crane and placed inside a containment. Many dealerships lack adequate space to build a secondary containment dike for these large tanks. State regulations regarding large tanks vary. Proposed methods for containing

these tanks are so varied, one state issues experimental permits for designs not explicitly defined in the regulations (Illinois Department of Agriculture, 1989).

In new installations the tank can be built within a concrete containment or some other watertight basin. The aim is to be able to detect leaks in the tank inside the containment. Providing some type of impervious barrier beneath existing tanks is a problem with no simple solution. The most common method for detecting leaks is a false bottom. A false bottom is a steel floor welded inside the tank over a thin layer of sand (Figure 9). If the tank has a sump, it is cut out and a steel plate is welded in its place. A layer of sand is placed over the old tank floor. There are two methods for attaching the new floor over the layer of sand. One involves sliding steel sheets for the new floor through slits cut in the wall just above the sand. The steel plate is welded to the wall and when the new floor is complete the slit circles the entire wall separating the old bottom from the tank. The old bottom merely becomes a shallow pan full of sand. Some contractors weld the old bottom to the edge of the false bottom and install leak detection ports in the sand layer.

The other method for attaching the false bottom to the tank wall involves the use of an angle iron which is bent to match the curvature of the wall. The angle is welded to the wall and provides a surface on which to attach the new floor. Steel sheets for the new bottom are delivered through a large opening cut in the the top of the tank.

The area around the tank is usually sealed with a clay lined earthen dike. Clay lined earthen dikes are made by uniformly incorporating bentonite or attapulgite clay into the top 6 inches of soil. Large rocks and gravel must be removed as well as soil high in organic matter. A thorough analysis of the soil is required to determine the amount of clay required per square foot of soil. An engineering recommendation or the recommendation of the appropriate regulatory agency should be followed concerning clay addition. In most state regulations, the maximum permeability is one-millionth centimeters per second (one-third of an inch per day). The clay seal should cover the area inside the dike and up to the top of the dike (Figure 10). The top of the dike should be three feet wide and the sides should slope no more than one foot per two feet of run. A six-inch layer of gravel or soil should be placed over the clay liner to protect it from erosion and desiccation.

Natural soil can be used for an earthen dike without the addition of clay if the soil has the following physical properties; 50 percent or more of the soil passes through a No. 200 sieve and no more than 5 percent is retained on a No. 4 sieve. The soil must also contain less than 2 percent organic matter and have a plasticity index of at least 15 (Wisconsin Department of Agriculture, 1988).

Synthetic liners are an alternative to clay liners. Sheets of synthetic liner material are bonded to form a solid barrier inside the containment. The walls and floor of the basin can be made of packed earth or the floor can be earthen with walls made of concrete or prefabricated panels bolted together and anchored in concrete. Properly installed, synthetic liners are available with a guaranteed service life of 20 years. The disadvantage of clay and synthetic liners is the problem associated with cleaning up a spill. Their advantage is their lower cost compared to concrete or steel.

Some large tanks have been contained in a large steel tub to conserve space. The idea is bizarre but not as impractical as it sounds when one considers that a million gallon tank requires a dike over an acre in size if the walls are 3 feet high. The steel containment, coined the elephant ring, for a million gallon tank occupies an area smaller than one-fifth acre. An elephant ring is typically half as deep as the tank is high. With this ratio in height, 110 percent of the tank can be contained in a tub having a diameter 1.5 times that of the tank. A tub diameter 1.6 times that of the tank will contain 125 percent of the tank. The tank and tub combined require nearly twice as much steel plate to build as does the tank. The walls of the ring must be reinforced with members attached to the tank and the tank should rest on a 2 to 4 inch layer of gravel or sand to reduce corrosion and for leak detection. As with other secondary containments, rainwater has to be dealt with. A variation of the elephant ring that eliminates rain water problems is a ring that has a radius about 4 feet larger than the tank radius with a roof over the space between the tank and ring. This system has been proposed but has not yet been built.

Though large tanks are not easily moved, there are some methods for moving large tanks into a containment basin, eliminating the need for a false bottom that is costly compared to a synthetic or a clay liner. Since large tanks are easily damaged, an engineer or experienced contractor should be contacted for assistance in moving them. Large tanks have been moved by floating them in water. Some of these tanks are made primarily of steel only three-sixteenths of an inch thick and will float in water no deeper than 10 inches. A clay lined dike is built around the tank and water is pumped into the dike until the tank begins to float. It is then moved to a clay lined area in the dike. Water is pumped or drained out of the dike and the area where the tank was previously located is then sealed with clay. To reduce the chance of damaging the tank, projections, such as the sump should be removed. Interior braces may be required to support the bottom against the buoyant forces of the water.

Tanks as large as 300,000 gallons have been moved by the same method as houses are moved. Two large beams which pass through holes cut in the in the tank wall are used to support the weight of the tank while being moved. After moving the tank, the holes must be patched and tested for leaks.

Four tanks in Nebraska were moved two miles using three dollies made from semitrailer axles. The dollies consisted of a framework that bolted to brackets welded to the side of the tank. Hydraulic jacks on the dollies were operated simultaneously to raise each tank. One of the three dollies had a fifth wheel that allowed a tractor to pull the tanks.

A fourth way to move large tanks is on a cushion of air. This involves attaching a skirt around the bottom of the tank and using large blowers welded to the tank to provide a cushion of air on which the tank can ride while being pulled on a relatively smooth surface.

Another alternative to false bottoms for leak detection involves subsurface drainage that spills into a sump or containment basin around the tank. Equipment used by utility companies to bore under roads can be used. The containment would resemble a moat with perforated piping discharging into a moat. Someone specializing in subsurface drainage should be consulted to determine the suitability of the site for this type of leak detection.

