To the Graduate Council:

I am submitting herewith a thesis written by Brian Keith Corwin entitled "Design and Management of a System to Store, Concentrate, and Degrade Pesticide-Contaminated Wastewater." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Agricultural Engineering.

Daniel C. Yoder, Major Professor

We have read this thesis
and recommend its acceptance:

Accepted for the Council:

Associate Vice Chancellor and
Dean of The Graduate School

DESIGN AND MANAGEMENT OF A SYSTEM TO STORE, CONCENTRATE, AND DEGRADE PESTICIDE-CONTAMINATED WASTEWATER

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Brian Keith Corwin

August, 1996

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This thesis is dedicated to my mother, Marjorie C. Corwin,
who passed away on July 24, 1993.

I miss you.

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ABSTRACT

One of the consequences of modern agriculture's reliance on chemicals is the production of pesticide-contaminated wastes. Much of this waste is made up of equipment rinsewater and spray tank rinsates, inappropriate disposal of which threatens the quality of the nation's water resources. One promising disposal technique employs an evaporation/degradation system, which consists of a lined bed or pit filled with soil and into which the wastewater is placed. The water evaporates, and the pesticide residues are adsorbed onto the soil and are eventually degraded by soil micro-organisms. Researchers have investigated variations of this system and obtained promising results. However, none of the previous reports indicate that much background analysis went into the designs. The goal of this research was to seek the combination of factors resulting in the optimum combination of evaporation and degradation. The variables that influence both of these processes include: (1) temperature, (2) soil texture, (3) evaporation rate, (4) mode of application of the pesticide solution to the soil, and (5) time.

A test apparatus was constructed employing individual soil columns to simulate conditions in a soil bed. Individual column treatments consisted of all possible combinations of two temperature levels, two soil types, two airflow rates, four application methods, and four run times. A mixture made up of water and the herbicides atrazine and

fluometuron at low concentrations (10 parts per million) was continually supplied to the columns. Records were kept of the amount of herbicide solution supplied to each soil column to meet its evaporation requirements. At prescribed time intervals, the soil in the columns was tested for herbicide concentration levels as an indication of the rate dissipation.

Results indicate that substantial volume reduction (water evaporation) and decontamination (herbicide dissipation) of pesticide rinsate material in a soil disposal system can be achieved through simple application techniques. Under conditions of continual loading, the columns ability to degrade the herbicides was not overwhelmed by the increase in concentration levels. Soil type plays an important role in both processes. Although evaporation in the sandy soil columns was slightly greater (about 10%) than in those containing silty soil, the overall average herbicide degradation was much higher in the silty soil columns. The silty soil columns experienced an average of 85% atrazine and 59% fluometuron degradation (of that applied to the columns). Additionally, the evaporation (per surface area) from the silty soil columns averaged 3095 L/m^2 [76 gal/ft^2] under low temperature, low airflow conditions and 7168 L/m^2 [176 gal/ft^2] under high temperature, high airflow conditions. In the proper design of such a system, greater emphasis should be placed upon elevating temperatures rather than facilitating air movement.

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CHAPTER I:

INTRODUCTION

RESEARCH JUSTIFICATION

Today's farmers rely heavily on pesticides to provide the quantity and quality of food and fiber needed to feed and clothe the ever-growing world population. Ware (1994) reports that 8.34 million pounds of pesticides were used in the production of food, clothing and durable goods for the more than 250 million persons living in the United States in 1991. With the world's population increasing at an exponential rate, greater pressure will be placed on increasing agricultural production to meet future demands. However, one must realize that as the need for increased production is desired, the amount of land on which to produce these commodities remains the same or has lessened. Therefore, in order to meet the increasing demand, farmers must produce greater quantities of food and fiber from the same acreage that is currently under production (Klassen, 1989). Agricultural chemicals, in the form of pesticides and fertilizers, can help farmers accomplish this goal by increasing productivity and efficiency. Thus, the demand for and use of agricultural chemicals will remain steady or even increase in the future.

Agricultural chemicals also have an enormous economic impact. Private industry benefits greatly from the sale and use of these chemicals. Ware (1994) points to 1992 reports which estimate the world market for pesticides to be valued at $25.5 billion.

America comprises the world's largest market at 32% of this total. In 1991, U.S. manufacturers produced 1.3 billion pounds of pesticides valued at $7.8 billion, with a retail sales value reaching $8.3 billion. Additionally, Ware (1994) reports that in the U.S. alone, about 30% of crops are destroyed by pests each year despite the use of pesticides. This represents an annual loss of about $30 billion to American farmers. This figure would surely skyrocket if the use of pesticides were eliminated.

These are not the only areas in which agricultural chemicals have an economic impact. Consumers in the United States spend less of their income on food than any other people in the world (Bohmont, 1990). Klassen (1989) estimates that since 1951, American consumers have saved $202.8 billion on food expenses due to reduction of disposable income spent on food. Without the use of these chemical products, the world food supply would be reduced by as much as 40% and food prices would increase drastically. Thus, it is very apparent that agricultural chemicals are responsible for part of the physical well-being enjoyed by most people in the U.S.

Although these chemicals are clearly indispensable in modern agriculture, they do not come without serious drawbacks. At the forefront is the growing concern that their use and/or misuse has the potential to adversely affect the environment. Concern is especially growing with regard to the contamination of water resources, both groundwater and surface water. Shortle et al. (1989) point to earlier studies which estimate that the drinking water of 50 million people in the U.S. could potentially be contaminated by agricultural chemicals. In literature obtained from Smoot (1994), it is interesting to note

that pesticides and nitrates rank in the top three as contaminants considered by states and territories in the U.S. to be a major threat to groundwater quality. Lisa Heacox, in the December 1990 issue of *Farm Chemicals*, points to an Environmental Protection Agency (EPA) report which states that about 10% of the nation's community drinking water wells have detectable residues of at least one pesticide. However, less than 1% of the wells have pesticide residues above levels considered damaging to human health. Burgess (1989) cites a 1988 EPA interim report indicating that normal agricultural use has apparently led to residues of 46 different pesticides in the groundwater of 26 states. A total of 74 pesticides from all sources have been detected in the groundwater of 38 states. It should be noted that although the vast majority of the residues detected were below EPA's maximum contaminant level, Heacox (1990) quotes EPA deputy administrator Henry Habicht, "The finding (EPA study) underscores the need to be ever-vigilant in order to avoid more serious problems in the future."

One of the unfortunate consequences of modern agriculture's reliance on pesticides is the production of pesticide-contaminated wastes. These include empty pesticide containers, tank rinse waters, unused portions of chemical mixes, equipment wash-waters, incompatible mixtures, and/or spilled materials (Ehart, 1988). Aside from empty containers, the bulk of this waste is made up of very dilute solutions resulting from left-over tank mixes and equipment wash waters. There is much effort being given to developing realistic disposal methods for these pesticide-laden materials. This effort is fueled by the growing public concern that inappropriate pesticide disposal is threatening

the quality of ground and surface water resources.

As with any waste problem, the first response is to minimize the amount produced. For pesticides, this entails the development of a complete, well-planned waste management strategy. Implementation of such a plan is a key to preventing these chemicals from entering the water resources. It is important to realize that the best way to address this problem is through a systems approach. Up to the point the crop protection chemical gets into the applicator's hands, the possibility of the chemical causing any environmental pollution is rare (except in extreme cases such as spills or accidents). What the applicator does in the way of managing his use of the chemical will make the difference as to whether the chemical contaminates water resources. The Midwest Plan Service (MWPS, 1991) offers many suggestions for reducing the volume of containers and liquids that a farmer must properly manage. Therefore, for an applicator, proper waste management should actually begin before the chemicals are purchased and continue until well after they are applied.

During the pre-application period, one of the most important factors is the actual purchase of chemicals. Applicators must make logical judgements for their individual needs. According to Burgess (1989), an understanding of the chemical's properties, the soil properties, the specific site conditions, and the best available management practices is necessary in order to most appropriately choose the correct chemical and mode of application. Additional practices that the applicator should follow during the pre-application phase include following the label directions exactly, proper selection of

application equipment, careful mixing and equipment calibration, use of anti-backflow devices on all water supplies, and proper container disposal.

While the pesticides are being applied, the applicator should ensure that proper label rates are being observed. Actual application also depends on limiting factors including weather conditions (and their impact on drift control) and the proximity of water resources (such as lakes, streams and wells). After applying the chemical, the first step in the post-application phase involves equipment cleansing, both internally and externally. An excellent choice for internal equipment cleansing involves utilizing some form of in-field rinse system. This type of system internally washes the equipment, then this material is re-applied over the crops without exceeding the recommended label rates. External equipment cleansing needs to take place in a covered rinse pad facility which provides a means of collecting and storing all rinse water. Additionally, all chemical mixing should take place in this facility so as to contain any spills. Ideally, all of the pesticide-laden wastewater collected from this rinse pad facility should then be pumped to a proper wastewater disposal system.

Although good management minimizes the amount of waste through efficient storage, mixing, and use, it is unavoidable that some waste will be produced. The problem then becomes one of disposing of these unwanted residuals in a manner which is both environmentally sound and economically feasible (Yoder, 1992, Wentz, 1989, and Seiber, 1992).

APPROACH

In the early 1990's the University of Tennessee Experiment Station farm superintendents solicited help in addressing their ever-growing problem of and concern with properly dealing with their residual pesticide rinsate waste material. This research initiative evolved from and is the direct result of the need to address their particular problem. Our approach and philosophy in dealing with this problem can be broken down into four distinct steps:

1) to intelligently address their problem through a thorough understanding of not only the waste itself, but also of the currently available disposal options/methods;
2) to choose the available technology deemed the best;
3) to investigate ways of optimizing the chosen disposal option;
4) to install pilot- and full-scale units for use on the experiment station farms.

This manuscript will follow this outline, and the thrust of this initial study will revolve around laboratory research efforts to optimize the chosen approach.

CHAPTER II:

BACKGROUND

Since liquid waste constitutes a large portion of the pesticide waste stream, one important but often overlooked aspect of any comprehensive pesticide management strategy is the proper treatment/disposal of all contaminated waste solutions. Before properly addressing this issue, one must have a thorough understanding of this type of waste. Two questions come to mind: what is it, and is it regulated?

RINSATE PRODUCTION

The Midwest Plan Service (MWPS, 1991) describes rinsates as water, and sometimes solids, contaminated with pesticides or fertilizers of relatively low concentrations (i.e., less than field strength application rates). Rinsate comes from several sources, including:

- precipitation-induced runoff from a mixing/loading pad,
- wash water collected from the rinsing of mixing/loading pad,
- debris collected in the sump of the mixing/loading pad,
- wash water collected from both internal and external spray equipment cleaning, and
- spills.

The majority of rinsate is produced through the equipment cleaning process. In general, equipment tanks, hoses, pumps, booms, nozzles, and exterior surfaces will contain

pesticide residue which needs to be removed when changing from one chemical to another. Seiber (1992) notes that this is critical if changing to different types of chemicals (i.e., herbicides, insecticides, fungicides, or fertilizers), or if changing from chemicals not registered for use on a particular crop being sprayed. This is a very common occurrence, since the majority of farmers rely on limited equipment for a variety of application needs. This washwater typically consists of a dilute pesticide solution along with adjuvants, dirt, oil, and miscellaneous debris.

These rinsates constitute a large volume of material. Heacox (1991) states that average-sized applicators can easily produce 3785-15140 liters [1000-4000 gallons] of mixed pesticides and rinsates during a normal cropping year. In Tennessee, both the Knoxville and Highland Rim Experiment Station farms of The University of Tennessee produce approximately 3785-5678 liters [1000-1500 gallons] of pesticide-laden waste per year (Yoder, 1992). Estimates reported by Taylor et al. (1988) indicate that a typical custom applicator in Illinois is capable of generating in excess of 41,635 liters [11,000 gallons] of contaminated rinsewater during a single spraying season.

Much of the literature refers to these wastewaters as "dilute pesticide solutions." Seiber (1988 and 1992) gives some insight into what is meant by dilute. Considering that a typical tank mix concentration is roughly 10,000 ppm of active ingredient, that 3.8-30.3 liters [1-8 gallons] of unused material remains in the tank after application, and that 38-303 liters [10-80 gallons] of water are used to flush this residue out of the spraying system, he concludes that typical washwaters will contain approximately 100-1000 ppm of pesticide

active ingredient. This is consistent with MWPS recommendations of using a 10:1 ratio of fresh water to field-strength pesticide for adequate rinsing of spray equipment, thus diluting rinsates to about 10% of field strength (MWPS, 1991). Additional pad rinse waters and precipitation-induced runoff waters will further dilute this material, perhaps down to the 10-100 ppm levels.

REGULATORY ISSUES

As with the treatment and/or disposal of any potentially hazardous waste, it must first be determined if these pesticide waste solutions are regulated under the Resource Conservation and Recovery Act (RCRA). The current status of these materials as hazardous waste is somewhat confusing.

Definition of a hazardous waste

According to Wentz (1989), in the RCRA legislation of 1976 the U.S. Congress defined a hazardous waste as

> "a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may (1) cause, or significantly contribute to, an increase in mortality or an increase in serious irreversible or incapacitating reversible illness or (2) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported or disposed of or otherwise managed."

Wentz (1989) points out that while this definition refers to "solids," it has been interpreted to include semisolids, liquids, and contained gases as well. Although Congress defined the

term "hazardous waste" in RCRA, it was left up to the EPA to develop regulations actually identifying those substances deemed to be hazardous wastes. As specified in the 1993 U.S. code of federal regulations (40CFR parts 260-299), the EPA defined a waste to be hazardous if it meets any of the following criteria:

- is a substance that is not excluded from regulation under RCRA §261.4(b)
- exhibits characteristics of ignitability, corrosivity, reactivity, and/or toxicity as outlined in part 261, subpart C
- is a listed waste as outlined in part 261, subpart D
- is a mixture containing a listed hazardous waste

There are over 20,000 different pesticide products currently produced (Ware, 1994). While the vast majority of technical grade agricultural chemicals are not toxic enough to be classified as hazardous, some are and can be found on lists outlined in the RCRA regulations. Both Ehart (1988) and Krueger (1988) provide tables of numerous pesticide active ingredients and inert ingredients which are listed RCRA hazardous wastes. Specific agricultural chemicals regulated by the EPA (under the RCRA legislation) generally exhibit the characteristic of toxicity. From discussions with Miller (1994), he points out that any waste is considered hazardous due to toxicity when: (1) it is fatal to humans at low doses, or (2) the LD_{50} (oral rat) $\leq$ 50 mg/kg, or (3) LD_{50} (dermal rabbit) $\leq$ 200 mg/kg. LD_{50} means median lethal dose, or the dosage level at which 50 percent of the subjects given a substance die (Wentz, 1989). For a comprehensive listing of the LD_{50}'s of specific pesticide chemicals, consult the appendices of Ware (1994).

As pointed out by Davis (1992), one must consider inert as well as active ingredients when determining if a particular crop protection chemical is regulated as a hazardous

waste. He illustrates this point by comparing two common herbicides (2, 4-D and atrazine). The active ingredient of 2, 4-D has been identified by the EPA as a toxic listed hazardous waste. On the other hand, technical grade atrazine is not regulated, but formaldehyde, which is an inert ingredient of some atrazine formulations, is a listed hazardous waste. Therefore, atrazine formulations containing formaldehyde as an inert ingredient are regarded as hazardous wastes due to the mixture rule outlined above. Thus, wastes generated from the use of both of these herbicides are regarded as hazardous and are subject to RCRA regulations, although for different components (Davis, 1992).

According to Wentz (1989), it is important to realize that the responsibility of determining if a particular waste is hazardous falls on the generators. They must either test their waste using standard methods (approved by EPA), or have sufficient knowledge about their waste to assess whether it exhibits any of the characteristics used to define a hazardous waste.

Hazardous waste generators

The EPA classifies hazardous waste generators into three categories: 1) conditionally exempt small quantity generators, 2) small quantity generators (SQG's), and 3) "generators." As can be seen in Table 1, conditionally exempt SQG's include those who produce less than 100 kg [221 lb.]of hazardous waste (or < 1 kg[2.2 lb.] of acutely hazardous waste) at a site per month or who accumulate less than 1000 kg [2205 lb.] of hazardous waste (or < 1 kg [2.2 lb.]of acutely hazardous waste) at any one time (Wentz,

Table 1. Matrix listing the criteria defining the various types of hazardous waste generators.

Waste Type	Exempt SQG	SQG	Generator
Acutely hazardous waste	0 - 1 kg/mo	0 - 1 kg/mo	> 1 kg/mo
Acutely hazardous residues or contaminated soil	0 - 100 kg/mo	0 - 100 kg/mo	> 100 kg/mo
Hazardous waste	< 100 kg/mo	100 - 1000 kg/mo	> 1000 kg/mo
Accumulation limits:			
1) Quantity	1000 kg	6000 kg	no limits
2) Time period	no limit	180 days	90 days

Source: Miller (1994)

1989). SQG's include those who produce between 100 and 1000 kg [221 and 2205 lb.] of hazardous waste per month, while "generators" are those producing in excess of 1000 kg [2205 lb.] of hazardous waste.

According to §262.34 of 40CFR (1993), a SQG may accumulate hazardous waste on-site for up to 180 days (270 days if the waste must be transported over a distance of 200 miles for off-site treatment, storage or disposal) without a permit or without having interim status, provided that the accumulated quantity never exceeds 6000 kg [13,230 lb.]. On the other hand, "generators" may accumulate hazardous waste on-site for up to 90 days without a permit or without having interim status, provided that the "generator" complies with all necessary requirements outlined in §262.34. If any of these accumulation times are exceeded (without a granted extension) the "generator's" status is changed to that of an operator of a storage facility and is thus subject to a completely different set of

requirements and regulations.

Triple rinse process

Although we are only interested in the liquid waste stream, it is necessary to briefly mention regulations regarding the solid waste stream. As alluded to previously, solid waste generated in the use of these products is made up of the leftover containers, the vast majority of which are empty plastic jugs. Once the original contents have been removed, what the user does next determines whether the containers are considered hazardous waste and regulated under RCRA.