Large tanks must also be anchored. Weights can be attached to the tank or tanks can be constrained using cables attached to anchors outside of the dike (Kammel et al. 1990). Concrete deadmen or earth anchors can be placed beneath the liner if the clay or synthetic liner is properly sealed. Since the bouyant force on a large tank can exceed 100,000 pounds, an alternate method to protect the tank and dike is to constrain the tank from lateral movement while allowing it to float. Flexible plumbing is required to allow the tank to move without damaging plumbing. It is also a good practice to leave fittings and manholes open when tanks are empty to equalize liquid levels inside and outside the tank in the event of a spill or rainfall accumulation.

Pesticide Storage Containment--

Pesticide storage containment is similar to fertilizer storage containment with the exception of earthen containments which are not permitted for pesticides. It is also important to separate pesticide containment from fertilizer containment. The two can be adjacent inside one containment area with a dividing wall between the two. The dividing wall can be lower than the outside wall to allow the whole area to be used as one containment during a catastrophe. Pesticides should also be kept under roof because of the problems associated with contaminated rain water. Packaged pesticides should be stored in a separate warehouse and not inside a secondary containment for bulk pesticides or fertilizer. Flammable pesticides should be separated from non flammable ones and the warehouse should be curbed to contain large spills or water used in extinguishing fires.

Dry Fertilizer Storage Containment--

Dry fertilizer storage buildings should be elevated above ground level to prevent rainfall runoff from entering the building. The floor should be paved with concrete and cracks should be routinely repaired to prevent the downward movement of fertilizers. The roof and walls should be free of leaks that will allow rain water to come in contact with fertilizer. Floor sweepings and scrap fertilizer materials should be kept under roof as are other dry fertilizers. Limestone is generally the only dry fertilizer material that can be stored outside.

Until recently, wood was the material of choice for dry fertilizer buildings. Some new buildings are being made primarily of reinforced concrete. The floor is poured with slots wide enough for walls to be stood edgewise in them. Wall sections are then poured horizontally on the floor. Reinforcement steel and clips for connecting wall sections are accurately placed in each wall section. A crane is then used to erect the walls and connect adjoining panels. The bin walls are supported laterally across the top of the open end with steel or concrete beams. The advantage to this type construction is the savings in labor compared to wooden buildings.

WATER-TIGHT CONCRETE CONSTRUCTION

To ensure that concrete for load pads and containment structures will resist penetration by moisture and chemicals and have a durable finish, the following specifications should be followed (Noyes, 1988):

Use Type IIA or Type II cement with air entrainment at 4,000-4,500 psi compressive strength. Type II provides moderate sulfate resistance.

Use water-cement ratio of 0.40-0.45 for a stiff (1.5"-3" slump), relatively dry mix for maximum strength, chemical resistance, freeze/thaw resistance, and watertightness.

Use 5.5% to 7% air-entrainment in cement to improve workability at placement, and improve watertightness and strength of low slump concrete.

Use concrete plasticity admixture for easier workability at placement and for improved watertightness and strength.

Vibrate concrete during placement at 5,000 to 15,000 vibrations per minute for minimum aggregate segregation.

Powered steel trowel surface finish to minimize coarse surface texture to improve washing and cleanup.

Immersion or moist cure concrete at least 14 days (28 day immersion or moist cure preferred for maximum strength).

Allow no more than 30 minutes between concrete truck loads during placement.

Mix concrete 70-100 revolutions at mixing speed, then an additional 200-230 revolutions (maximum of 300 total revolutions) at agitating speed.

Discharge mixed concrete within 1.5 hr per ACI C94.

Minimize discharge drop distance by using a discharge chute.

Use large (1" - 1.5"), clean, impervious aggregate or aggregate 1/3 the size of the slab thickness for maximum strength and watertightness.

Use clean, drinkable mixing water at a pH - 5.0 - 7.0.

Oven test aggregate for excess moisture and adjust water added accordingly. If oven testing is not possible, reduce total added water assuming 3.5% excess water in sand and 1.5% excess in aggregate.

Continuous pour in one day - no cold joints.

Expansion joints should be spaced close enough to prevent cracks from forming in undesirable places. Joints should be machine cut to a depth of one-fourth to one-fifth the slab thickness. The rule of thumb is that the minimum joint spacing in feet be 2.5 times the slab thickness in inches. That is, a 8-inch slab should have joints no farther than 20 feet apart. Joints should be located in areas where they can be monitored, for example, not under a tank. Joints should be sealed with a material resistant to fertilizers and pesticides and should be periodically checked for repair or replacement. The sections between joints should be square. If not square the length-to-width ratio should not exceed 1.5.

A vapor barrier should not be used beneath pours as this may cause the concrete to retain moisture and increase degradation of the concrete from freezing and thawing.

Frost heave problems can be reduced by keeping the area around concrete slabs dry. The area beneath the concrete should be higher than the surrounding area and surface drainage should be provided to keep water from standing near containment structures. The drainage around concrete structures should be monitored for two or three years after construction to ensure that the area is well drained after the structure settles. Runoff from buildings and paved areas should be kept away from containment sites using curbs and gutters.

Steel reinforcement bars are recommended for containment structures. Wire mesh or fiber additives will not provide resistance to cracking over the life of the facility. Generally, No. 4 reinforcement rod is required and spaced 12 inches in both horizontal directions. The steel in sumps is usually spaced 6 inches. Since steel reinforcement requirements vary with soil bearing capacity, strength of concrete, and the anticipated loads, an engineering recommendation should be followed regarding steel requirements.