The industry standard, the label advisories, and RCRA rules all point to the triple rinse process as the proper means of container treatment. These containers can be treated as nonhazardous waste and recycled, re-used or disposed of otherwise, so long as they meet RCRA's criteria of "empty." Under §261.7 of RCRA (CFR,1993b), a hazardous waste container is considered empty if it has been triple rinsed via a solvent capable of removing the commercial chemical product from the inside of the container (i.e., for pesticide containers, triple rinsing with water is the method of achievement). Although this eliminates the containers from hazardous waste consideration, the rinsewaters now become hazardous pesticide solutions. This same triple rinse process applies to all other pesticide containers, such as mixing tanks. Thus, one can see that this triple rinse process can be a major contributor to the liquid waste stream.

Exemption

Currently, farmers are treated differently than other generators of hazardous waste materials. In the 1993 revision of RCRA, Subpart G of 40 CFR262 (i.e., §262.70) states that a farmer is not required to comply with federal hazardous waste regulations provided all empty pesticide containers are triple rinsed and all pesticide residues are disposed of on his own property in accordance with disposal instructions on the label. However, Krueger (1988) points out that commercial applicators do not enjoy the luxury of this exemption. They must comply with all RCRA regulations as necessary.

While on the surface this exemption appears favorable for farmers, closer inspection reveals some limitations. In many instances, disposal instructions printed on container labels are lacking. Although they generally provide adequate information concerning the solid wastes (i.e., empty containers), guidance concerning the actual pesticide waste is usually insufficient. In such cases, it may be necessary to obtain professional technical assistance. Krueger (1988) brings to light another concern stating that this exemption is quite narrow and quite specific. Excess tank mix and rinsates may be applied over an area allowed by label directions (such as the margins of the field where the chemical was sprayed) or recycled as dilutant in future tank mixes. However, it does not mean that an applicator can dump or bury these pesticide-laden wastes anywhere on his property. In an additional note, the EPA reclassified pesticide rinsewaters and rinsates in 1990. Noyes (1991) points out that pesticide rinsewater and rinsate which is separated and identified is not considered a hazardous waste by the EPA, and can be stored

indefinitely. However, mixed or combined rinsates that are not identifiable are considered hazardous wastes by the EPA and must be legally disposed of within 90 days.

Violation penalty policy

Except for small quantities as permitted by federal, state and local regulations, it is illegal to dispose of any pesticide-related waste via open dumping or burning. Further, the MWPS (1991) states that "no pesticide or pesticide-related waste can be disposed or stored in such a manner that it may contaminate food, feed, or food and feed packaging materials." These regulations are issued under the authority of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), and are subject to penalty violations as with any other provision of federal law. As reported in the MWPS (1991), FIFRA violations by private and commercial applicators are punishable by fines reaching $1000 and $5000, respectively, per offense. Additionally, "per offense" could conceivably be interpreted as each illegally disposed pesticide container, for example.

Also, violations of hazardous waste regulations are subject to penalties established under RCRA and enforced by EPA. The RCRA penalty policy is designed in such a way that penalty amounts reflect the severity of the violations (Hill, 1988). A 3 x 3 matrix (see Table 2) is initially used for determination of penalty amounts, and then it may be adjusted based upon the following:

- economic benefit derived from non-compliance
- good faith efforts to comply
- degree of willfulness and/or negligence
- history of non-compliance

- ability to pay
- other factors

Table 2. Penalty Policy Matrix. All penalty amounts are per day violations.

Potential for Harm	Extent of Deviation from Requirement		
	Major	Moderate	Minor
Major	$25,000 to $20,000	$19,999 to $15,000	$14,999 to $11,000
Moderate	$10,000 to $8,000	$7,999 to $5,000	$4,999 to $3,000
Minor	$2,999 to $1,500	$1,499 to $500	$499 to $100

Source: Hill (1988)

Similar to the FIFRA policy, RCRA violation penalty amounts are considered on a per day of non-compliance basis. Hill (1988) notes, as seen in the matrix, that the maximum penalty authorized by RCRA is $25,000/day/violation. Davis (1992) discovered that these offenses are also punishable by a maximum five year prison sentence or both. He further notes that non-compliance with hazardous waste transportation laws are punishable by civil penalty fines up to $10,000 per violation per day.

Confusion

Are farmers and applicators hazardous waste generators? This is no easy question to answer. As previously demonstrated, there is a lot of "gray area" in the interpretation of whether pesticide-contaminated wastewaters are hazardous. The RCRA regulations appear to contradict themselves at times, and therein lies much of the confusion. The point made above is simply that the solutions are not hazardous except under two conditions:

1) if an applicator generates more than 114-L [30-gal.] per month above and beyond that which can be re-applied to the land in accordance with label recommended rates, or 2) if an applicator ships the waste solution off-site for treatment and disposal instead of disposing of it on his own land. It appears that the manner in which a farmer chooses to handle these waste solutions will alleviate this confusion and directly determine whether the wastes are considered hazardous and applicable to RCRA regulations.

TECHNOLOGY OVERVIEW

Now that one has a clear understanding of this waste material, what should be done with it? The treatment/disposal technologies investigated in the literature are targeted toward applicators unable to comply with the exemption conditions previously outlined. Currently, there are numerous options available for the proper disposal of these waste solutions. Of those, there are varying ranges of complexity and cost. However, before addressing these options more closely, it is interesting to observe some of the most commonly used disposal practices of today's farmers, whether good or not. In a waste assessment survey of Nebraska farmsteads, Reed et al. (1994) indicate that the most common practice of disposing of leftover rinsates is via re-application on fields just sprayed. This is in contrast to earlier reports cited by the authors, which indicated that storage for future use was the preferred method of disposal. Other less common disposal methods for the unused chemicals included such practices as: 1) burning, 2) returning to the dealer, 3) selling to neighbors, friends, or relatives, 3) diluting with water and spraying

on non-crop land or idle acres, 4) letting commercial applicators take care of it, 5) spraying along fence lines and ditches, 6) following label recommendations, 7) pouring on the ground away from farm buildings/houses, and 8) hauling it to a landfill (Reed et al., 1994).

The manner in which an applicator of crop protection chemicals chooses to handle the generated waste solutions can be categorized as either disposal practices or treatment options. This is an important distinction. Treatment options either destroy wastes or render them harmless to the environment (Wentz, 1989), while disposal practices do not actually destroy or eliminate the waste. Disposal practices generally include recovery (recycling) processes, waste minimization practices, or handling of the material such that it is basically "out-of-sight, out-of-mind." Treatment options applicable to pesticide-laden wastes can further be classified as physical, chemical, or biological in nature (Seiber, 1988 and Wentz, 1989), or some combination thereof. Table 3 lists the rinsate disposal practices and treatment technologies overviewed in this section and gives a brief summation of thier strengths and weaknesses. A more in-depth discussion of each of these methods follows the table.

Table 3. Overview of pesticide rinsate disposal practices and treatment options outlined in this chapter.

Treatment/Disposal Technologies	Advantages	Disadvantages
Disposal practices:		
1. Do nothing approach	quick and easy	illegal and environmentally unfriendly
2. Leach fields	low cost; readily installed with minimal complications	not isolated from groundwater; potential contamination
3. Treat as hazardous waste	legal: complies with RCRA regulations	extensive compliance requirements; costly; generally requires technical assistance
4. Rinsate recycling (collection/storage)	widely used; if properly managed is environmentally acceptable	requires careful mgmt. and modern equipment and facilities; potential FIFRA conflicts; only a volume reduction method - residual requires further disposal
5. In-field rinse system	excellent volume reduction technique if carried out properly; fairly simple and inexpensive; most advantageous in conjunction with another disposal method	some residual material requiring further disposal
Treatment options:		
1. Evaporators	simple concept; low cost; excellent volume reduction technique	residual material requiring further disposal; potential air contamination via volatilization
2. Activated carbon filtration	well known and understood process; simple concept; fairly low cost; excellent decontamination efficiency; compliance of RCRA if managed properly	only a volume reduction technique; residual waste stream requiring further disposal; may require additional pre-treatment steps (coagulation, flocculation)
3. Biologically-based sorbents	comparable removal efficiencies to activated carbon; major appeal lies in potential to biodegrade; low cost	still in research and development stage; residual waste stream, but easier to handle; some materials not yet commercially available

Treatment/Disposal Technologies	Advantages	Disadvantages
4. Ozonation and/or ultraviolet irradiation	both greatly detoxify waste into a more environmentally acceptable residual; commercially available; potentially mobile; easily operated and highly versatile	fairly high investment cost; still produces a residual waste stream requiring further disposal
5. Photolysis	complete mineralization of waste yielding simple products of reaction	research stage only
6. Hydrolysis and other simple chemical reactions	simple chemical reagents for waste detoxicant; fairly good neutralization of pesticides	only in research stages
7. Microwave plasma destruction	high levels of destruction with simple products of reaction	very technical and extremely expensive
8. Wet air oxidation	high destruction levels	very complex and technical; not extensively evaluated for pesticide wastes; extremely high cost
9. Molten salt process	excellent destruction levels	fairly exotic, technical, and complex process; experimental stages only; expected high investment cost
10. Activated sludge treatment system	complete destruction of waste is possible	developed for industrial pesticide manufactures; some pre-treatment is necessary; residual sludge; requires intensive management and sampling
11. Trickling filter	can handle highly toxic wastes; effective on a variety of compounds without future disposal of residuals; technology is transferrable to small above-ground units	initially developed for industrial use; some pre-treatment is necessary; costly to build and maintain; requires intensive management and monitoring
12. Enzymatic methods	greatly accelerates detoxification (promotes hydrolysis) yielding residuals more susceptible to further degradation processes; excellent potential when used in conjunction with other methods	does not completely destroy waste, therefore a residual material; this biotechnology method is still in the research and development stages
13. Microbial acclimation and genetic engineering	promising for enhanced degradation when utilized with other processes	research stage only; uncertainties surrounding its application to pesticide mixtures

Treatment/Disposal Technologies	Advantages	Disadvantages
14. Composting	early indications of good destruction of a limited number of compounds; potentially useful as a follow-up treatment process for other methods	somewhat inconclusive, thus more research needed especially regarding pesticide mixtures and a wider variety of compounds; possibility of residual waste stream
15. Double stage concentration/degradation system	dual phase concept; combination of biologically based sorbents and composting; potential for yielding no residual waste stream	although good early indications from individual stage studies, not yet incorporated into and studied as one complete process; further research needed on wider variety of compounds and on mixtures
16. Single stage evaporation/degradation process	employs both volume reduction and degradation concepts into a single process; simple concept; environmentally friendly; requires minimal management and operational skills; no residual waste stream; realistically transferrable to farm-scale operations at reasonable costs; early indications of excellent performance of the system	potential regulatory issue concerns, although may be circumvented

Disposal practices

Do Nothing Approach

In the past, pesticide users had no reasonably-priced option available to them for the safe disposal of their pesticide waste solutions. This often led to the improper and illegal dumping of the wastes along fence rows, gravel roads, or simply "out back." Another common practice in the past was to wash the excess spray material and rinsate down the drain and into the sewer. In some cases this material was allowed to simply run

off into adjacent ditches and drainageways. Still other applicators dumped their pesticide wastes into soil-lined pits such as those used for septic tank effluent (Brown, 1986a and 1986b). However, these methods are no longer acceptable because of the potentially adverse effects they have on water resources. Hopefully, today's farmers are more environmentally conscientious than this. In addition, it is likely to only be a matter of time before state or federal regulatory agencies require greater accountability in the use of crop protection chemicals and in the disposal of their associated wastewater.

Leach Fields

This technology is widely used by small fruit farms in the state of New York. These leach lines were installed as part of Chemical Control Centers (CCC) developed in conjunction with the United States Department of Agriculture Soil Conservation Service (USDA/SCS). In addition to the leach lines, these facilities consisted of a water source, a catch basin, and a pesticide storage building (Spittler et al., 1984). Seiber (1988) describes this concept as lines embedded in the soil to distribute the collected pesticide-laden water back to the field for subsequent weathering. Generally, the leach lines are entrenched two to four feet below the soil surface and within the field operations area (either between the orchard rows or along the orchard border). This technology is of low cost to the operator and can be ready for use within a couple of weeks. However, the major drawback of this approach is potential contamination of water resources since the system is not isolated from groundwater.

Due to concerns voiced by the New York State Department of Environmental

Conservation, Spittler et al. (1984) initiated a study to evaluate the environmental impact of these leach fields. Water and soil samples were taken from three CCC facilities and analyzed for six pesticides. Their research indicated that the pesticides had not leached into the groundwater; in fact, the chemicals had traveled less than 46 cm [18 inches] from the leach lines during five years of operation. However, the author suggests that a long-term, follow-up study would be useful for further monitoring of groundwater. Additional soil analysis and anthropod population monitoring revealed no adverse environmental effects. Consequently, the State of New York ruled these installations as "normal agricultural operations" and not subject to regulations and permits required of "classified point-sources polluters" (Spittler et al., 1984).

Treat as Hazardous Waste

On the expensive end of the scale, another option is to collect the pesticide waste solutions for shipment to EPA-approved disposal facilities. There are numerous drawbacks to this option, the most notable being compliance requirements and cost. First, pesticide users who choose to handle their waste in this manner must comply with all local, state, and federal hazardous waste regulations. Compliance with these can be quite extensive. Table 4 summarizes the requirements and lists other useful regulation information. There are five major RCRA requirements which must be met by hazardous waste generators/transporters.

Table 4. EPA and DOT Hazardous Waste Transportation Regulations

Required of	Agency	Code of Federal Regulations
Generator/shipper		
1. Determine if waste is hazardous according to EPA listing criteria	EPA	40 CFR 261 and 262.11
2. Notify EPA and obtain I.D. number; determine that transporter and designated treatment, storage, or disposal facility have I.D. numbers	EPA	40 CFR 262.12
3. Identify and classify waste according to DOT Hazardous Materials Table and determine if waste is prohibited from certain modes of transport	DOT	49 CFR 172.01
4. Comply with all packaging, marking, and labeling requirements	EPA	40 CFR 262.32 (b),
	DOT	49 CFR 173, 49 CFR 172, subpart D, and 49 CFR 172, subpart E
5. Determine whether additional shipping requirements must be met for the mode of transport used	DOT	49 CFR 174-177
6. Complete a hazardous waste manifest	EPA	40 CFR 262, subpart B
7. Provide additional placards to transporter	DOT	49 CFR 172, subpart F
8. Comply with record-keeping and reporting requirements	EPA	40 CFR 262, subpart D
Transporter/carrier		
1. Notify EPA and obtain I.D. number	EPA	40 CFR 263.11
2. Verify that shipment is properly identified, packaged, marked, and labeled and is not leaking or damaged	DOT	49 CFR 174-177
3. Apply appropriate placards	DOT	49 CFR 172.506
4. Comply with all manifest requirements (e.g., sign the manifest, carry the manifest, and obtain signature from next transporter or owner/operator of designated facility)	EPA	40 CFR 263.20
5. Comply with record-keeping and reporting requirements	EPA	40 CFR 263.20
6. Take appropriate action (including cleanup) in the event of a discharge and comply with the DOT incident reporting requirements	EPA DOT	40 CFR 263.30-31 49 CFR 171.15-17

Source: Wentz, 1989. Provided by the U.S. Environmental Protection Agency.

A generator's first requirement is to determine whether the waste is classified as a regulated hazardous waste. Hill (1988) states that if testing is required for this determination, many waste pesticide generators lack the necessary training, and a higher level of expertise will be needed. This testing can be quite burdensome and costly. Once a generator has determined that the waste is regulated under RCRA, he must notify the EPA and obtain an EPA Identification Number. The third step for generators is fulfillment of pre-transport requirements. These involve standards for packaging, labeling, marking, placarding and accumulation time. All packaging, labeling and placarding must additionally be approved by the Department of Transportation (DOT), including the use of special DOT-approved containers. The EPA also mandated that generators are required to mark each container of 417 liters [110 gallons] or less with the following specific hazardous waste statement (completed in full)(Hill, 1988):

> HAZARDOUS WASTE: Federal Law Prohibits Improper Disposal
> If found, contact the nearest police or public safety authority or the U.S. Environmental Protection Agency.
> Generator's Name and Address _____
> Manifest Document Number_____

For many, Hill (1988) suggests that the use of specialized transporters experienced in farm waste may be beneficial.

Compliance with the manifest system is the fourth requirement and one that Hill (1988) feels to be the most important aspect of a generator's responsibilities. The Uniform Hazardous Waste Manifest (UHWM) is a form containing information about a specific hazardous waste. This manifest must accompany the material during shipment

from the generation point to the ultimate destination (i.e., from "cradle to grave"). Further, it is the responsibility of the generator to originate the manifest forms and secure all appropriate signatures (Wentz, 1989).

The fifth and final RCRA requirement involves proper record keeping and reporting. Generators are responsible for retaining a copy of each signed manifest for a period of three years, whether or not a signed copy is returned to him by the designated treatment, storage, or disposal facility. Similarly, records of all test results, waste analyses, and all other EPA-submitted reports must be kept for a period of three years. Finally, the EPA requires all generators who ship their waste off-site to submit biennial reports to the Regional Administrator by March 1 of every even-numbered year (Wentz, 1989 and Hill, 1988).

As Davis (1992) points out, cost of disposal in this manner will vary depending on the waste, the distance to disposal site, and method of disposal. Generally, generators of pesticide wastes have two EPA-approved disposal options: 1) in a RCRA-approved landfill, or 2) in a RCRA-approved incinerator. Neither option is readily available or easily accessible. In a survey of Nebraska farmers, Reed et al. (1994) found that the majority of farmers did not know the location of nor distance to the nearest permitted landfill capable of accepting pesticide-laden wastes. Further, many were uncertain if their county sanitary landfill accepted these types of wastes. Philipbar (1988) indicates that the 1984 Hazardous and Solid Waste Amendments of RCRA require that most regulated pesticide wastes be disposed of via RCRA-approved incinerators. According to him, there are only five major

commercial incinerators in the U.S. approved to incinerate pesticide wastes. Thus, most of these wastes must be transported long distances for disposal. Although incineration typically achieves 99.99% destruction efficiencies (Oberacker, 1988 and Philipbar, 1988), there are several drawbacks aside from accessibility. Certain pesticide formulations may contain various amounts of heavy metals or halides, which would preclude incineration unless either suitable pre-treatment steps are employed or effective pollution control devices are installed in the incinerator (Oberacker, 1988). Additionally, Davis (1992) discovered that incineration usually costs $350 per 208-L [55-gal.] barrel, excluding transportation. He further cites reports indicating shipping costs via commercial/licensed hazardous materials handlers to range as high as $1000-$3000 per 208-L [55-gal.] drum. Brown (1986a and 1986b), on the other hand, reports typical shipping costs to be about $250 per barrel. On a per distance basis, Philipbar (1988) states transportation costs for shipping truckloads of hazardous wastes to be about $2.75 to $3.00 per loaded mile and rail shipments to be about $1.00 per loaded mile.