To prevent secondary containment basins from leaking beneath the containment wall, waterstops are needed between containment floors and walls. Molded vinyl waterstops are available in several shapes. These must be embedded in the concrete floor beneath the wall. Other water stops are available which can be placed on the perimeter of the slab after it has cured.

Many fertilizer and pesticide handling facilities have concrete slabs beneath tanks that may be incorporated into a secondary containment design by attaching walls. The suitability of the slab for supporting the wall should be determined. In most instances this is not the case. If the concrete is in good condition and free from cracks it can serve as part of the containment floor and the pad can be extended. The wall can then be built above new concrete. It is important when joining new concrete to old concrete to seal the crack between the two slabs and to connect the slabs using dowels inserted into holes drilled into the existing concrete. In some instances even where existing concrete is in good condition the best decision is to remove the concrete if the slope is incorrect or the pad is too low due to settling. An engineer experienced in concrete design should be consulted regarding the use of existing concrete.

MANAGEMENT PRACTICES

Containment systems are an essential part of environmental security at fertilizer/pesticide dealerships, but they are no substitute for good management. Environmental management involves, 1) the proper handling of fertilizers and pesticides, 2) the security of the facility during periods of nonoperation, and 3) the reliability of equipment designed to transport or contain these materials.

Proper handling of materials begins with employee training and education. Employees should understand the sources of groundwater contamination and the importance of keeping fertilizer and pesticides contained. The rinsate storage scheme should be understood by all and all storage containers should be labeled, including rinsate containers. A typical scheme may involve rinsate storage tanks designated as corn, cotton, soybean, and pesticide free make-up water. Schemes vary according to the variety of crops treated and the amount of rinsate that is handled at the facility. To prevent contamination of materials, spills should be cleaned up immediately after they occur. To minimize the amount of rainwater that must be collected and used, the loading pad and containment system should be cleaned and sumps should be pumped out at the end of each working day or prior

to rainfall events. To help determine if water is suitable for discharge kits are now being marketed to test liquids for contaminants. Some tests can be completed in a few minutes, others require a few hours.

There are two approaches to pesticide handling; mixing pesticides to the carrier in the batch mixer and mixing pesticide with carrier at the application site. Mixing pesticide and carrier at the facility is the common practice. This practice ensures formulation accuracy because an experienced mixer operator oversees the addition of pesticides to the mix. This approach also requires less equipment since pesticides are not mixed and handled in equipment separate from fertilizer. The disadvantage of mixing pesticides and fertilizers at the facility is the amount of equipment that has to be cleaned to prevent contamination when switching products. The mix tank, nurse equipment, and application equipment must all be cleaned to purge the system of a particular material. Another disadvantage is the hazard associated with the transport of large volumes of material containing pesticides.

Many dealers have begun mixing pesticides with fertilizer at the site of application. Pesticide laden rinsates can practically be eliminated from the facility if the applicator is rinsed in the field. On-board rinse systems are available which have nozzles mounted inside the applicator tank to clean the tank walls and baffles. Portable sprayers are also available for cleaning pesticide residues from the outside of applicators. To ensure formulation accuracy some operators weigh or meter out batches of pesticide at the facility for each load of fertilizer. The pesticide is then transported to the field in separate containers on nurse equipment. The containers should be approved by the Department of Transportation for transporting pesticides.

Applicators can be equipped with on-board injection or impregnation systems. These systems add pesticide to fertilizer in the output stream of the applicator. These systems are ideal for reducing rinsate since pesticide never enters the applicator tank. Direct injection and impregnation systems, however, are limited in the number of products they can handle and some dealers are skeptical of their accuracy.

Regardless of where pesticides and fertilizers are mixed, the amount of rinse water handled at the facility can be reduced by rinsing as much equipment as possible in the field. To reduce the chance for rinsates to enter surface water the rinsing should be done a safe distance from ditches and creeks. When on-board rinse systems are used, the rinsate left in the applicator should be broadcast over the field last treated. Good judgement should be exercised to maintain the total pesticide application rate within label recommendations.

Other methods for reducing the volume and cost associated with handling rinsates include (Gredler and Cole, 1987):

Job scheduling. For example, a dealer who plans to apply fertilizer and herbicide to corn and cotton can group the jobs so that equipment must only be rinsed only once per day.

Equipment can be modified to reduce the amount of residue remaining after being emptied. The pump on large application equipment, for example, is driven by a belt from the engine and is nearly 10 feet from the tank drain. As an option, the pump can be driven hydraulically and placed directly beneath the applicator tank.

Using high-pressure rinse equipment can also reduce the volume of rinsate reduced. Though centrifugal pumps are well suited for handling liquid fertilizer, their high output and low operating pressure make them poorly suited for washing out equipment. High pressure washers do a better job of cleaning for the amount of water used.

Proper equipment calibration and accurate measurement of the acreage to be applied will minimize the amount of pesticide that must be rinsed out of the applicator or hauled back for recycling.

The security of the facility during periods of nonoperation requires daily inspections of the security system, closing of valves, and disabling of pumps and electrical circuits. Facilities in areas subject to theft or vandalism must have a security fence with locks on gates around the property or should have the area patrolled. At the end of each working day the facility should be locked and valves on tanks and all pumps should be turned off. Some facilities are equipped with a single switch which locks out all electrical circuits to pumps or electrically driven valves.

Facilities in areas not subject to vandalism may not require a security fence, however, all valves on tanks should be locked in the closed position. Since valves on tanks and valves at the bottom of external sight gages both need to be locked, the two can be positioned on each tank so that a single lock can be used to lock both valves. Gravity drains on containment areas are not recommended, however, in some areas drains are permitted to discharge rain water. The discharge of rainwater must be closely supervised and drain valves should otherwise be locked at all times. During extended periods of nonoperation storage areas and containment systems should be checked frequently. Prior to the winter season the facility should be "winterized". Water trapped in lines should be discharged and water in containment basins should be removed to prevent damage to the system due to freezing.