Rinsate Recycling (Collection and Storage)

One of the most widely used and environmentally acceptable methods of disposal is to collect the rinsewater and store it in holding tanks to be used as make-up water for future tank mixes. Previous applications of this method (Rester, 1988 and Taylor et al. 1988) usually employed the use of a concrete wash pad with a sump for collection of these washwaters. The collected wastewater is then pumped from the sump to storage tanks for later use (see Figure 1 for conceptual view of a typical facility). This approach may have

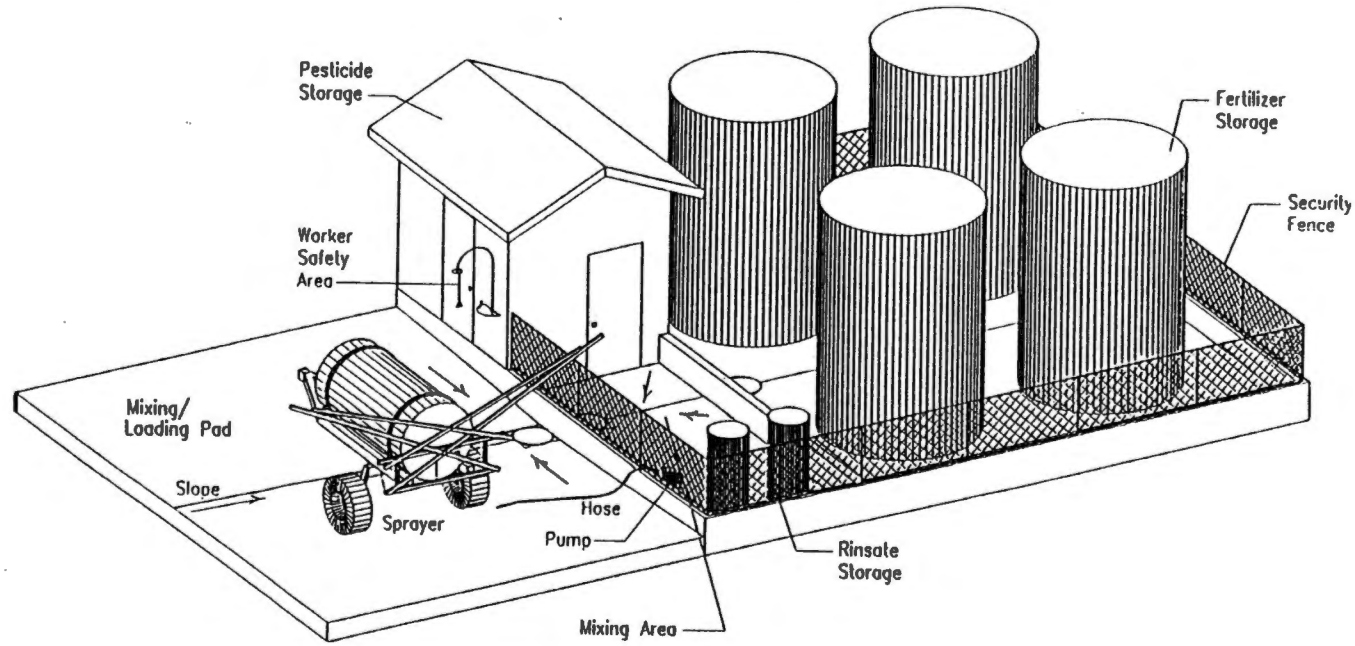


Figure 1. Typical medium sized pesticide storage, containment, and mixing/loading facility perspective (Mid West Plan Service, 1991).

limited utility for all but large operations, as the initial investment can be expensive and require a complex system of tanks and pumps. Similar facilities in Louisiana and Illinois both reported construction costs in the range of $10,000 to $12,000 (Rester, 1988 and Taylor et al., 1988).

Though attractive, this approach involves many considerations and several limitations. The biggest concern revolves around potential conflicts with FIFRA with respect to 1) improper tank mixing and 2) application of chemicals to non-target areas (MWPS, 1991). Thus, it is extremely important that the pesticide-laden washwater is segregated and stored in separate, well-identified tanks to avoid label violation, incompatible mixtures and potential crop damage due to phytotoxicity (Brown, 1986a and 1986b; Rester, 1988; Taylor et al., 1988). However, in situations where applicators apply pesticides to a limited number of crops there are times in which the chemicals are registered for use on several crops, thus negating this concern. Areas such as the Midwest are well suited to this process, since only a few crops are primarily grown. As the variety of crops increase, however, the feasibility of rinsate recycling diminishes (Taylor et al., 1988).

Additional considerations include the need to filter the wastewater before storage to remove foreign materials introduced in equipment rinsing, and the danger of microbial growth in the tanks limiting storage time (Brown, 1986a and 1986b). It is best to only store this material when there is a known future application in which this wastewater can be utilized as a dilutant and promptly applied (MWPS, 1991 and Rester, 1988). Ideally,

Rester (1988) suggests that this wastewater should be stored no longer than about two weeks. It is further recommended by Taylor et al. (1988) that the reuse of this rinsewater be limited to preplant or preemergence applications in order to better expose the pesticide to the beneficial degradation processes found in soil. However, the rate of reuse should be restricted to no more than 5% (by volume) of the new spray mixture to prevent overapplication to the extent of hindering these soil reactions. Brown (1986a and 1986b) states that the amount of residue remaining in the rinsate is unknown, and that this uncertainty affects the accuracy of the formulation of new solution. However, at a 5% blend rate, studies indicate that the rinsate will only slightly influence (additional 2% maximum) the total concentration of active ingredient in the new tank mix (Rester, 1988; Taylor et al., 1988; Noyes, 1991). This falls well within the allowable label rates for most crop protection chemicals when used alone.

It is also important to realize that this approach is actually only a volume reduction method, since it does not completely get rid of all the waste. The remaining material still requires further disposal. Proper rinsate re-use only utilizes a small portion of the stored washwater. Additionally, the sludge and other debris collected in the sump is laden with pesticide residue and may be considered hazardous waste (MWPS, 1991) and subject to RCRA regulations.

In-field Rinse System

Hart et al. (1991) feel that a major concern associated with conventional pesticide application systems is the cleaning of the tank and associated sprayer components, and

dealing with the subsequent rinsates. A partial solution to the problem of proper rinsate disposal is to reduce the volume of material remaining after application. A method suggested by the authors for achieving this goal is to rinse chemical application equipment in the field. The studies point out that the resulting diluted spray material can then be re-applied over the crop so long as the total application rate does not exceed those recommended and authorized by the label (Brown, 1986a and 1986b; Noyes, 1992; MWPS, 1991; Wills and Burcham, 1992; Hart et al., 1991). Both Davis (1992) and Hart et al. (1991) cite several earlier researchers and their investigations into in-field sprayer rinse systems. These early designs, although promising, revealed several limitations. In addition to inadequate components, Hart et al. (1991) felt that the major drawback to these early designs was the potential for the operator to come into direct contact with pesticide residues during rinsing. They further suggest that an improved design would encompass automatic operation and minimal applicator exposure.

Davis (1992) set out to accomplish this goal. The result was the development and evaluation of the Tennessee In-Field Sprayer Mounted Rinse System (TISMRS). The TISMRS incorporates a permanently-mounted rinsing device and associated plumbing, which greatly improved early design attempts by limiting operator exposure. The TISMRS is very economical and easily added to most existing sprayer systems. Wills and Burcham (1992) report that the rinse tank and most other necessary plumbing components can be purchased from local sources at a cost of about $200. A special tank rinsing nozzle can be purchased from an agricultural spray product supplier for roughly $180. A

schematic of a typical in-field sprayer mounted rinse system can be viewed in Figure 2. The authors suggest installing a funnel-bottom type tank sized at 10% of the primary sprayer tank capacity or 57 liters [15 gallons], whichever is larger. Further, the authors provide detailed installation procedures for this system. In his evaluation of a TISMRS prototype, Davis (1992) obtained results consistent with label advisories, industry standards and EPA's requirement of triple rinsing pesticide containers as adequate cleansing. These findings were comparable to earlier studies, which indicated that as the number of rinse sequences increased, the rinsate concentration decreased (Trask, 1988). Davis (1992) noted that other than rinse sequence and rinsing volume, little else (including operating pressure, tank geometry, or commercially available nozzle types) significantly impacted the system's performance.

As pointed out by Wills and Burcham (1992), it is important to realize that an in-field rinse system is not a "cure-all" remedy for the problem of pesticide-laden wastewater disposal. It is only a partial solution in that it has the potential to greatly reduce the volume of material generated; nonetheless, some waste will remain, requiring further disposal. The in-field rinse system does not address, for instance, the issue of external equipment washing and the associated waste mixture. However, it is most advantageous when incorporated into a complete pesticide waste management strategy and used in conjunction with a complete pesticide handling facility.

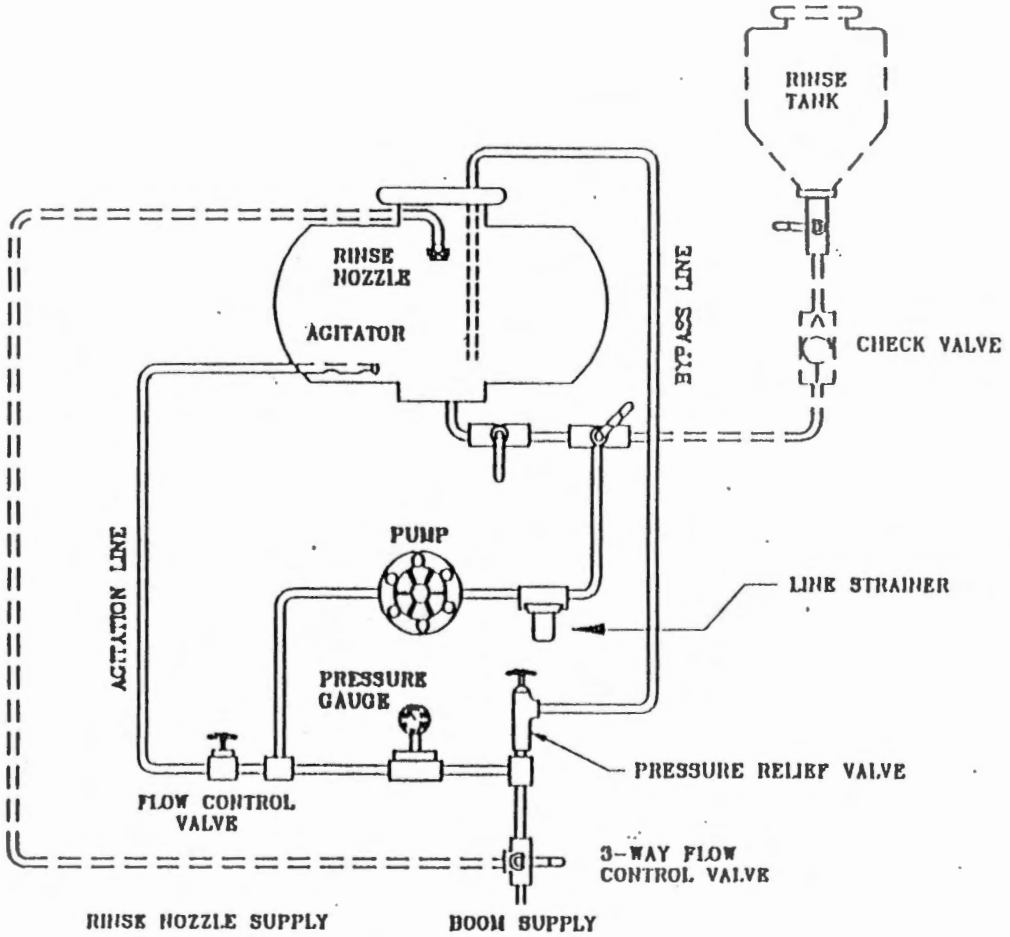


Figure 2. Schematic of a simplified in-field sprayer mounted rinse system. Dashed lines indicate additional components and plumbing required to modify a conventional sprayer (Hart et al., 1991).

Treatment options

Physical Treatment

Physical treatment options generally involve some form of separation technique. Since it is usually a simple and inexpensive solution to a variety of waste management situations, Wentz (1989) feels that physical separation should be the first consideration anytime a waste contains both solids and liquids. Thus, many methods will utilize a separation technique in conjunction with one or more other processes to obtain a better quality treatment. Separation includes such techniques as screening, sedimentation and clarification, centrifugation, flotation, filtration, sorption, evaporation and distillation, stripping, and reverse osmosis. In terms of pesticides, physical treatments typically center around a concentration approach. This class of approach attempts to address the problem by reducing the volume of aqueous pesticide waste requiring further attention. In terms of economic efficiency, Yoder (1992) states that in addition to waste containment, waste volume reduction may provide the greatest cost savings and risk reductions. The importance of volume reduction techniques becomes apparent when considering the potential quantity of waste solutions produced by applicators, as outlined earlier. Most efforts in this type of disposal method center around either evaporation systems or sorption/filtration systems.

Evaporation systems

The former system includes such concepts as evaporation pits/ponds and commercially available evaporators. The basic principal behind these concepts is to reduce

the volume of rinsate waste by evaporating the water, resulting in a highly concentrated liquor along with any waste residue (Wentz, 1989 and Seiber, 1988). Design of an open evaporation pit is relatively simple. Egg et al. (1980) reports early uses of such pits in 1974 on the Texas High Plains for disposal of cattle dip solutions at feedlots. Construction of these facilities generally consists of either concrete pits or lined lagoons. Of the materials available for use as pit liners, Egg et al. (1980) suggest that reinforced concrete, although expensive, is likely the safest and most durable. They also report that several synthetic flexible membrane liners are available and should perform adequately. Unless proper precautions are undertaken, entry of rainfall and/or runoff could potentially hinder the system's effectiveness. This can be especially true in areas of high precipitation and low evaporation. However, Egg et al. (1980) addressed this issue by evaluating the impacts on evaporation rates of various types of roofing materials. They found that most roofing materials reduced overall evaporation rates by about 25%.

An off-shoot to this concept is the utilization of a commercially available evaporator. The University of Alabama at Huntsville, in conjunction with the Tennessee Valley Authority's National Fertilizer and Environmental Research Center, developed one such system to reduce the volume of rinsewater after collection. As reported by Heacox (1991), this flat-plate solar evaporator is simply a box constructed mainly of concrete, stainless steel and glass, measuring approximately 2.4 x 1.5 x 2.1 meters [8 x 5 x 7 feet]. As seen in Figure 3, it consists of a basin covered by a transparent lid. This lid emits solar radiation and restricts heat loss. It is tilted to not only help drain precipitation but also to

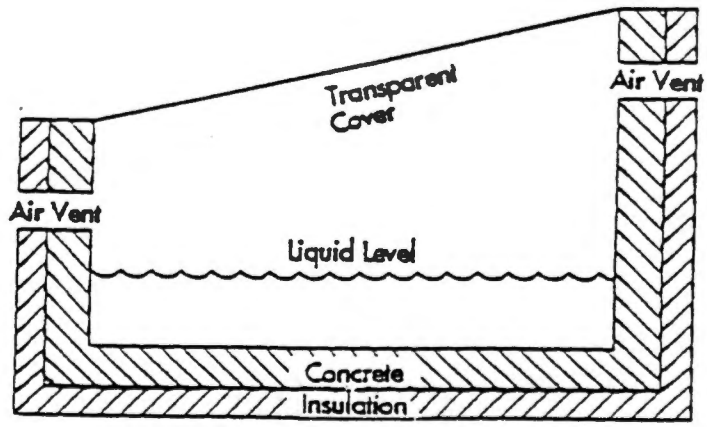


Figure 3. Simple solar evaporator concept (Heacox, 1991).

maximize the quantity of solar radiation. Furthermore, insulation is added to the basin in order to help retain collected energy and air vents facilitate the removal of vapors. This evaporator is well-suited for operations generating between 3785 and 15,140 liters [1000 and 4000 gallons] of rinsate per year at an investment of less than $4000. Once the majority of rinsewater has evaporated, the quantity of pesticide residue remaining can be determined, and the remaining material can be used in the next application (Heacox, 1991).

Robert Claunch (1988) reports a technology transfer concept with the capability of being successfully applied to agricultural chemical waste solutions. The toxic substance solvent evaporator (TSSE) was originally intended to help small quantity hazardous waste generators and is applicable to all chemical waste streams containing dilute quantities of toxic material. The TSSE utilizes a wick to adsorb the pesticide waste material onto a large surface area, thus accelerating evaporation and reducing the volume of waste material. Claunch (1988) further reports of a pilot unit TSSE operating in New Orleans for the purpose of collecting evaporation rate data. Although mechanical components can be added to facilitate evaporation, the basic system derives its energy from the sun and, according to the author, should be operable throughout the U.S. during the growing season. Due to the simplicity of this concept, he suggests supplying the applicator with a do-it-yourself kit to minimize costs.

Although these systems are generally simple concepts, cost little and provide an excellent means of reducing the volume of contaminated waste material, they have several drawbacks that may be of major concern. All of the above authors point out that the

residual material, although substantially less than original volume, would still require further disposal, usually regulated and expensive. Possible groundwater contamination resulting from container leaks is another major concern. In addition to double lining these containment facilities, monitoring wells will most likely need to be installed to insure no contamination of surrounding soil and water sources (Brown, 1986a and 1986b and Seiber, 1988). The costs associated with well installation can easily range in the thousands of dollars, not to mention the considerable expense incurred for routine sample collection and analysis which, according to Brown (1986a and 1986b) can easily cost upward of $500 per sample. Finally, there is a potential for air pollution via volatilization of these pesticide materials (MWPS, 1991). The escape of these airborne materials can also be quite odiferous (Seiber, 1988). Thus, Seiber feels that the negatives outweigh the positives unless progress is made toward developing degradation enhancements for these systems.