The integrity of containment systems, storage containers, and other equipment designed to keep fertilizer and pesticides from entering water supplies should be checked frequently. Tanks, valves, and piping systems should be frequently checked for leaks. In some proposed regulations, a considerable number of inspections of these systems with documentation of inspections is required. This practice is recommended as a part of an overall inspection and maintenance program for the facility. Tanks and plumbing, for example, should be inspected annually for leaks and trouble areas should be physically tested by either a vacuum or pressure test. A strict maintenance schedule should be followed, not only to protect water supplies, but to reduce down-time during the season.

COST AND WORK SCHEDULING

Containment of materials at fertilizer dealerships can be a costly proposition. A concrete slab can usually be poured for about \$100 per cubic yard. A survey of dealers in the Midwest and Great Plains has shown that the cost for loading pads, including site preparation, reinforcement, form work, and finishing has ranged from \$140 to \$200 per cubic yard of concrete. This high cost was due, in part, to the special requirements for retrofitting new and existing concrete, site preparation, and the labor associated with forming sumps. Other costs associated with a load pad include the cost of rinsate holding tanks

and pumps and plumbing to transfer material to and from these tanks. At most facilities, three or four 500-gallon tanks are needed. The total cost for a rinsate recycling system should be around \$2500, depending on the amount of material that must be purchased.

The cost of secondary containment will depend on the materials used for construction. Concrete has the advantage of conserving space but is more costly than synthetic or clay liners. The following cost comparisons for alternative diking systems were presented by Hansen (1990). In each alternative, a 10 percent contingency was included in the total cost. Also security fencing at \$10 per linear foot was included in each alternative. A typical secondary containment for six tanks, all 12 feet in diameter, the largest having a capacity of 30,000 gallons, costs \$26,000 if made of concrete. Per square foot of floor area the concrete dike costs about \$11.00.

A clay-lined-earthen-dike with the same floor area would cost \$14,000. Due to the sloping sides, the earthen dike can contain a tank with a volume up to 45,000 gallons. Per square foot of floor area the earthen dike costs about \$6.00.

A similar dike with a hypalon liner sandwiched between polypropylene liners will cost \$19,500, or \$8.25 per square foot of floor area. The polypropylene liners, geotextile liners, are needed to protect the main liner from damage during installation. In some synthetic liner installations one or both geotextile liners can be omitted if clean sand or smooth pebbles are adjacent to the hypalon liner and steps are taken to protect the liner during installation. This can result in a savings of 13 to 40 cents per square foot of floor area.

Dealers typically spread containment construction over a two- or three-year period and regulations generally have a compliance schedule spanning a similar time period. The areas and materials at dealerships requiring containment are prioritized in most regulations and should be prioritized by dealers scheduling containment work over an extended period. Containment work should be prioritized in the following order; water system protection, pesticide storage containment, loading/mixing/equipment washing area containment, and fertilizer storage containment.

CONCLUSION

Before designing a complete containment system, dealers should visit sites and study existing systems. Dealers with containment systems are a valuable source of information, particularly if they have operated a system for some time. Experience and hind-sight are invaluable. A good system design should incorporate methods for expanding in the future. Provisions for the construction of roofs over areas subject to incidental spills should be included in the long-range plan.

Even in states where there are no containment regulations, dealers should contact local agencies involved with water supplies, such as the Health Department, Local Emergency Management Agency, and the local Environmental Regulatory Agency when modifying a facility. For assistance in designing containment, the Cooperative Extension Service, State Department of Agriculture, fertilizer and ag-chemical dealer organizations and TVA's National Fertilizer and Environmental Research Center can be contacted.

Fertilizer and pesticide containment provides opportunities for the retail fertilizer industry to take a leadership role in protecting our water resources. Indications are that there will be more and not less regulation for fertilizer and ag-chemical dealers in the future. It is everyone's responsibility to protect our water resources. After all, we are only borrowing this water from our descendants.

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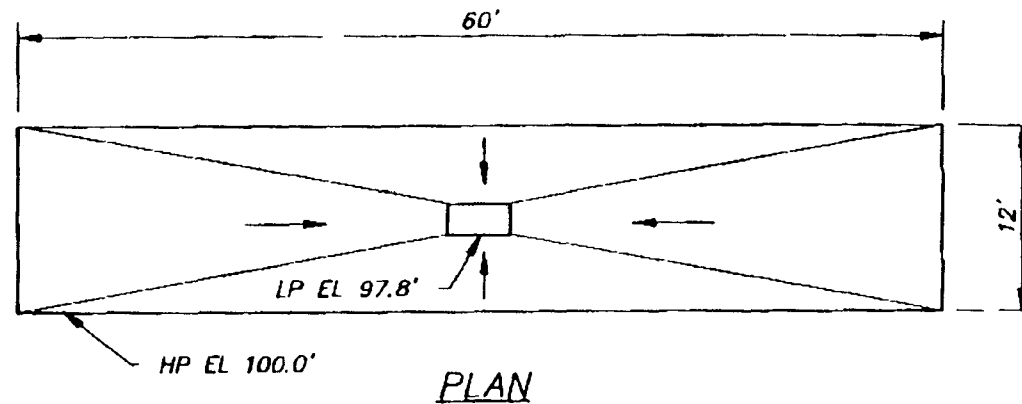
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Liquid Holding Capacity in Gallons

$$LHC = \frac{7.5 \times L \times W \times D}{3}$$

Where,

L = pad length in feet

W = pad width in feet

D = depth at sump inlet in feet

7.5 = gallons per cubic foot

$$LHC = \frac{7.5 \times 60 \times 12 \times 2.2}{3}$$

$$= 3960 \text{ gallons excluding sump}$$

By adding a 4" high rollover curb around the pad the LHC is increased by 1800 gallons.

LHC of the curb is computed as follows:

$$LHC = 7.5 \times L \times W \times CH$$

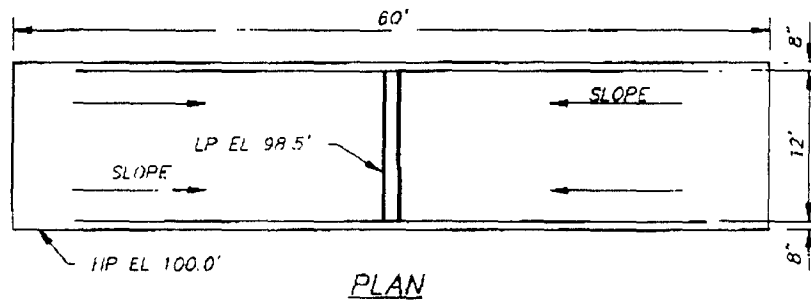
where,

CH = curb height in feet

$$LHC = 7.5 \times 60 \times 12 \times 0.33$$

$$LHC = 1800 \text{ gallons}$$

Figure 1
LOAD PAD FOR SINGLE VEHICLE



The Liquid Holding Capacity for this pad is computed by the equation

$$LHC = \frac{7.5 \times L \times W \times D}{2}$$

$$LHC = \frac{7.5 \times 60 \times 12 \times 1.5}{2}$$

$$LHC = 4,050 \text{ gallons excluding the trough}$$

Figure 2
SINGLE VEHICLE LOAD PAD WITH TROUGH

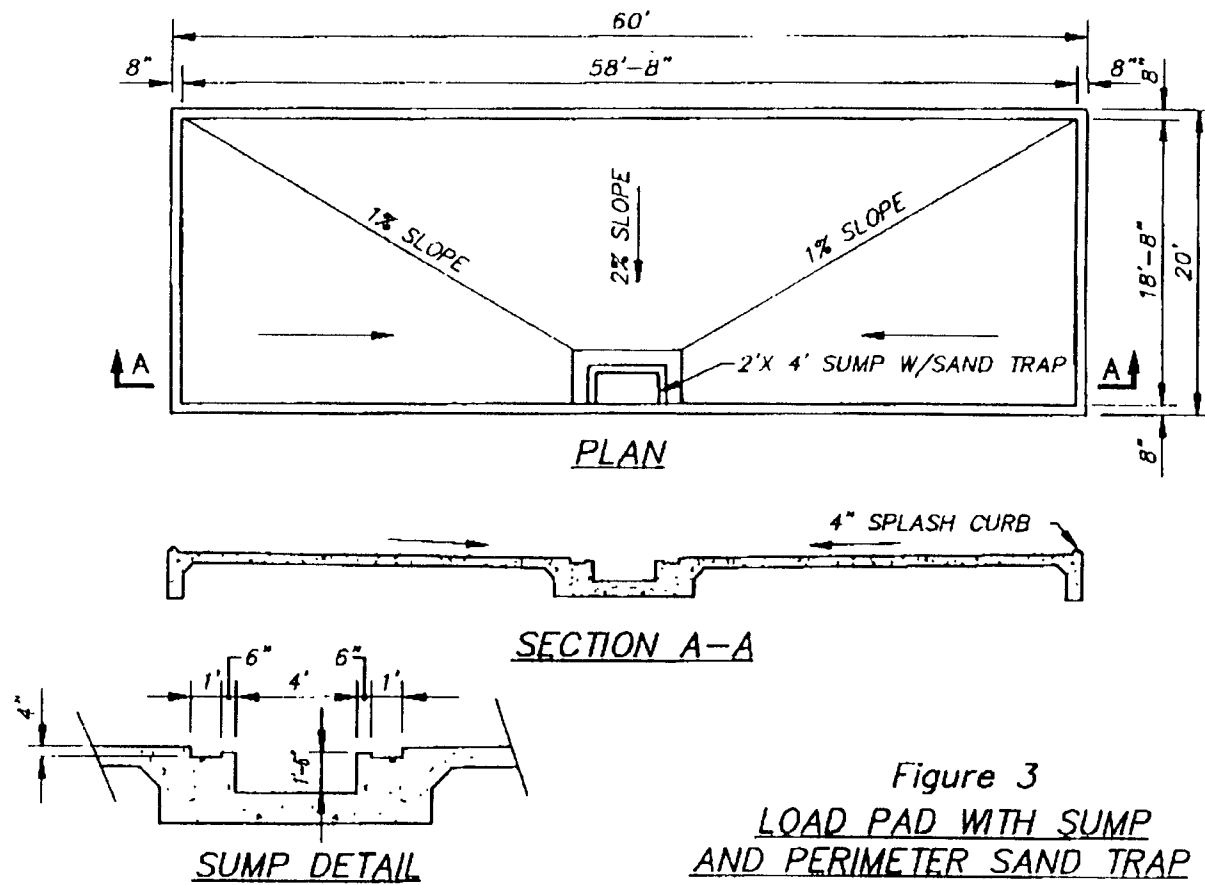
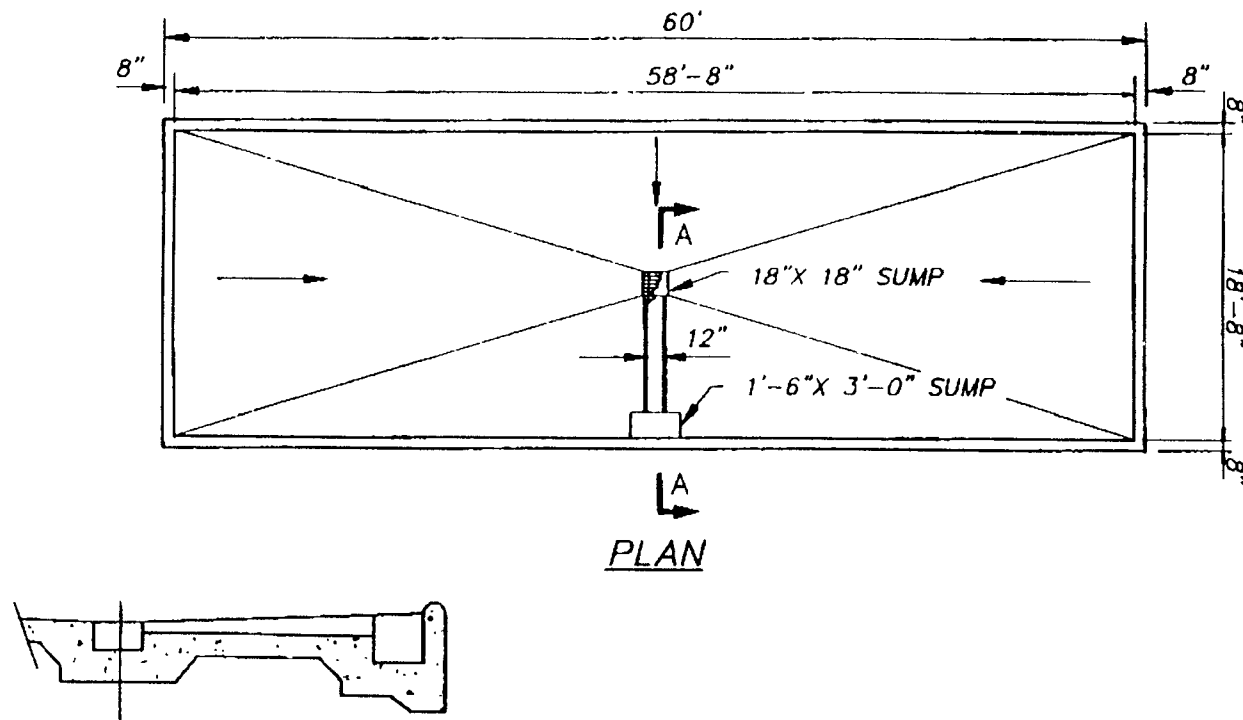