Adsorption/filtration systems

Wentz (1989) describes "sorption" as a commonly used term referring to both adsorption and absorption, because both may occur simultaneously in wastewater systems. He defines adsorption as the physical adhesion of molecules or particles to the surface of a solid adsorbent without a chemical reaction. Absorption, however, involves the penetration of the molecules/particles into the absorbent. A widely used treatment method for pesticide rinsates involves passing the solution through an adsorption medium, generally granulated activated carbon (GAC), to remove the pesticide residues from the

rinsewater (Brown, 1986a and 1986b and Dwinell, 1992). Both Dennis (1988) and Dwinell (1992) note that removal of organic chemicals from wastewater via GAC filtration is a well-known and understood phenomenon with broad applications as evidenced in its widespread use by various industries.

This concept is accomplished through adsorption of the pesticide constituents onto the actual carbon matrix. Since adsorption is a surface reaction, the effectiveness of GAC to remove these substances from wastewater is directly dependent upon its surface area (Wentz, 1989; Kobylinski et al., 1988; Dwinell, 1992). Kobylinski et al. (1988) describes numerous methods of introducing wastewater to the carbon media, including batch slurry and upflow or downflow through packed columns/beds. These can be either recirculating systems or plug flow type systems. According to Dwinell (1992) the critical factors in the design and operation of any GAC system are the adsorptive capacity of the carbon and the exposure time. The carbon has a finite adsorptive capacity, which once exceeded renders the system ineffective. Nye (1988) points to earlier studies on the evaluation of 30 classes of pesticides, generally finding that 100-300 mg of pesticide can be adsorbed onto a single gram of carbon. This capacity is influenced by the concentration and volume of pesticide rinsate treated. Basically, the higher the pesticide concentration in the waste stream, the smaller the amount of rinsate the system can successfully treat (Dwinell, 1992). This necessitates that the system be continually monitored and the carbon periodically replaced. The author states that this required testing and analysis is not only expensive, but is also of limited availability.

A CARBOLATOR 35B® recirculating carbon filtration unit was evaluated and reported on by Kobylinski et al. (1989) and Dennis (1988). The CARBOLATOR 35B® is a commercially available water purification unit from Sethco Corporation, and was modified by the authors in order to treat pesticide-contaminated wastewater. The unit consists of an 72-L [19-gal.] reinforced epoxy tank with an O-ring sealed lid, within which are placed two porous polypropylene bags of GAC. In a pilot-scale study, the authors recirculated a waste solution containing seven pesticides (i.e., baygon, dimethoste, diazinon, ronnel, malathion, dursban, and 2,4-D ester) through the unit. In their most stringent test, a 1514-L [400-gal.] batch of solution was formulated with a 100 ppm concentration of each active ingredient. All pesticide concentrations decreased exponentially with time, as was predicted mathematically. The results demonstrated an extraction efficiency of 94% or better for all seven chemicals. These efficiency factors were further validated through two separate field studies. After 24 hours of treatment, the authors reported that all pesticide in the effluent were below the limits of detection. In conclusion, the authors expressed that the CARBOLATOR 35B® system could provide an economical, dependable, and effective means for SQG's to treat their aqueous waste streams. Even with the necessary addition of an in-line filter for removal of suspended solids, the total cost of the system was reported to be around $3000 (1981 costs).

Several researchers have investigated the potential of installing an additional stage to the typical carbon adsorption process in order to enhance filtration. This second stage generally involves an additional pretreatment process such as flocculation, coagulation, or

sedimentation for the removal of suspended solids in the hope of eliminating potential clogging of the carbon charge. Sedimentation, as described by Wentz (1989), is a physical process whereby suspended solids are separated from liquids via gravitational settling. Flocculation and coagulation, on the other hand, are chemical treatment steps employed to enhance sedimentation in cases where the settling rates are too slow for effective clarification. Although related, these two chemical means of clarification are different. Coagulation, Wentz (1989) states, is the "addition and rapid mixing of a coagulant to neutralize charges and collapse the colloidal particles so they can agglomerate and settle." Common coagulants used include alum [$Al_2(SO_4)_3$], ferris chloride ($FeCl_3$), and ferris sulfate [$Fe_2(SO_4)_3$]. In some instances, water-soluble polymers may be more effective in the promotion of coagulation than are alum or iron salts.

These materials also promote flocculation under controlled pH conditions and gentle agitation. Large settable flocs are produced through the binding of agglomerated colloidal particles and the flocculation chemical. Wentz (1989) further indicates that pH, along with the dosage and nature of the coagulant, are the chief factors affecting these chemical treatment processes. In cases of insufficient alkalinity, lime or soda must be added to raise the pH level of the wastewater. Nye and Way (1988) report that the inability to flocculate the pesticide wastewater can be a major deterrent in the utilization of this important pre-treatment process. This problem can be attributed to the fact that most pesticide formulations include emulsion, organic solvents, or other compounds to enhance their mixability with water. These authors investigated this problem and concluded that

the use of ferric salts or aluminum followed by the addition of hydroxide yielded the most consistent results.

In two separate articles, Nye (1984 and 1988) reviewed the research activities of earlier scientists investigating multi-stage carbon adsorption processes. As seen in Figure 4, the pre-treatment step involved flocculation/coagulation and sedimentation of the contaminated solution, followed by passing the supernatant through columns of GAC. This system utilized a 208-liter [55-gallon] drum of flocculent capable of treating over 3785 liters [1000 gallons] of wastewater. Four 15.24 cm [6 in.] diameter, 1.22 m [4 ft.] long PVC columns containing approximately 200 lbs of GAC had the capacity of handling up to18,925 liters [5000 gallons] of rinsate. In one reported case, a mixture of five herbicides (trifluralin, alachlor, dinoseb, 2,4-D, and paraquat) was successfully treated by this system. At that time (early 1980's), the pesticide concentration in the effluent was reduced to below the detection limits of the Indiana State Chemist Office's pesticide residue lab. Nye (1988) further indicates that the system cost, excluding carbon, should typically run about $1000. Additionally, pre-treatment chemicals can be purchased for around 5¢ per liter [20¢ per gallon] of treated wastewater.

Dwinell (1992) reports another multi-stage carbon filtration system, this one commercially produced by Imperial Chemical Industries, Ltd. (ICI). The ICI system first utilizes a flocculation agent and then passes the contaminated solution through a sand filter and two carbon filters. This unit is designed to be portable and modular with the capabilities of treating discrete batches of about 1000 liters [265 gallons] of rinsate. A

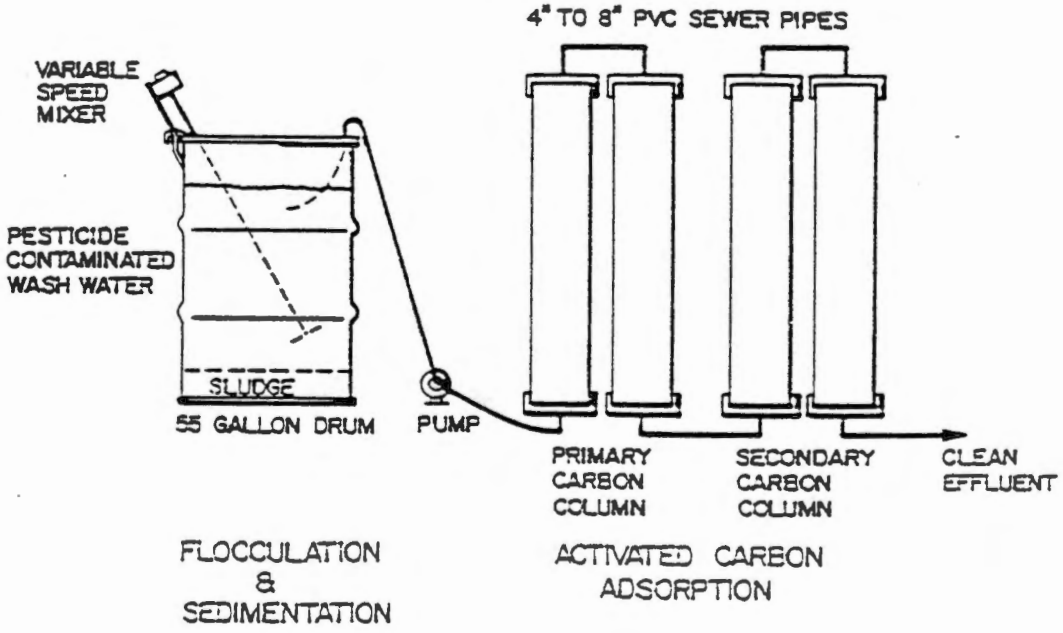


Figure 4. Multi-stage carbon adsorption process for the treatment of pesticide-contaminated wastewater. Pre-treatment step involves flocculation, coagulation and sedimentation of the contaminated material. After which, the supernatant is passed through columns of granular activated carbon (Nye, 1984).

dye is added to the flocculation step to serve as an indicator that the carbon charge has reached its capacity and requires exchanging. The treated effluent can either be re-used in subsequent cleaning operations, or discharged with a proper National Pollutant Discharge Elimination System (NPDES) permit. Capital costs can range anywhere from $20,000 to $50,000, which Dwinell (1992) feels can be considerably less than the fines and clean-up costs if this material is not properly managed.

The September 1992 issue of *Farm Chemicals* magazine reported yet another commercially available multiple-stage carbon-type treatment system. The SENTINEL® utilizes CARBO-FLO® technology developed by ICI more than 20 years ago. In addition to carbon filtration, the system incorporates a chemically-induced flocculation and settling process to remove suspended and dissolved organics. Davis (1992) reported a study which evaluated the SENTINEL® system and which revealed that the system removed virtually all of three pesticides (alachlor, atrazine, and permathrin) from wastewater. It further concluded that the system's efficiency was limited upon the chemical's active ingredient, formulation, and type, and conceded that flocculation was less important than actual filtration. Including installation and personnel training, *Farm Chemicals* indicated expenditures of $14,000 for the system and treatment costs of approximately 8¢ per liter [30¢ per gallon].

Klassen (1992) reports that Calareo, Inc., in Corcoran, CA, developed a self-contained rinsate filtering system that is a variation of the above described carbon adsorption processes. The first of three stages utilizes a chemical flocculation tank to

induce organic settling. The liquid is then transferred to a sedimentation tank, where additional solids are allowed to settle out. The supernatant is then passed through a diatomaceous earth filter for removal of any remaining solids and certain chemicals. All contaminated sludge produced during this process is compressed into a "cake," sealed in drums, and disposed of at an appropriate landfill. The resulting effluent can then be re-used as future wash water. Although the initial capital cost was high, about $50,000 plus another $25,000 for concrete containment, the system is capable of treating a maximum of 2650-L [700 gal.] of rinsate at a time at a rate of 26¢-40¢ per liter [$1 - $1.50 per gallon]. The owner indicated to Klassen (1992) that a scaled-down version of this system could be developed for considerably less.

A major advantage to these carbon filtration/adsorption-type processes is that they are apparently in compliance with all applicable regulations. Dwinell (1992) reports that RCRA authorities at both the state and federal levels have indicated that these systems may be exempt from RCRA facility permits so long as the following conditions are met:

- they are operated as a closed loop system, thus complying with RCRA recycling provisions (i.e., the treated effluent is re-used as wash water and there is no discharge of this effluent)
- all residual waste (i.e., spent carbon charges and waste sludges) are removed prior to the applicable accumulation time frame (i.e., 180 days for SQG's and 90 days for "generators")
- the systems are safeguarded against treatment of RCRA regulated pesticides

Although advantageous because of their simplicity and high decontamination efficiency, these carbon filtration/adsorption-type processes have several drawbacks. Other than the often expensive capital investment, the major concern is the further disposal

need for the residual waste. It is important to realize that these systems are at best only volume reduction techniques, the operation of which produce at least two additional waste streams: the spent carbon charges and the accumulated flocculation/sedimentation sludge. In the system described by Nye (1988), approximately 91 kg [200 lbs.] of spent carbon and 379-L [100 gal.] of sludge are produced during the treatment of 18,925 liters [5000 gallons] of pesticide-laden water. These wastes will likely have to be disposed of in EPA-approved hazardous waste facilities, which as alluded to earlier cannot only be expensive but burdensome. Dwinell (1992) reports that such disposal can range on the order of $500 to $1000 per instance.

Although spent carbon is commonly regenerated thermally, Massey et al. (1992) feels this technique is not economically feasible for the small quantities of spent carbon usually generated from pesticide filtration processes. This leaves incineration as the preferred available disposal option of this material. However, incineration requires that the waste carbon be transported off-site, and is thus regulated under RCRA. As a means of on-site disposal of the spent carbon, these authors evaluated the feasibility of biologically degrading the pesticide bound to the carbon. Their study looked at charcoal contaminated with a mixture of 10 various pesticides. They observed little success in biodegrading these contaminated carbon charges, and further feel that it would be almost impossible to enhance the composting ability of this material due to the high concentration, limited bioavailability and mixture-effects associated with these pesticide sorbed carbon charges (Massey et al., 1992).

Nye (1988) reports that another possible option for the disposal of the residual sludge and spent carbon is that of encapsulation in cement. This is a form of stabilization which Wentz (1989) describes as a chemical treatment process designed to limit or reduce the ultimate release of hazardous constituents from a waste. Solidification, he further reveals, is a widely practiced disposal option for hazardous waste liquids and sludges. Utilizing inert nondegradable binding agents or polymers, most of these processes incorporate the waste into a solid matrix. In earlier studies cited by Nye (1988), the contaminated carbon was powdered and, along with the waste sludge, mixed with portland cement. Wentz (1989) states that portland cement, a mixture of oxides of calcium, silica, aluminum, and iron produced from clay and limestone in high temperature kilns, is a common binding agent in the hazardous waste industry. In the study conducted using pesticide wastes, this procedure reportedly met the EPA Extraction Procedure test (Nye, 1988) and thus would not necessitate disposal at a RCRA-approved hazardous waste facility (Wentz, 1989). Thus, Nye (1988) feels that it is a promising technique for the simple and safe handling of the waste sludge and spent carbon charges.

Alternatives to activated carbon

Instead of using the standard granular activated carbon medium, researchers at Virginia Polytechnic Institute and State University (VPI or Virginia Tech) are examining the potential of other organic materials for the sorption of aqueous pesticide wastes. Their research is fueled by the biggest drawback of GAC: the concern raised by the need for further disposal of the sorbent material. Thus, their goal centers around employing

biologically-based materials which might be better suited for future degradation processes. In particular, they have extensively investigated various lignocellulosic materials (such as peat moss and steam exploded wood) and shown that they will readily sorb pesticides from solution as effectively as activated carbon.

Using laboratory procedures, they simulated a two step batch demulsification, sorption and column filtration process. The batch-sorption step involves mixing the sorbent directly with the rinsate solution. The effluent is then filtered through a column packed with more organic material. Numerous pesticides, formulations, and sorbents have been evaluated with this procedure.

In one of their studies, Hetzel et al. (1989) used diazinon solutions with additions of peat moss to show that either concentrated or diluted pesticide solutions could be absorbed into organic material. Treatment with peat moss of solutions containing initial concentrations of diazinon and chlorpyrifos ranging from 1,250 to 20,000 mg/L resulted in reductions ranging from 55% to 91% after 24 hours. It was noted that for high levels of chlorpyrifos, peat moss absorbency was not as effective as it was at lower concentration levels. In a second batch equilibrium study, Hutchinson et al. (1993) appraised the ability of three different sorbents (rubber, peat moss, and steam-exploded wood) for their effectiveness in removing metolachlor from an aqueous solution. They report that at the highest concentration levels (400 mg/L), shredded rubber stoppers removed close to 85% of formulated metolachlor from the solution, while peat and steam-exploded wood were less effective, at 72% and 55%, respectively. The authors feel that shredded rubber from

old car tires could potentially be utilized for the benefit of two waste problems.

Another VPI research effort, reported by Mullins et al. (1992), evaluated the efficiency of three sorbents (sphagnum peat moss, steam-exploded yellow poplar wood fibers, and activated carbon) for the removal of aqueous solution pesticides formulated as either emulsifiable concentrates (EC), wettable powders (WP), or flowables (F). The 10 pesticides were mixed at concentrations of 5000 mg/L[ppm], and included atrazine (F), carbofuran (F), azinphos-methye (WP), captan (WP), folpet (WP), chlorpyrifos (EC), diazinon (EC), lindane (EC), malathion (EC), and metalachlor (EC). Employing only the batch-sorption phase of the process, the authors achieved large reductions in pesticide concentrations for most cases. Mullins and his associates feel that not only sorption, but also alkaline hydrolysis and filtration contributed to the reduction of these pesticide levels. However, removal of a few pesticides, specifically metolachlor, carbofuren, and chlorpyrifos, was significant but not as good as they anticipated.

Their desire for improvement prompted the addition of column filtration as a second sorption-step. Testing this two-step process with aqueous suspensions containing either atrazine, metolachlor, or chlorpyrifos, chemical removal was improved, and in most cases the sorbents achieved greater than 99% reduction in concentration levels. Additionally, the researchers looked at modifying these sorbents by adding vegetable oil to them. They discovered that "pretreatment with vegetable oil provides better sorptivity of certain pesticides onto specific lignocellulosic matrices and is capable of enhancing the bioreactivity of sorbents" (Mullins et al., 1992).

A final study by Mullins et al. (1993) evaluated some other lignocellulosic materials (peat moss, steam-exploded newspaper) for sorptivity of aqueous pesticide suspensions. Using their two-step sorption process, the investigators report reduction of chlorpyrifos (initial concentration of about 4000 mg/L[ppm]) and metolachlor (initial concentration of about 6000 mg/L[ppm]) levels to range from 97.6% to > 99% for all sorbents.