Figure 3
LOAD PAD WITH SUMP
AND PERIMETER SAND TRAP



SECTION A-A
SCALE: 1/4" = 1'-0

Figure 4
LOAD PAD WITH TWO SUMPS

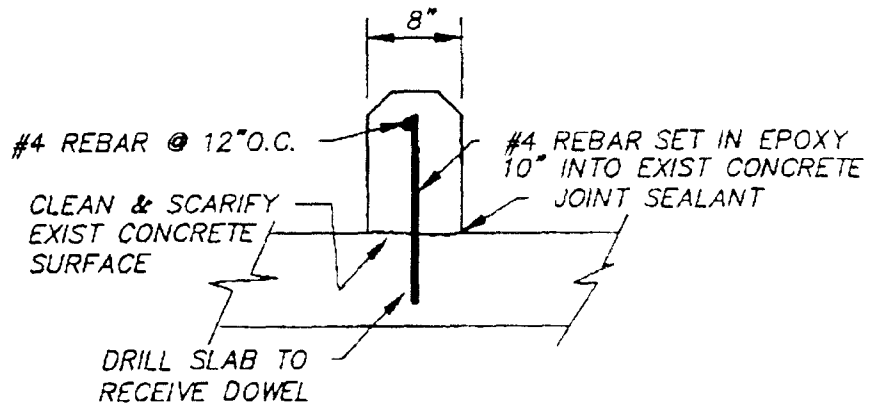


Figure 5
NEW CURB ON EXISTING CONCRETE