These research efforts at Virginia Tech have clearly shown the promise that bio-based materials have for removing high concentrations of pesticides from rinsate solutions. In addition to their sorbtivity comparable to that of activated carbon (Hetzel et al., 1989 and 1991; Mullins et al. 1992 and 1993; and Hutchinson et al., 1993), the major appeal of these materials lie in their potential to be readily degraded in a further disposal processes, unlike activated carbon (Massey et al., 1992). In a 1993 publication, Mullins and his colleagues evaluated the "bioreactivity potential" of several bio-based materials. Both small-scale and field-scale compost studies were conducted by the research team on seven lignocellulosic substrates: ground peanut hulls, steam-exploded peanut hulls, ground peanut hulls + steam-exploded peanut hulls, peat moss, peat moss + 8% vegetable oil, steam-exploded wood fibers, and steam-exploded wood fibers + 8% vegetable oil. In conjunction with possibly enhancing the hydrophobic sorption capacity of the substrates, additional oil treatment may improve the microbial activity of their compost process. In this instance, the sorbents were amended with waste oils obtained from fast food restaurants, a by-product themselves requiring proper disposal. As for the peanut hulls, an abundant crop residue in certain geographic locations, these lignocellulosic by-products

naturally contain 2-3% lipids. Gauged by the production of carbon dioxide (CO_2) and compost pile temperatures, the research team deduced that all of the peanut hull-type substrates were highest in degradability. The steam-exploded wood- and peat moss-based materials, respectively, were comparatively less bioreactive than the peanut hull-type sorbents (Mullins et al., 1993).

Although it has been clearly shown that lignocellulose is readily compostable, the true test of these materials lie in their degradability when contaminated with sorbed pesticides. As of yet, this specific scenario has not been addressed and is an area compelling further study. However, this text later reviews the exploration of these same Virginia Tech scholars into the fate of several pesticides applied directly onto various bio-based compost materials. Noteworthy is the fact that, although relatively low in cost, $0.15 and $0.11/kg [$0.07 and $0.05/lb], respectively (Hutchinson et al., 1993), steam-exploded materials are not yet commercially available, whereas peat is (Mullins et al., 1992 and 1993).

Chemical Treatment

The second major classification of available treatment options is that of chemical techniques. They involve, according to Wentz (1989), the use of reactions to transform hazardous waste streams into less hazardous substances. In essence, these procedures generally serve to chemically detoxify the waste, thus resulting in a residual material more environmentally acceptable. In addition to detoxification, these methods are successfully employed as a means of volume reduction. This class of technologies, some of which were

previously discussed, include neutralization, precipitation, coagulation/flocculation, oxidation/reduction, color removal, disinfection, ion exchange, and stabilization/solidification, to mention a few. Due to their nature, many of these technologies lend themselves for use in conjunction with other disposal methods in a multi-stage process such as seen with settling techniques added to carbon adsorption processes. In terms of agricultural wastes, current available techniques of this nature can range from exotic, technologically-intensive systems to simple, basic chemical reactions or combinations thereof (Honeycutt et al., 1988 and Seiber, 1988).

Oxidation/ultraviolet irradiation

The use of ozone (O_3) to detoxify pesticide waste solution is a technique gaining interest by scientists, and is being thoroughly studied. Ozone is widely used in some municipalities for the disinfection of potable water, and Wentz (1989) describes it as a very powerful oxidant. Produced by an electric corona discharge through air or oxygen, it is relatively unstable in aqueous solution and cannot readily be stored, thus dictating on-site production (Wentz, 1989). In terms of pesticide decontamination, several authors report research combining ozonation with ultraviolet (UV) irradiation processes. The most widely recognized study in this research area involved work with a field-scale system developed at the USDA, Beltsville, Maryland research center. The literature (Honeycutt et al., 1988; Kearney et al., 1984; Seiber, 1988) reports that the above-mentioned study successfully processed rinsate containing such compounds as atrazine, 2,4-D, and the animal parasite control agent coamophos. This UV-O_3 unit alters the pesticide molecule,

resulting in a more polar, less toxic, and more biodegradable end product. In their research, Kearney et al. (1984) report that more than 80% of atrazine and 2,4-D degraded in 2-3 hour time period, while paraquat degraded somewhat more slowly. In addition to increased dwell time, their research also revealed that a reduction in active ingredient concentrations drastically increased degradation rates (Kearney et al., 1984 and Honeycutt et al., 1988). Although the initial cost of the unit is high ($35,000), operational costs (based primarily on the UV unit's energy usage) are relatively low ($650 annually) (Kearney et al., 1984 and Kearney, 1988). With additional advantages of being commercially available, potentially mobile, easily operated, and highly versatile, this technique holds immense promise for on-site treatment of farm production rinsates. However, researchers feel that its greatest potential lies in being used in conjunction with some sort of microbial metabolic process (Honeycutt et al., 1988; Kearney, 1988; Seiber, 1988; Kearney et al., 1984).

Ozonation and bioremediation

A 1990 issue of *Environmental Science and Technology* reports on such a microbial metabolic combination process. Developed by Somich et al., the system utilizes ozonation plus bioremediation as a means of treating rinsates. The researchers performed ozonolysis on collected rinsate containing the following twelve herbicides: alachlor, atrazine, cyanozine, 2,4-D, dicamba, glyphosate, malathion, metolachlor, paraquat, permethion, sikazine, and trifluralin. The pesticide-laden solution was first treated with O_3, and then the products were placed in a soil column for further degradation by

microorganisms (microbes). As ozone gas was pumped through the wastewater, the bubbles gradually broke down the pesticides into harmless biodegradable products. This aqueous material was then filtered through soil, where microbes degraded the byproducts, leaving only water, ammonia, and carbon dioxide (Somich, 1990). The scientists concluded that in all cases rinsate ozonation greatly improved the rate of microbial mineralization of the parent chemicals. Additional tests revealed that this process eliminated all herbicidal activity from the waste solution, with no observable mutagenic activity. The danger in relying completely on these disinfection techniques is that, in order to safely dispose of the effluent, total removal/degradation of the chemical is required. Although not specifically mentioned in the literature, the effluent could possibly be re-used as subsequent rinsewater.

Filtration/ozonation/adsorption

A final multi-stage ozone process is the system produced by the Wilbur-Ellis Company. Dwinell (1992) describes their system as one featuring a solid particle filter, a settling tank, an oil filter, and an ozonation unit all in conjunction with a carbon adsorption filtration stage. These four features are included to augment the useful life of the carbon filters. First, the solid particle filter and the settling tank remove debris, which might obstruct filter pores downstream. Next, in order to facilitate the removal of grease and oil which might disrupt both the ozonation and carbon adsorption processes, the rinsate flows through an oil filter. Finally, the rinsate enters an ozonation chamber, where organics, algae, bacteria, and other organisms are oxidized. This not only diminishes potential

clogging of the carbon filters but possibly enhances the adsorptivity of the chemical to the carbon (Dwinell, 1992). For further degradation, the system has the capacity to add an UV light source downstream of the three carbon filters. After treatment of about 189,250 liters [50,000 gallons] of rinsewater, the first carbon charge in the series is removed and the remaining two are rotated forward with a new charge being placed in the third position. As with the aforementioned carbon filtration systems, all spent carbon requires subsequent disposal, but the resulting effluent may be recycled for future cleaning operations. Dwinell (1992) additionally feels that both capital and operational costs parallel those of other carbon adsorption techniques.

Photolysis

Alluded to earlier in the form of ultraviolet irradiation, a second general type of chemical treatment technique receiving notable attention is that of photolysis. Early on, the American Chemical Society (ACS) recognized the scientific evaluation of photochemical destruction as a potential and practical means of addressing the pesticide waste problem (Crosby, 1978 and Plimmer, 1978). Some of this early research centered around the photodegradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) (Honeycutt et al., 1988 and Crosby, 1978). More recent research ventures concentrate on solar photodecomposition with the addition of photoactive catalysts to the wastewater. These photocatalytic semiconductor powders are suspended in the wastewater and then subjected to solar illumination. When exposed to solar irradiation, these catalysts absorb sunlight and promote photoredox reactions. Complete mineralization of the organic constituents

occurs, yielding only carbon dioxide (CO_2), water (H_2O) and hydrochloric acid (HCl) (Nozik and Cooper, 1988 and Seiber, 1988). Although only studied in the laboratory with model compounds such as phenol and chlorinated hydrocarbons, these scientists report that nearly complete removal of the chemical is possible in about four hours. Since the technique is in the research stage no actual costs are available, but the experts feel that it could be easily implemented at minimal cost. Both authors (Nozik and Cooper, 1988 and Seiber, 1988) strongly believe that its greatest potential lies as an addition to existing holding/evaporation pond technologies.

Hydrolysis and other simple chemical reactions

Both Seiber (1988) and Honeycutt et al. (1988) indicate that varying levels of degradation can be achieved through the use of hydrolytic and/or other oxidizing agents. Hydrolysis research activities from several scientific teams are presented in the ACS Symposium Series No. 259 text. Although different in nature, both studies report successful pesticide detoxification utilizing hydrolysis (Macalady and Wolfe, 1984 and Lemley et al., 1984). Various other chemical reagents have been analyzed for their potential ability to neutralize pesticides. Honeycutt et al. (1988) cite an earlier study in which metallic sodium in liquid ammonia, evaluated along with several other reagents, successfully degraded in excess of 92% of several organophosphate insecticides. However, they concede that its use is prohibitive due to human hazards, its corrosive nature, and high costs. On the other hand, according to Lee et al. (1984), sodium perborate is a commercially available stable powder, extremely reactive with phosphorus

esters. Thus, they recommend solutions of this non-chlorine industrial bleach as an effective chemical detoxicant for organophosphate insecticide wastes. In a study of various common simple reagents, researchers at Ciba-Geigy Corporation found that hypochlorite (household bleach - NaOCl) was the most effective at degrading a variety of their formulations. In seven out of 10 products they tested, hypochlorite reduced the level of active ingredient upward of 50%. Similarly, Seiber (1988) reports on a study in which household bleach was added to MCPA-DMA wastewater and rapidly reduced concentrations from >1000 ppm to <100 ppm, under outdoor sunlight conditions. Seiber (1988) is hopeful that a simple chemical reagent capable of neutralizing pesticide wastes can be found. The idea of simply adding and mixing such a chemical is very appealing to him, and thus he feels research in this area should be vigorously pursued.

Microwave plasma destruction

Bailin et al. (1978) report that destruction of organic compounds via passage through a microwave discharge was first researched in 1967 at the Lockheed Palo Alto Research Laboratory. Microwave discharges, or plasmas, are known to promote a variety of reactions. The plasma is a gaseous mixture consisting of free electrons, ions, and various neutral species (Bailin et al., 1978). In general, the waste material is passed through a plasma detector tube in which free electrons are produced by microwave radiation. The plasma reaction is initiated by the free electrons. As these electrons collide with the pesticide molecules, free radicals are formed, which undergo a series of rapid reactions resulting in final products. Utilizing oxygen as the reactant gas, Honeycutt et al.

(1978) and Bailin et al. (1978) reported destruction levels upward of 99% for the pesticides malathion, polychlorinated biphenyl (PCB), methyl bromide, phenylmercuric acetate, and keptone when passed through a microwave plasma system.

These detoxification levels are consistent with those reported by Honeycutt et al. (1988). Additionally, both authors report simple products of reaction such as CO_2, CO, SO_2, and Br_2 ,for example. Although quite effective, this method is fairly technical and extremely expensive, and thus would not be conducive to farm application for the disposal of rinsates. In 1978, Bailin et al. report that the capital cost of the unit alone ranged on the order of $100,000. On the other hand, Honeycutt et al. (1988) feels that microwave plasma destruction could be a valid tool for some large dealers/applicators and for industrial use.

Wet air oxidation (Zimmerman Process, Zimpro®)

Another more complex chemical treatment technique is that of wet air oxidation. In principal, this process utilizes sufficient heat (up to 340°C [644°F]) and pressure (up to 13,790 kPa [2000 psig]), in the presence of air or oxygen, to oxidize any organic solution (Wilkinson et al., 1978 and Honeycutt, 1988). In relatively short order (less than one hour), this process is capable of oxidizing sewage sludge to the final products of CO_2 and H_2O. While it has yet to be widely applied to pesticides, both sets of authors do report limited data. Atrazine and Amiben® herbicide wastes processed in this manner yielded active ingredient destruction levels of 100% and 88-99.5%, respectively (Wilkinson et al., 1978 and Honeycutt, 1988). Although not extensively evaluated, the costs of this process

are estimated to be extremely high, thus negating its use at the farm level.

Molten salt process

Finally, another fairly exotic chemical treatment process mentioned by Honeycutt et al. (1988) is that of molten salt combustion, developed by Rockwell International. As can be seen in the schematic (Figure 5), waste material is combined with air and continuously blown beneath the surface of a molten salt bath. Some of the original researchers into this concept, Yosim et al. (1978), say that the waste material is introduced in such a manner that any gas formed during combustion is forced to pass through the melt before being exhausted. Prior to being released into the atmosphere, this off-gas, containing carbon dioxide, steam, nitrogen, and oxygen, is passed through either a venturi scrubber or a baghouse for removal of any particulate matter. Ash and other noncombustible by-products tend to build up in the melt and require removal. This spent melt mixture can be reprocessed to recover and recycle the salt to the combustor. The remaining waste ash is then disposed of.

In both bench-scale and pilot-scale combustors, the scientists at Rockwell International utilized molten sodium carbonate at an operating temperature between 800 and 1000°C [1472 and 1832°F] to destroy a variety of test wastes (Yosim et al., 1978). At these temperatures, they report complete and odor-free destruction of the contaminated material. Of the limited pesticides tested, DDT, malathion, chlordane and 2,4-D, the authors report achieving destruction levels in excess of 99.9% for every case. Honeycutt et al. (1988) estimate the cost for processing waste in this manner to be around $1.10/kg

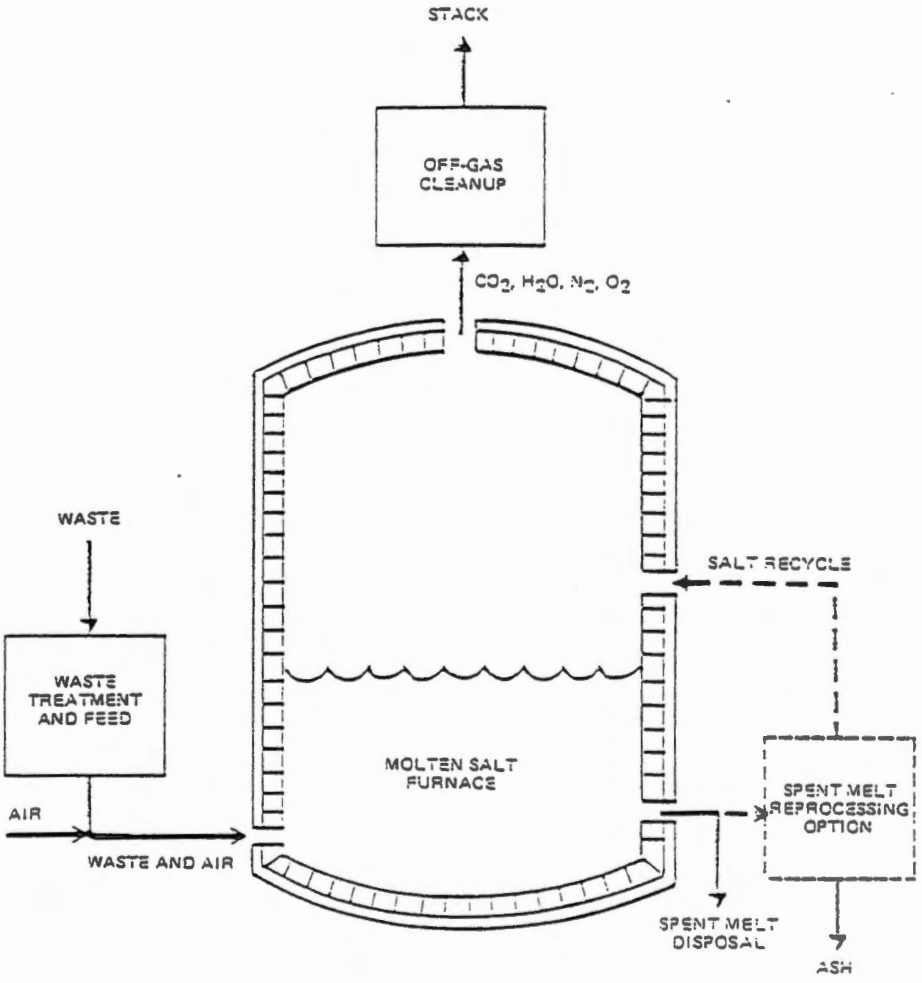


Figure 5. Molten salt combustion process concept (Yosim et al., 1978).

[$2.43/lb.] of pesticide. Conceptually, Rockwell International envisions a mobile molten salt unit mounted on a truck bed and capable of processing 227 kg/hr [500 lbs./hr] of waste.

Biological Treatment

Biological techniques comprise the third and final major classification of available treatment options. Biological degradation, as defined by Craigmill and Winterlin (1988) for pesticide-laden wastes, is the chemical breakdown of pesticides mediated by microorganisms, plants and subcellular systems (such as enzymes) that have originated from living cells. In contrast to volume reduction techniques, biological treatment techniques are generally targeted towards destroying the actual pesticide molecules or rendering them less toxic. This classification of technologies include activated sludge systems, trickling filter systems, enzymatic methods, microbial acclimation techniques, genetic engineering approaches, and composting processes.

Microbial degradation

Before delving into the variety of actual treatment technologies encompassed by biological degradation, one must first possess a limited amount of background knowledge. As Craigmill and Winterlin (1988) so importantly point out, the majority of pesticides formulated in this day and time are designed such that they readily break down into low toxicity compounds when exposed to natural environmental conditions. Along these lines, one of the major pathways for pesticide degradation (after application) is via metabolism by soil microorganisms (microbes). Microbes can be categorized in a number of ways.

One such classification is based upon their source of nutrients, making them either heterotrophic or autotrophic. Heterotrophs utilize organic matter, while autotrophs utilize inorganic matter. A second important classification method described by Wentz (1989) is according to their utilization of oxygen; they can be either aerobic, anaerobic, or facultative. Aerobic microbes require oxygen molecules for the conversion of organic matter into the needed energy for growth. Anaerobes, on the other hand, require the absence of free oxygen molecules. They utilize oxygen which is chemically combined with other elements. Facultative microbes can essentially survive in either aerobic or anaerobic conditions (Wentz, 1989).