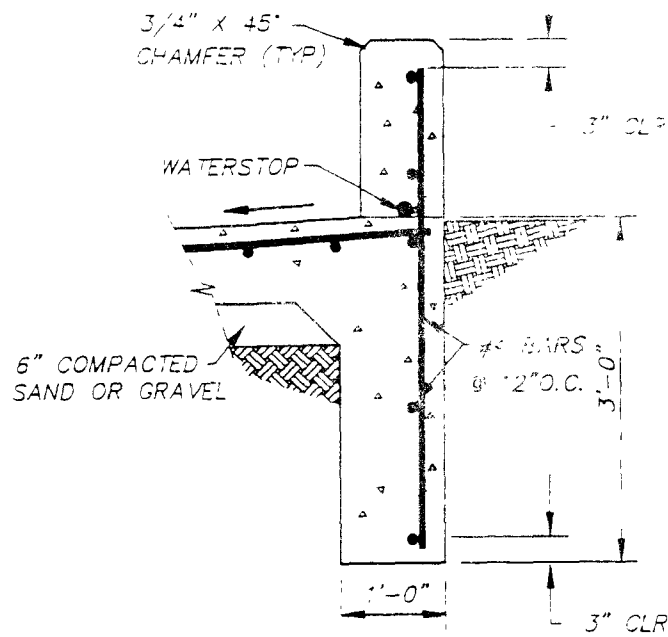


Figure 6
CONTAINMENT WALL

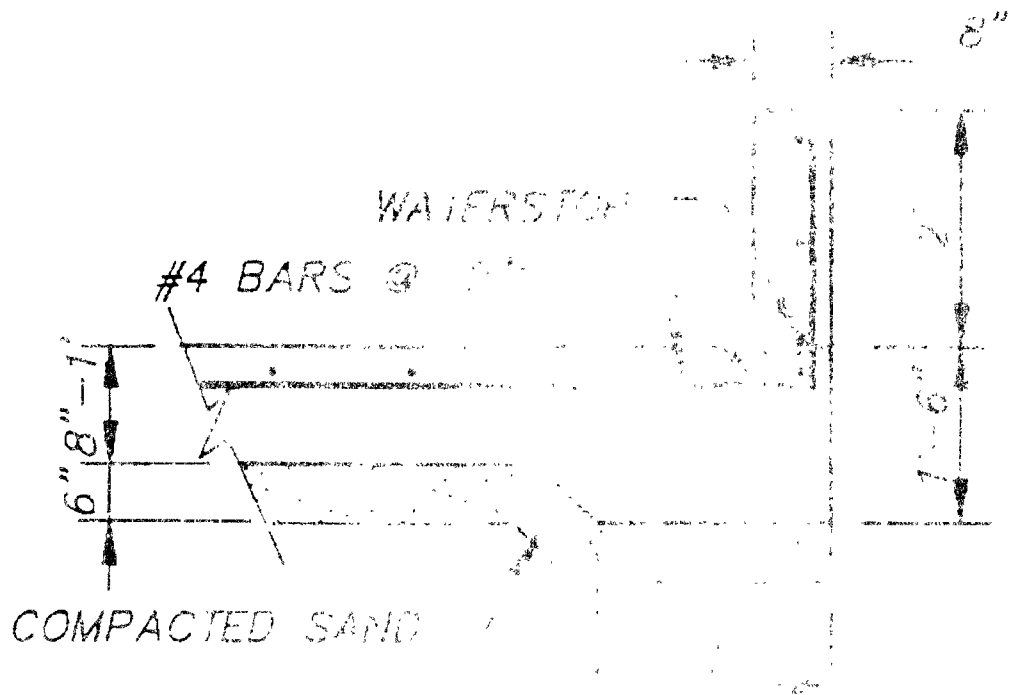


FIG. 10
FLOATING SLAB

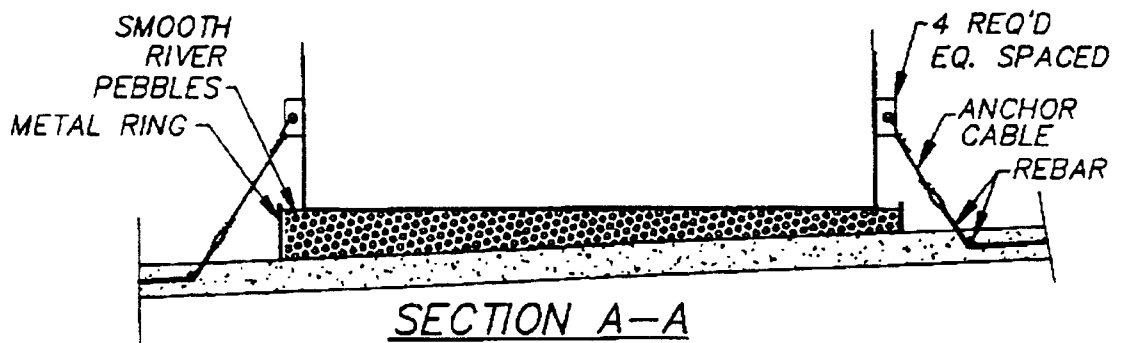
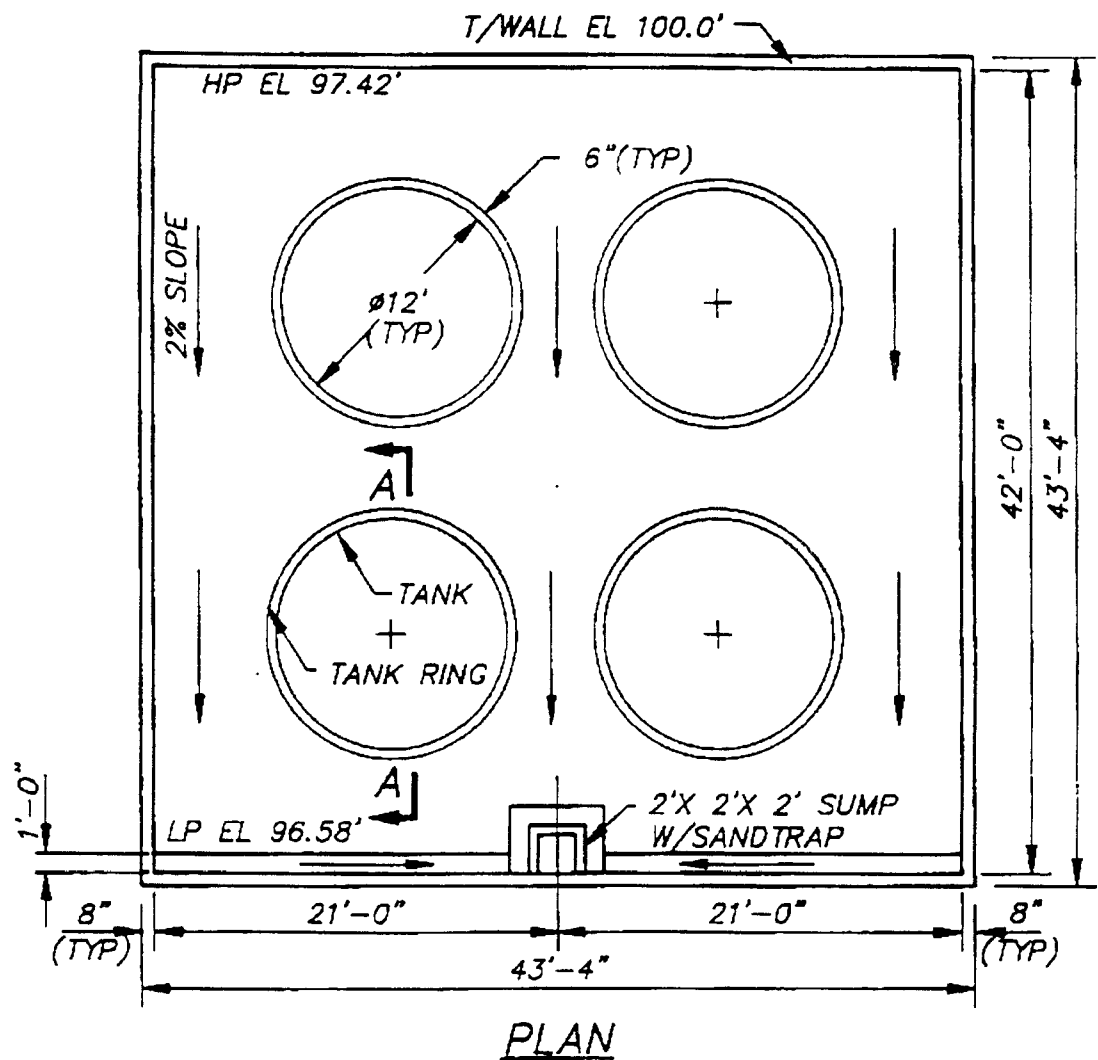