Both Mueller (1993) and Craigmill and Winterlin (1988) point out that microbial pesticide degradation can take place either directly or through incidental transformation. Catabolism is described as the process in which the pesticide directly serves as an energy source supplying microbial growth. In such cases, the chemical is viewed as a carbon source or nutrient where the products of metabolism are actually incorporated into the chemical structure of the microbe. Conversely, when an organism metabolizes a pesticide (or other such nutrient) but the products of metabolism are not incorporated into the microbe, the process is termed co-metabolism (Mueller, 1993 and Craigmill and Winterlin, 1988). The most important metabolic reactions, according to Craigmill and Winterlin (1988), include oxidation, reduction, and hydrolysis. They go on to say: "The results of these reactions are metabolites that are generally more water soluble than the parent compound, and that are less toxic. In many cases the metabolites may be further

metabolized and the ultimate end products are carbon dioxide, water, and salts."

The biological degradation of pesticides is dependent upon numerous factors, most importantly environmental conditions and the chemical properties of the compound. These degradation processes are very dependent upon the pesticide involved (Craigmill and Winterlin, 1988), specifically its susceptibility to microbial degradation and its volatility/photostability (Mueller, 1993). Among the many influential soil factors, these researchers mention soil type, organic matter content, temperature, microbial population characteristics, pH, oxygen, and moisture as a few being instrumental in biological activity. Craigmill and Winterlin (1988) generalize that warm, moist, oxygen-rich soils high in organic matter are most conducive to microbial metabolism.

Activated sludge treatment system

Some of the earliest documented reports of biological disposal techniques are those developed by industrial pesticide manufacturers for the treatment of organophosphate manufacturing wastes. Craigmill and Winterlin (1988) refer to the development of an activated sludge treatment system by Monsanto in the mid-1960's for treatment of such wastes. As they describe it, the "system is composed of a concentrated biomass which is supplied with nutrients and oxygen in order to promote the most efficient use of the waste by the microorganisms." Their system included some pre-treatment processes to control odor and to neutralize acidity. The scientists at Monsanto reported complete destruction of parathion and paranitrophenol after seven to ten days of treatment. After allowing the sludge to settle, the effluent was discharged into the city sewer system. The remaining

sludge was then recycled and mixed with new waste. Due to the extreme biotoxicity of the parathion waste, the authors report that this system required intensive management and sampling (Craigmill and Winterlin, 1988). A similar system was reportedly developed a few years later by Chemagro Corporation for the treatment of a mixture of organophosphate wastes. Their design was slightly different from the Monsanto concept in that it was a two-stage process, both stages being activated sludge processes. The first-stage activated sludge process was utilized to absorb some of the shock that the waste had on the microbes, while the second stage provided the definitive degradation (Craigmill and Winterlin, 1988).

Trickling filter

Another early documented biological technique developed for industrial use was reported in the early 1970's. It utilized a combination of activated sludge and trickling filter process for the successful treatment of 2,4-D wastes. Craigmill and Winterlin (1988) describe the trickling filter system as a bed filled with 5-10 cm [2-4 in.] diameter stones. This filter medium not only provided sites for microbial attachment, but also created voids to facilitate the passage of air and wastewater (Wentz, 1989). As the effluent was dripped over the rocks, air was forced up from the bottom and through the bed. A biological slime layer formed on the surface of the stones and utilized the waste as a food source while it passed through the bed (Craigmill and Winterlin, 1988). As Wentz (1989) explains, these systems actually contain both aerobic and anaerobic zones. The biological film consists of microbes which are aerobic to a depth of only 0.1 to 0.2 mm [0.004 to 0.008 in.], while

the layer next to the rock's surface is anaerobic. It is felt by Craigmill and Winterlin (1988) that a trickling filter process is advantageous because it is capable of handling large pulses of toxic wastes which might otherwise render some biological processes ineffective.

A more recent variation of this trickling filter process was investigated in Illinois by Schmidt et al. (1988). They evaluated the performance of both acidic and alkaline trickling filter systems on a multitude of pesticide compounds. To promote alkaline hydrolysis, one disposal bed was filled with coarse grade limestone. In the other pit, acidic strip mine waste material was added to facilitate acid hydrolysis. A simple PVC pipe recirculation system distributed the waste solution across the top of the filter media. Additionally, in order to enhance microbial degradation, the scientists injected pesticide-decomposing bacteria into the system. For a mixture of alachlor, atrazine, butylate, cyanazine, linuron, metalochlor, metribuzin, pendimethalin, and trifluralin, they generally observed higher degradation rates (up to 30% per day) in the acidic system. The alkaline disposal bed averaged 2.5% degradation per day. The triazine class of pesticides especially tended to persist in the alkaline bed, while low rates of effluent infiltration were experienced through the acid medium. Although far from perfect, Schmidt et al. (1988) feel these types of systems are advantageous due to their apparent effectiveness on a variety of commonly used insecticides and herbicides without the need for further disposal of any residuals. Although the early industrial-type trickling filter systems reported by Craigmill and Winterlin (1988) were costly to build and maintain, and required intensive management and monitoring for proper operation, the design by Schmidt et al. (1988) was

much simpler and more applicable to the needs and skills of smaller pesticide waste generators. Realizing that the size and capacity of these systems is dictated by an individual's rinsate production, capital and operating costs were estimated at roughly $6000 and $2,500/year, respectively. Although their original systems were placed in the ground, Schmidt et al. (1988) report that this technology is easily transferrable into an above-ground unit conforming to recent regulatory trends.

Enzymatic methods

In the area of biotechnology, several researchers have investigated the enzymatic activity of microbial cell-free extracts for the degradation of pesticides. The literature points to one scientist in particular, Dr. Douglas Münnecke, as the initiate of this research. In his initial studies, Wilkinson et al. (1978) reports that Münnecke utilized parathion, an organophosphate insecticide, as the sole carbon and energy source for a mixed bacterial culture. These cultures experienced exceptional growth, due in part to the production of the enzyme parathion hydrolase. Münnecke was able to successfully isolate and extract this enzyme from the parent cells. As cited by numerous other reports, Münnecke showed that his extracted enzyme promoted hydrolysis of various organophosphate pesticides at a much higher rate than did chemical hydrolysis methods (Wilkinson et al., 1978; Craigmill and Winterlin, 1988; and Honeycutt et al., 1989). It is reported by Honeycutt et al. (1989) that some of Münnecke's subsequent studies revealed that the enzyme degraded diazinon in soil by 97% in a 24-hour period.

Researchers at Ciba-Geigy Corporation obtained purified parathion hydrolase from

Dr. Münnecke with the intention of testing the efficacy of the enzyme under field conditions. The thrust of their effort was to evaluate the usefulness of parathion hydrolase as a simple and inexpensive means of cleaning up diazinon spills. Using greenhouse soil treated with various levels of diazinon, Honeycutt et al. (1984) simulated spill situations which would result in localized, high concentrations of the pesticide in the soil. As Craigmill and Winterlin (1988) summarize: "They found that parathion hydrolase was very effective in promoting the hydrolysis of diazinon at levels as high as 5000 ppm." Although less effective in diazinon concentrations greater than 2000 ppm, the enzyme rapidly and effectively degrades the pesticide in the soil, reaching safe environmental levels within 24 hours (Honeycutt et al., 1984).

Karns et al. (1988) successfully utilized this same enzyme as part of a treatment process for the elimination of cattle-dip pesticide wastes. In a tick eradication program along the Texas/Mexico border, authorities treat cattle via dipping operations containing the organophosphate insecticide and acaricide coumaphos. These operations produce vast quantities of waste coumaphos solution, which is highly resistant to degradation. Utilizing Flavobacterium, a strain of bacteria which produces the parathion hydrolase enzyme, these scientists were able to enhance the degradation of coumaphos. The addition of this enzyme facilitated the hydrolysis of the coumaphos molecule, yielding a product referred to as chlorferon. This microbial hydrolysis by-product proved to be very susceptible to further degradation by UV-ozonation. Further exposure of these biological/physical treated by-products to a soil medium provided rapid and complete oxidation by the

naturally occurring soil microbes, yielding only carbon dioxide and water. Karns et al. (1988) performed both laboratory studies and field tests with encouraging results from both. In the field test, they treated 2460 liters [650 gallons] of waste cattle dip solution. Under ambient temperature and vigorous aeration, the microbial hydrolysis of coumaphos was virtually complete within 48 hours. Ozone was then pumped into the waste for an additional 20 hours, after which less than 50% of the chlorferon remained.

Along these same lines, Bumpus and Aust (1988) and Karns (1992) report that the white root fungus *Phanerochaete chrysosporium* is capable of degrading a variety of pesticide compounds. As Karns (1992) explains, it is widely known that this white root fungus degrades lignin through the action of a lignin peroxidase enzyme. It is this enzyme which attacks compounds such as DDT, methoxychlor, lindane, chlordane, dieldrin, 2,4,5-T, and pentrachlorophenol. Karns (1992) indicates that additional lignin-degrading actinomyces which produce lignin peroxidase may hold similar promise.

Clearly, there is substantial evidence to suggest that biotechnological techniques such as these hold promise for helping treat pesticide-laden wastes. Through systematic isolation and characterization of such organisms, Karns (1988) feels that an "arsenal of enzymatic weapons" may be developed for the remediation of pesticide contamination. Even though such enzymes do not totally destroy the pesticides, they greatly accelerate their detoxification, yielding residuals more susceptible to further degradation processes. Although much more research is needed in this area, Karns (1992) thinks that "it is just a matter of time and effort before the proper organisms are found, characterized, and utilized

for this type of waste treatment." Along with his associates, he even forsees the distribution of these enzymes in the form of packets which the farmer or applicator could directly add to their tanks for rinsate treatment (Karns et al., 1988).

Microbial acclimation and genetic engineering

Craigmill and Winterlin (1988) indicate that "microbes can be acclimated to utilize pesticides as a carbon source by growing them in increasingly higher concentrations of pesticides." They report that the majority of research in this area centers around the microbes becoming accustomed to and tolerant of extremely high concentration levels. Along these lines, Smith and Mortensen (1991) isolated a microorganism from field soils which had received annual treatments of 2,4-D formulations since 1947. They report that soils in these plots contain higher quantities of 2,4-D-metabolizing organisms than did soils in control plots. This 2,4-D-degrading bacterium, identified as *Pseudomonas testosteroni*, utilizes the herbicide as a carbon source. In tank tests, these researchers added the organisms to an aerated solution of simple mineral salts and 2,4-D amino formulations. They showed that *P. testosteroni* metabolized the herbicide, and over time achieved complete breakdown of the chemical. The bacterium was successfully tested over a range of concentration levels and temperatures. Their system was then effectively transferred to a farm operation for the biological destruction of 2,4-D amino tank and container residues (Smith and Mortensen, 1991). Although potentially useful for the clean-up of concentrated spills, this research approach is of limited utility due to uncertainties surrounding its application to pesticide mixtures.

Another area of research, called promising by Craigmill and Winterlin (1988), centers around the genetic engineering of bacteria to degrade organic pollutants. The use of these "super-bugs" for the clean-up of crude oil spills has been widely recognized. In terms of applying this type of technology to the degradation of pesticides, the research is more or less in its infancy. One such effort centers around the transfer of plasmids from one species of bacteria to another. Craigmill and Winterlin (1988) describe bacterial plasmids as small, extrachromosomal, replicating closed DNA molecules. Functions transferred via these plasmids may include fertility, antibiotic resistance, or degradative pathways, for example. Catabolic plasmids are those coded for chemical degradation (Quensen and Matsumura, 1984). The literature reveals that, of the degradative plasmids discovered so far, the majority have been found in *Pseudomonas* species, which are commonly found in soils. In addition, plasmids are transmissible between bacterial strains and/or species. In research coordinated by Quensen and Matsumura (1984), they were able to partially transfer the chemical degradative capacity of one *Bacillus* species to another *Bacillus* species. Although they were unable to fully assess the characteristics and performance of the transformants, the researchers feel that important strides were made in the direction of engineering microorganisms capable of degrading organic pollutants. Although further research in this area is needed, biotechnology of this type holds immense promise. As Quensen and Matsumura (1984) state: "they (plasmids) may be used to genetically alter microorganisms already present in a polluted environment so that they gain the ability to better degrade a pollutant without losing their ability to survive field

reducing paraquat levels, they did achieve positive destruction results for the other compounds. For these, analysis indicated concentrations were reduced to extremely low or undetectable levels.

In another case cited by Craigmill and Winterlin (1988), researchers at Virginia Tech also reached mixed results. Radiolabeled diazinon and chlordane was added to a compost mixture of dairy cow manure and sawdust, and the material was then incubated for three weeks, after which analysis revealed varying degrees of volatilization for both compounds in addition to measurable amounts of metabolism of diazinon only. In contrast to these somewhat favorable indications, a third referenced article from Craigmill and Winterlin (1988) concluded that parathion was not effectively degraded via composting. In this particular case, after seven days of composting with garbage, no parathion metabolites could be detected.

Encouraged enough by the results of their earlier study, a flurry of subsequent experiments were carried out at VPI. Several sources cite their field studies regarding the composting of various pesticide compounds. Their field-scale bioreactors were elementary in design, in some cases simply consisting of plastic trash cans fitted with locking lids and in others, wooden-framed boxes lined with black plastic. In either instance, they were submerged in the ground (Mullins et al., 1989, 1992 and 1993; and Hetzel, 1989). In the first of these subsequent studies, Mullins and his associates (1989) added diazinon to a compost mixture of commercial peat moss and fresh dairy cattle manure containing 25% wood chips. They enriched this material with finely ground corn meal and fertilizer and

added water to achieve a moisture content of 60 - 65%. These pits were then monitored for the disappearance of diazinon and the appearance/presence of its hydrolysis metabolite IMHP. Their results showed rapid decreases in diazinon levels, with little concern for volatilization (Hetzel, 1989). By the end of three weeks, not only low but also high concentrations of the chemical were reduced to less than 1% of the initial application amounts. Further, they saw an initial increase in the IMHP level corresponding to this rapid decrease in diazinon, and then the IMHP levels declined with time. Thus, Mullins et al. (1989) conclude that in the early stages of the compost process, diazinon was quickly degraded to its metabolite IMHP, and then IMHP was further degraded as the microbial activity continued.

In another investigation, Mullins and his research team (1992) applied atrazine and carbofuran to the compost pits and monitored degradation and the appearance/disappearance of their associated metabolites. For this study, the organic matrix of the pile contained a mixture of sphagm peat moss, corn meal, and crushed limestone at 67:22:11, dry weight basis, respectively. The scientists inoculated the bioreactors with aged horse manure, agricultural soil, and activated peat. After three weeks of composting, they report no detectable carbofuran or carbofuran phenol, the pesticide's hydrolysis product. Atrazine, on the other hand, degraded at a much slower rate. Only 14% of the initial atrazine levels remained after 26 weeks of composting, and no detectable levels of hydroxyatrazine (the hydrolysis product of atrazine) could be found after 15 weeks. As in the previous study, Mullins et al. (1992) again theorized "that the

parent molecule undergoes further degradation as the composting process progresses" due to the disappearance of the pesticide metabolite. Although not conclusive, these initial efforts provide enough promise to warrant further investigation and as Haug (1993) states, composting should be recommended as a possible treatment technique for pesticide rinsates.

Combination Approach

Several of these studies revealed that the utilization of a multi-stage process incorporating more than one treatment technology (e.g., flocculation/carbon adsorption, ozonalysis/UV irradiation, ozonation/bioremediation) has the potential to yield more desirable results than a singly-applied treatment technique. As Craigmill and Winterlin (1988) summarize:

> "Because of the diversity of chemicals in use as pesticides, it is very unlikely that any one method of degradation will be able to handle all types of waste. By combining chemical, biological, and physical treatments it should be possible to develop pesticide waste disposal systems that can fill all needs."

Contrary to other classes of chemicals, a wealth of knowledge exists pertaining to the environmental fate of agrochemicals. As previously acknowledged, pesticides are unique from other toxic compounds in that they are specifically formulated to break down into low-toxicity compounds when exposed to natural environmental conditions. So, nearly all modern formulations are adsorbed on or readily degraded in soils. Armed with this knowledge, it is feasible to design treatment systems which exploit these properties. Unlike all of the above described treatment options which employ some form of either

volume reduction or destruction, there are several efforts underway to investigate the effectiveness of combining a concentration objective with a degradation objective, either in a single- or double-stage process.

Concentration/degradation system (double-stage process)

The barrage of published research from Virginia Tech scientists in the late 1980's and early 1990's gave insight into their efforts toward developing an acceptable means of disposing of unwanted pesticide rinsates (Hertzel et al., 1989 and 1991; Mullins et al., 1989, 1992, and 1993; and Hutchinson et al., 1992). The principal behind their approach revolves around first sorbing the pesticides from the rinsate solution via an organic material, and then applying this contaminated sorbent to a composting process to facilitate microbial degradation. This disposal philosophy has been the driving force behind their investigation and evaluation of various materials for their effectiveness as both a sorbent and a compostable substrate. As previously acknowledged, their earlier work revealed that certain lignocellulosic materials (e.g., peat moss or steam-exploded wood fibers) can sorb pesticides from waste solutions as effectively as can activated carbon. Additionally, with minimal management, these types of sorbents are also susceptible to microbial activity in a composting-type environment yielding less toxic degradation by-products. Based upon these encouraging indications, they envision combining this knowledge into a double-stage process whereby both pesticide concentration and degradation is achieved (Hetzel et al., 1989 and 1991; and Mullins et al., 1992 and 1993).

As Figure 6 depicts, the VPI researchers formulated a model for their concept. In

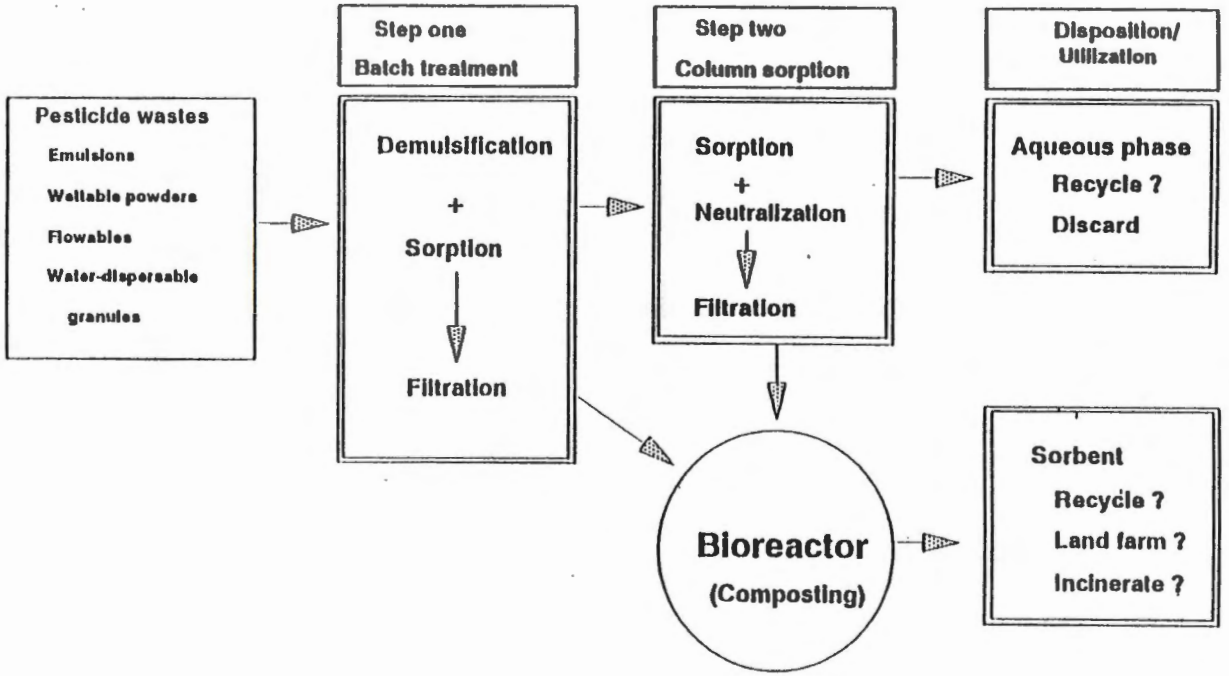


Figure 6. Flow diagram for pesticide wastewater disposal using organic sorption and microbial degradation. The process consists of two main components: a batch demulsification/sorption component, and a disposal component (Mullins et al., 1993).

their final design, the sorbent phase consists of two steps. First, a batch demulsification and sorption step is employed, in which the rinsates are mixed with organic sorbents (i.e., lignocellulosic materials) and demulsification agents [i.e., hydrated lime: $Ca(OH)_2$]. The solution is then passed through a column of lignocellulosic material in a column sorption/filtration step. At this point, the effluent can either be safely discarded into the sewer system or reused in the process. Finally, bioreactors are employed in the disposal phase of this process, whereby pesticides sorbed onto the spent sorbent undergo microbial degradation, yielding harmless end products (Mullins et al., 1992 and 1993).

The success of various laboratory trials evaluating the potential of such a system has led to the development of a pilot-scale system. The actual apparatus for the batch step consists of a 208-L [55-gal.] drum with an inner colander in which 132.5 - 151.4-L [35-40 gal.] of rinsate is mixed with 0.056 - 0.085m^3 [2-3 ft^3] of organic sorbent material and roughly 2.3 kg [5 lbs.] of demulsification agents. After thoroughly mixing for four hours with a motorized propeller mixer, the concoction is allowed to settle for 10-12 hours (Hetzel et al., 1991). The supernatant is then filtered through a PVC column packed with additional lignocellulosic material. Elementary field-scale bioreactors (described earlier) are then used to facilitate the composting process.

It is important to realize that, as of yet, the full concept incorporating both the sorption-phase and degradation-phase into a single process has not actually been evaluated. However, based upon the results of substantial individual laboratory-scale simulations, it appears to hold substantial promise for the disposal of pesticide rinsates.

The researchers have shown 1) that the two-step sorption-phase procedure can be extremely effective in the removal of chemicals from solutions, 2) that lignocellulosic materials are effective sorbents and compostable substrates, and 3) that successful composting of certain pesticides is achievable. Although the fate of several pesticides applied directly onto a compost matrix has been studied, Mullins et al., (1993) says that further efforts should center around "the fate of formulated pesticides sorbed onto lignocellulosic matrices during composting." It is also pointed out that there is some concern regarding the need for further disposal of the spent (or reacted) compost if it is removed from the bioreactors. Although this concern is limited, it still warrants further attention.

Evaporation/degradation systems (single-stage processes)

Whereas the VPI concept employs two distinguishable processes for the concentration and degradation of pesticide rinsates, efforts are underway at several universities across the U.S. to encompass these two objectives into a single process. In theory, the volume reduction and degradation objectives are combined into a single process by applying the contaminated wastewater to some form of a soil bed from which the water can evaporate and within which the pesticide will degrade. This technique is based upon two general ideas. First, volume reduction occurs through the evaporation of water from the soil surface, thus concentrating the pesticide in the soil. Second, the soil provides an excellent environment for degradation, where soil chemical and biological processes break down the pesticides. Early approaches implementing this concept took

place at Iowa State University and the University of California at Davis, and more recently at Texas A&M University and in the state of Florida.

Iowa State system: The idea of a contained soil disposal system began at Iowa State University in the late 1960's (Rogers and Allen, 1978; and Brown and Thomas, 1990). In 1969-70, the university constructed a concrete-lined disposal pit at its horticulture farm. This particular soil/evaporation pit, 3.7 m by 9.1 m by 1.2 m deep [12 ft. by 30 ft. by 4 ft. deep], was located below grade and filled with alternating layers of gravel (coarse river washed stone) and soil (silt loam typical of central Iowa). As seen in Figure 7, it was equipped with a mechanically activated roof to exclude precipitation. Additionally, a tile system was installed below the concrete floor of the pit to facilitate sampling of the surrounding groundwater. As of their 1984 publications (Hall; Junk and Richard), over 50 kg [110 lb.] of more than 45 different pesticide wastes had been deposited into the horticulture pit, and it had effectively evaporated approximately 22,710 liters [6000 gallons] of rinsate annually. Although perfectly sized for large operations, a soil pit of this size is not conducive for smaller applicators. Thus, Hall (1984) developed a small "micropit," modified from a precast concrete manhole structure, to serve as a model suitable for individual farmers and small applicators.

In 1977 a second pit was constructed at Iowa State's Agronomy-Agricultural Engineering Research Center (Junk and Richard, 1984). As can be seen in Figure 8, the agronomy pit is 13.7m x 7.3m x 1.7m deep [45 ft. x 24 ft. x 6 ft. deep]and roofed for protection from precipitation. This pit was double-lined with sheets of continuous black

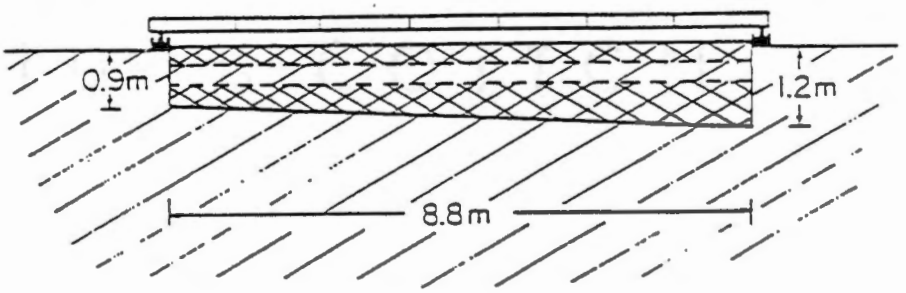


Figure 7. Cross-sectional view of covered concrete-lined Horticulture pit at Iowa State University, with alternating layers of rock (cross-hatched) and soil (slanted lines) (Junk and Richards, 1984).

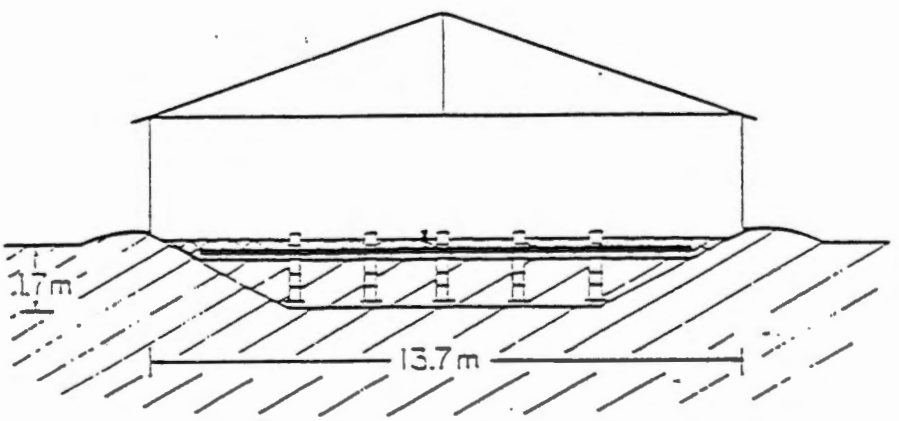


Figure 8. Cross-sectional view of canopied plastic-lined Agronomy pit at Iowa State University, with a distribution system (solid bar) embedded in rock (cross-hatched) and five sampling tiles extending through the rock and soil (slanted lines) (Junk and Richards, 1984).

polyethylene between layers of sand. Additionally, metallic hardware cloth was buried in the outer sand layer to deter burrowing rodents. The pit was then backfilled with the original silt loam soil to a depth of 1.22m and a 0.46m [4 ft. and 1.5 ft.] layer of crushed rock was added to the surface. To facilitate rinsate distribution throughout the pit, a manifold system is encased within the rock layer. As of their 1984 article, Junk and Richard report that about 150 kg [331 lb.] of 24 various pesticides had been applied to the pit.

In a 1984 article in the American Chemical Society Symposium Series No. 259, Junk and Richard reveal the results of extensive analytical sampling of both the horticulture and agronomy disposal pits at Iowa State. For both pits, samples were collected from the pit matrices, the underlying groundwater, all nearby water sources, and the vicinal air. As Junk and Richard (1984) appropriately point out, analysis of the samples from the actual pits only reveals, at best, a rough estimate of the characteristics of the system. They observed extreme variations in the chemical composition of samples extracted throughout the pit, thus indicating that samples representative of the entire pit were virtually impossible to collect. The interpretation of the sample analysis reflects the fact that these pits were, as the authors describe, actually "uncontrolled" systems, meaning that the amount and timing of waste deposits were haphazard rather than being scientifically structured. In general, the Iowa State scientists report no significant accumulation of any pesticides in either pit (Hall, 1984; Junk and Richard, 1984; Rogers and Allen, 1978). Samples from surrounding soil and water sources revealed no leakages or contaminations

that could be attributed to the operation of the horticultural (i.e., concrete-lined) soil pit. The agronomy (i.e., plastic-lined) pit, on the other hand, apparently had minimal seepage of chemicals into the surrounding groundwater. They further deduce that neither of these pits were a significant source of air contamination via pesticide volatilization (Junk and Richard, 1984). Thus, it appears that the systems are accomplishing the intended goal, and information supplied in 1992 revealed that the unit was still operating satisfactorily after nearly 20 years (Ilax, 1991).

California approach: At experiment stations throughout California in the mid 1970's, the University of California implemented the use of lined evaporation beds for the disposal of pesticide rinsates. Although similar in concept, these evaporation beds varied somewhat from the Iowa State idea. Typically 6.1 x 12.2 x 0.9 m [20 x 40 x 3 ft.], these pits were lined with a butyl rubber membrane and backfilled with 31 to 46 cm [12 to 18 in.] of sandy loam soil. As the cross-sectioned view in Figure 9 depicts, 10.2 cm [4-in.] diameter perforated PVC pipe lay underneath gravel along the bottom of the bed (Winterlin et al., 1984). The contaminated washwaters were collected from adjacent rinse pad facilities and first passed through a sedimentation chamber for the removal of debris and particulate matter. The solution was then distributed through the leach lines (Craigmill and Winterlin, 1988). Like the Iowa State system, the California evaporation beds provided roofing for the exclusion of rainfall. In this case, though, the roof was constructed from corrugated fiberglass, which gave the additional benefit of allowing sunlight to penetrate and heat the soil surface, thus promoting evaporation (Winterlin et

al., 1984).

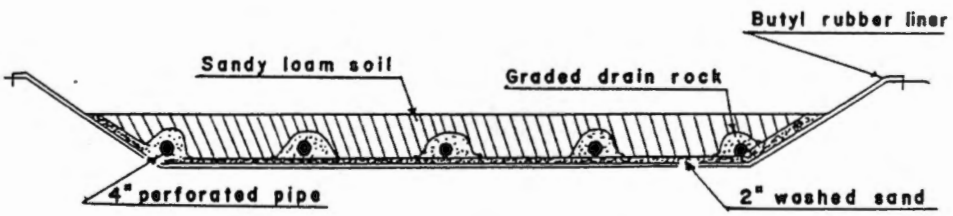


Figure 9. Cross-sectional view of a University of California evaporation bed (Winterlin et al., 1984).

The systems were designed such that capillary action pulls the solution up through the soil, and water evaporates off the soil surface (Winterlin et al., 1984). Ideally, Craigmill and Winterlin (1988) feel it would be best to keep the top layer of the soil only moist, not flooded. But, as they later reveal, "This is not always the case since the beds are sometimes overfilled during peak seasonal use, or the storage tanks are emptied into the beds faster than evaporation can occur." They further theorize that "this may not be detrimental since this process results in both aerobic and anaerobic conditions that are important when a broad spectrum of pesticides are introduced into the system" (Craigmill and Winterlin, 1988).

In 1981, Winterlin et al. (1984) initiated a study for the purpose of determining

whether these evaporation beds were performing as originally intended. They evaluated ten beds which had been in operation across the state of California for 4-10 years. Like the Iowa State pits, these soil beds were actually "uncontrolled" systems. It appears that when the pits were built, not much consideration was given to the scientific evaluation of their performance. This made future attempts at such somewhat difficult. Not only were the wastes haphazardly applied, but the pits themselves varied (e.g., different soil depth, lime incorporation, roofed, unroofed, different pesticides, variations due to geographic locations, etc.). Of the 100+ pesticides surveyed, only 46 were actually detected. In general, Winterlin and his colleagues (1984) feel that the levels of pesticides discovered in the evaporation beds were relatively low for disposal facilities of this size.

Additionally, the beds which received heavier use tended to have higher residue concentrations. Thus, the scientists surmised that the pesticides did not appear to build up in significant quantities within the beds over an extended period of time. However, they did notice higher concentrations within the upper inch of soil. It was theorized that chemical mass transport toward the top was facilitated by the "wick effect" (i.e., as evaporation occurs at the surface, more water is drawn upward through the soil via capillary action) (Winterlin et al., 1984). They also saw some evidence that the beds which had been amended with lime tended to accelerate the decay of certain pesticides. Finally, they generalized that the pesticide air levels detected paralleled both the vapor pressures and the residual levels of the compounds found in the upper surface of the soil.

Virginia system: A system similar in concept to the Iowa State systems was installed at the Virginia Agricultural Experiment Station in Winchester, Virginia in the late 1980's. The disposal unit at this orchard farm was nicely incorporated into a complete pesticide facility. This facility was designed with extreme forethought into and consideration of every aspect of pesticide usage and worker protection/safety. The disposal unit itself, as described by Horsburgh (n.d.), consists of adjacent concrete evaporation pits (8 m x 4.5 m x 1.8-2.1 m deep [26 ft. x 15 ft. x 6-7 ft. deep]) covered by a clear plastic panel roof and filled with alternating layers of soil and gravel. The wastewater enters the unit via gravity flow from the mixing/washing pad to a distribution manifold beneath the soil matrix surface. In contrast to the static system at Iowa State, this system provides a means of supplying compressed air to the pits for the purpose of aeration. Also, thermostatically controlled fans were installed to blow air across the pit surfaces to facilitate increased evaporation if needed. Finally, provisions were included for the sampling of not only the pit contents, but also the underlying groundwater (Horsburgh, n.d.).

Horsburgh (n. d.) concedes that the unit was extremely undersized and needed greater evaporation capacity. They approached this problem by constructing an additional evaporator to handle the excessive liquid material. A 6.1 m [20 ft.] long, 1.8 m [6 ft.] wide building housed 1.2 m [4 ft.] long corrugated paper filters on each side. As rinsate solution is pumped from the pits and trickles down the filters, fans blow air through the filter pads to induce evaporation. At its prime, Horsburgh (n. d.) reports that the

evaporator can eliminate approximately a quart of liquid per minute. However, as with any other filter material, he indicates that the spent pads are a residual waste requiring proper disposal. As another point of notice: although complete records are supposedly kept regarding the types and quantities of materials placed into the disposal unit, this system, like the ones in California and Iowa, was apparently built without any consideration for its scientific evaluations. Therefore, there is no data base pertaining to the performance of their soil digester. Finally, from personal observations of this unit, there is an odor problem associated with their pit, especially downwind from the pit. Although, this doesn't appear to be a major concern and could be addressed with minimal effort, they do advise their employees to stay away from the downwind side of the unit.

Texas variation: The biggest drawback of these early systems is the fact that the pit was placed directly in the ground instead of above ground. Dwinell (1992) indicates that a number of older systems are still in use which employ the original below-grade lined-pit design and are probably in violation of state groundwater protection laws. Thus, wells must be drilled alongside these soil beds in order to monitor the water table for possible contamination (Brown, 1986a and 1986b). Brown (1986a and 1986b) also states that in most cases as many as four groundwater-monitoring wells are needed for each disposal bed in contact with the soil surface. This becomes very costly. It typically costs several thousand dollars to install each well and as much as $500 to obtain and analyze samples on a quarterly basis.

In order to avoid this costly problem, specialists at Texas A&M University

(Brown, 1986a and1986b; and Brown and Thomas, 1990) suggest a soil bed system similar to the one at Iowa State with the exception being that the system is contained above ground. As Dwinell (1992) acknowledges, the majority of these types of systems in use now have been modified to eliminate concerns surrounding possible groundwater contamination. As he goes on to describe, current designs typically use above-ground tanks to contain the soil media in addition to providing secondary containment for the entire system. A general schematic of this concept can be seen in Figures 10 and 11. By using an above-ground bed instead of a pit, the systems may be operated without the need for monitoring wells, in addition to providing easy visual inspection for the monitoring and maintenance of leaks. A secondary containment structure adds further protection and assurance by capturing/preventing any leaks or spills from polluting the environment (Dwinell, 1992).