Figure 8
TYPICAL SECONDARY CONTAINMENT

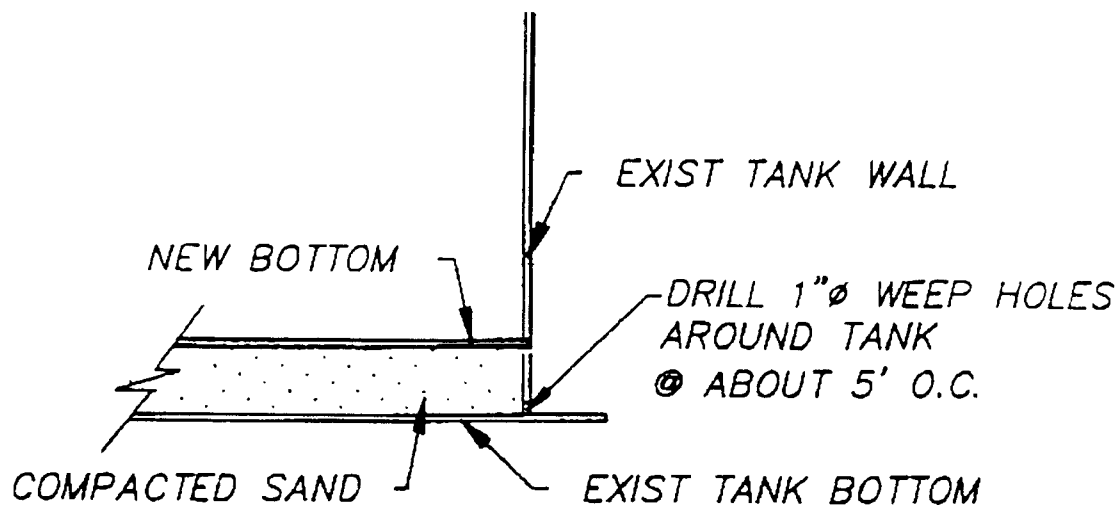


Figure 9
FALSE BOTTOM TANK

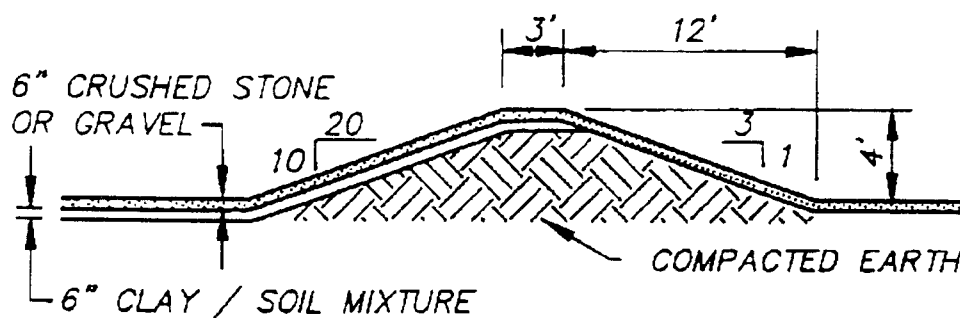


Figure 10
CLAY LINED EARTHEN DIKE

TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i>		
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16. ABSTRACT The International Workshop on Research in Pesticide Management, Disposal, and Waste Minimization was held in Cincinnati, Ohio, February 26-27, 1991. The purpose of this workshop was to provide government officials, pesticide user groups, pesticide producers and farm organizations practical solutions to pesticide treatment and disposal problems. The workshop focused on how to destroy pesticides and their residuals at low cost by the applicators and dealers. The technical program included presentations by government researchers and regulators, university agricultural station professors, industry experts and individuals involved in pesticide disposal and treatment.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
1) Pesticide 2) Herbicide 3) Insecticide 4) Fungicide		
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 208
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