Such a refined system was built by Texas A&M University several years ago. Their soil disposal bed unit operates in conjunction with a wash pad and collection sump facility. As can be seen in Figure 12, the bed consists of a lower chamber for liquid storage below a suspended 31 cm [12-in.] layer of a sandy loam soil. Liquid from the sump pump is distributed through a PVC manifold system lying on the surface of the soil. The rinsate solution drains through holes in the PVC lines, filters through the soil, and any excess is collected on the metal floor below the soil. A combination level switch/time clock is used to activate a second pump to douse the soil layer daily with the stored washwater. The disposal bed is built out of coated 6.35 mm [1/4-inch] steel plate and is

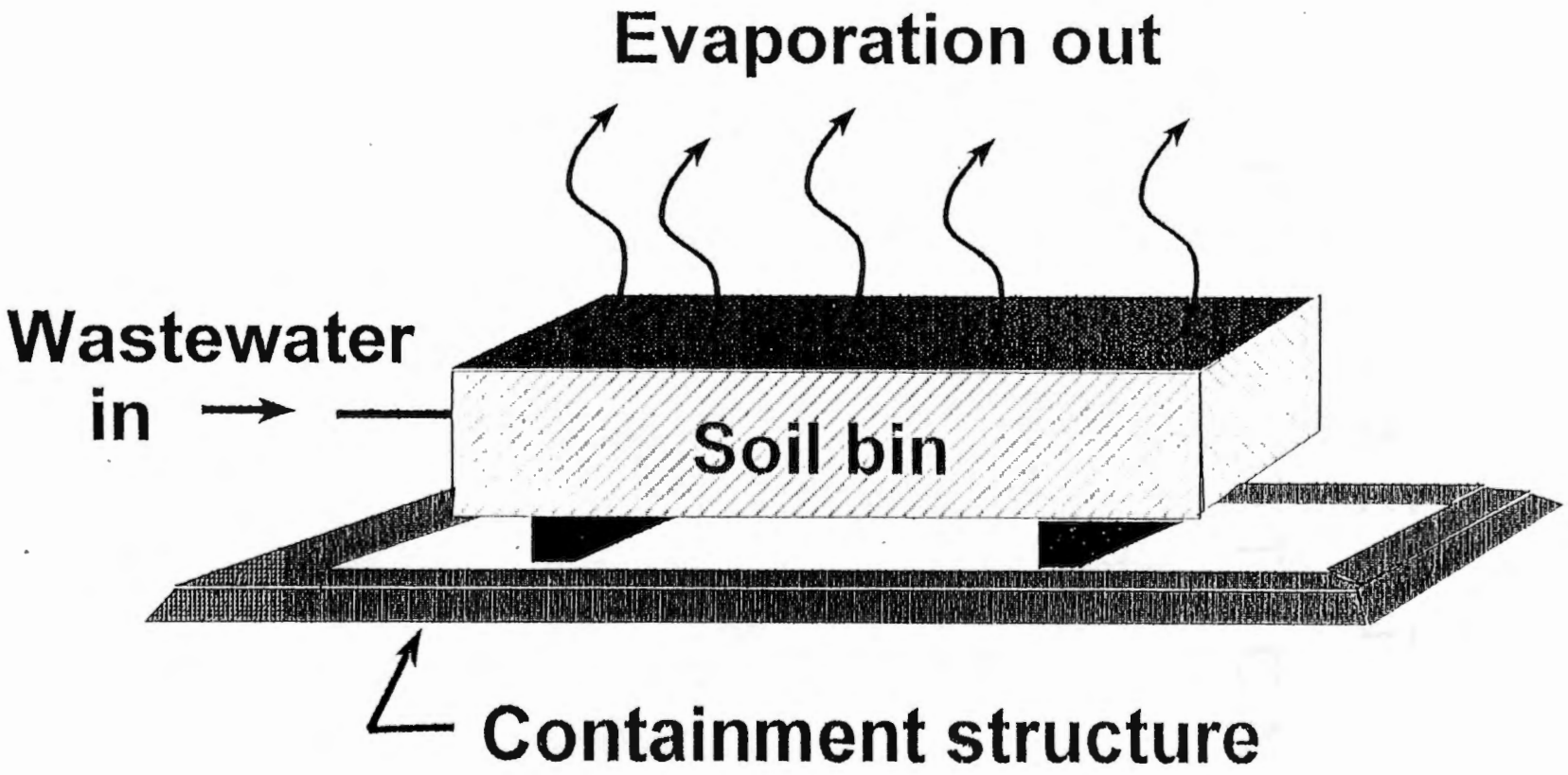


Figure 10. Conceptual view of evaporation/degradation soil bin system for the treatment of pesticide-laden wastewater (Yoder, 1992).

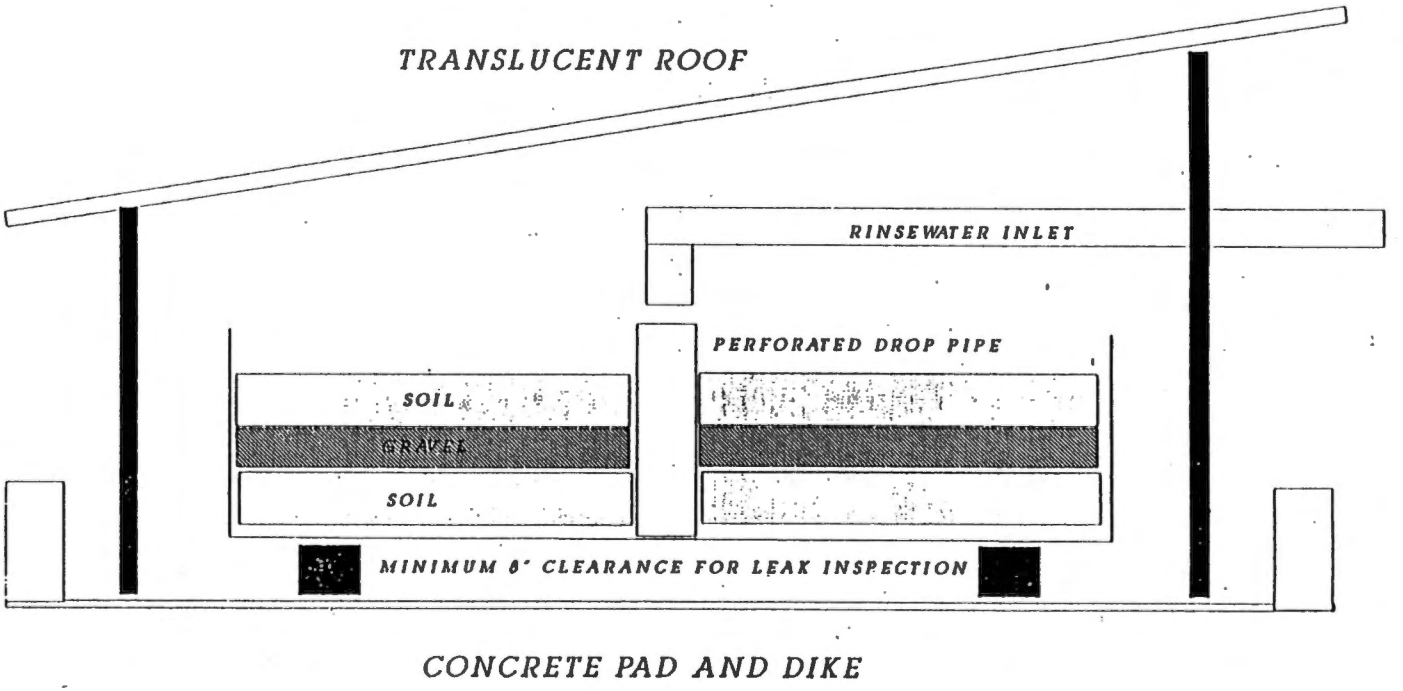


Figure 11. Conceptual drawing of evaporation/degradation system design used in Florida for the treatment of pesticide rinsewater (Dwinell, 1992).

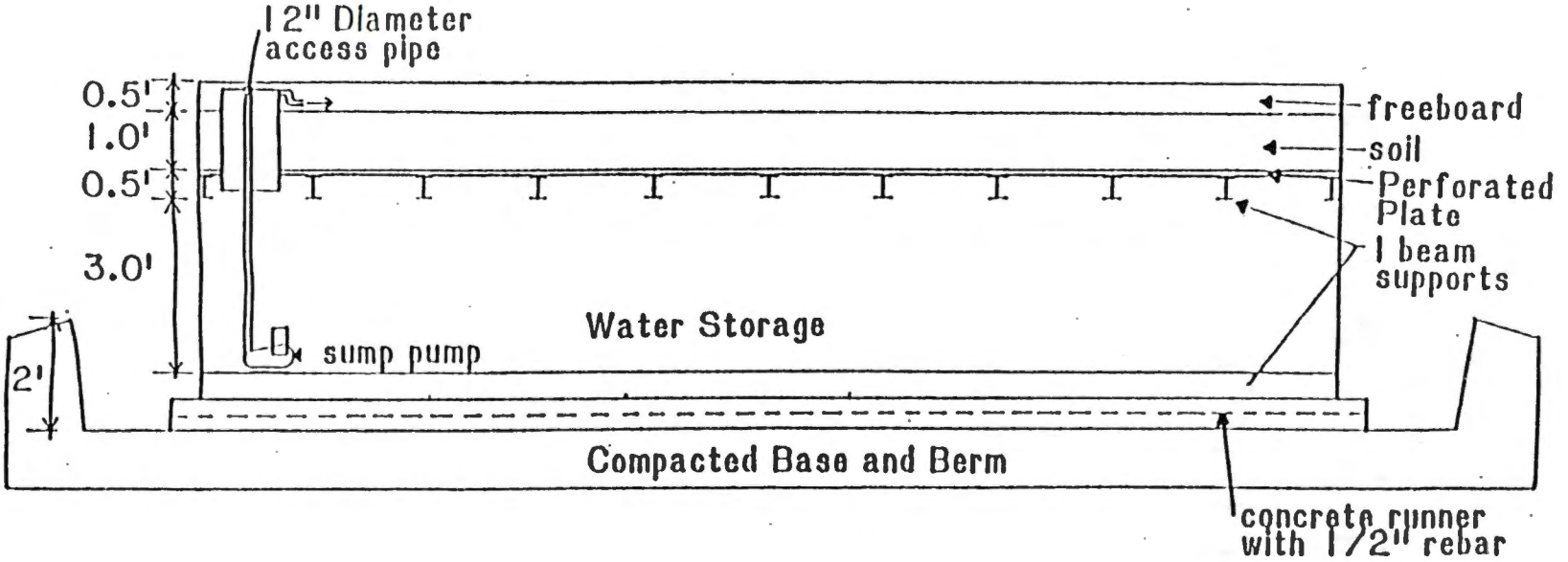


Figure 12. Cross-sectional view of disposal bed utilized for the treatment of pesticide wastewater at Texas A&M University (Brown, 1985).

equipped with skids to allow for easy transport and inspection for leaks. The entire disposal bed is surrounded by an earthern berm capable of containing the entire volume of the unit in case of a leak. The bed is also covered with a fiberglass roof that allows light to reach the soil but does not restrict air flow (Brown, 1985).

Brown (1985) envisions a typical unit to be approximately 2.44 m [8 ft.] wide by 12.2 m [40 ft.] long and 1.5 m [5 ft.] deep, and thus capable of handling between 30,280 to 37,850 liters [8,000 to 10,000 gal.] of rinsate per year based upon average Texas conditions. He further suggests the need for yearly soil sampling for possible pesticide buildup since the literature provides an inconclusive data base on pesticide degradation. In addition to eliminating environmental pollution concerns, this system differs from those at Iowa State and California in that it is a dynamic system. As Schmidt et al. (1988) point out, those earlier systems provided neither circulation nor aeration, and thus represented a static-type situation. Instead of allowing their unit to remain in a stagnant condition, the Texas researchers recirculate the wastewaster through their soil matrix.

Issues of concern: The initial systems constructed in Iowa and California provided the basis for the evaporation bed concept. However, it appears as if these first systems were built purely in response to application needs. They were not scientifically-driven systems. Only as an afterthought did researchers try to evaluate them scientifically. Although all indications of their performance appeared promising, several issues of concern were voiced by the scientific community. Included in these were possible problems due to pesticide volatilization and lack of information on the degradation

conditions. Hence, later studies were conducted to investigate such issues.

Pesticide volatilization: One concern associated with the evaporation of large amounts of pesticide-laden wastewater into the environment is the possibility of air contamination by pesticide volatilization. Pesticide volatilization may be viewed as either positive or negative. As Sanders and Seiber (1984) state:

> "Whether one would want to maximize or minimize volatilization rates from these systems is open to debate. The user may want to maximize this rate, for it can help decontaminate the system and keep pesticide concentrations under control. Alternatively, the user or the public may want to minimize volatilization, to reduce respiratory risks in the vicinity of the sites."

In any case, the rate of volatilization of these chemicals within the disposal bed facilities appeared to be minimal. As previously revealed, initial field measurements of both of these systems, by Junk and Richard (1984) in Iowa and by Winterlin et al. (1984) in California, indicated insignificant air contamination via pesticide volatilization. Junk et al. (1984) came to the same general conclusion during the evaluation of pesticide degradation in a mini-pit soil/water system study.

Confirming this, theoretical and laboratory work performed by Baker and Johnson (1984) and Sanders and Seiber (1984) indicates that there is little danger of excessive amounts of pesticide moving into the atmosphere with the evaporating water. This appears to be due to the strong binding potential between the soil and many pesticides. In their attempts to describe pesticide volatilization with water evaporation, Baker and Johnson (1984) noted that the saturation vapor pressure was very important in determining relative rates of volatilization of pesticides, with temperatures and ambient relative

humidity being much less so. Thus, they conclude that for agricultutal chemicals with vapor pressures greater than 1 x 10^{-3} mm Hg, volatility losses could be fairly significant. Pesticides with lower vapor pressures showed negligible volatility losses. Meanwhile, Sanders and Seiber (1984) employed a simple environmental chamber to model the volatilization of five organophosphorus pesticides (mevinphos, diazinon, methyl parathiom, malathion, and parathion) in soil pits and evaporation ponds. They ascertained that the soil in these systems was very influential in controlling the amount of volatilization. In general, they found that low solubility pesticides had a greater rate of volatilization from water than from soil. Essentially, there is a decrease in the amount of free pesticide in the water available for volatilization, due to the strong binding of the chemical molecules to the soil particles. Thus, in evaporation pond systems, with the absence of a soil matrix, they feel that volatilization could be a major route of loss of some pesticides.

Degradation trends: Although all indications from the systems at Iowa and in California point to reasonable amounts of degradation with no accumulation or build-up of pesticides over time, no qualitative or quantitative facts could be made concerning degradation conditions and trends. In order to address some of these issues, Rogers and Allen (1978) report on a secondary mini-pit experiment conducted at Iowa State for the evaluation of pesticide degradation in a soil-water system. Junk et al. (1984) partially buried fifty-six plastic garbage cans (110-L [30-gal]), used as containment devices, in the open ground. Six pesticides (atrazine, alachlor, trifluralin, 2,4-D ester, parathion, and carbaryl) were assessed in these receptacles. Blended individually and as mixtures at two

concentrations (0.4 and 0.02 weight percent of active ingredient), the pesticides were added along with 60-L [16-gal] of water and 15-Kg [33 lbs] of soil to the containers. Trials were conducted with additional variables being aeration and peptone nutrients supplied to half the mini-pits. Samples were collected from each container over a 68 week period and analyzed for not only the pesticides but their hydrolysis products.

Experimental results indicated that most of the pesticides were sorbed on to soil particles, thus guaranteeing almost complete containment. Their reports of insignificant losses through volatilization (even the volatile trifluralin was contained) further substantiates its correlation with the soil's binding potential. Varying degrees of degradation were observed, ranging from very rapid hydrolysis of 2,4-D ester and carbaryl to very persistent atrazine and alachlor. Additional items of note from their data: 1) addition of aeration and nutrients appeared to be of questionable value, 2) both concentration and mixture had an inhibitory effect on degradation; and 3) pH, although a consideration under certain circumstances with particular pesticides, seemed to be unimportant for a general soil/water disposal system (Junk et al., 1984).

In another secondary study of the concrete-lined disposal pit at Iowa State, Johnson and Hartman (1980) investigated its microbiology after eight years of continual use. From aqueous samples (both aerobic and anaerobic), soil samples, and submerged rock samples, these scientists characterized the resident microbial populations. As evidenced by not only the numbers but also by the fluctuation of bacteria in the samples, they reported substantial biological activity within the pit. Though they are quick to point

out that the mere presence of bacteria does not prove microbial degradation of pesticides, their laboratory tests support the notion that they played a significant role in pesticide destruction. It is further felt by these individuals "that the inclusion of soil and rock probably resulted in the presence of a more diverse flora than if the pit contained only liquid" (Johnson and Hartman, 1980).

Winterlin and his California-based colleagues (1989) performed a secondary study on one of their evaporation pits. In this particular pit, the upper layers of soil were highly contaminated with pesticides (> 1 kg [2.2 lb.]active pesticide per $0.1m^3$[$3.53 ft^3$] of top soil). Upon removal from the pit, this contaminated soil layer and a control soil were subjected to various tests for the purposes of "determining optimum conditions for degrading high concentrations of pesticides in soil." The control consisted of a similar soil type fortified with six pesticides (atrazine, trifluralin, malathion, diazinon, chlorpyrifos, and parathion). Both sets of soils were treated with various soil amendments including organic matter (peat), hydrated lime [$Ca(OH)_2$], acids (sulfuric acid) and nutrients (cornmeal and ammonium phosphate) under both moist (aerobic) and flooded (anaerobic) conditions. For the most part, they reported successful reductions of the pesticides' half-lives; although their data did indicate that the effects of the soil amendments were generally pesticide dependent (Winterlin et al., 1989). This was consistent with an earlier study along the same lines. In particular, Schoen and Winterlin (1987) reported that, with the exception of pesticide concentration, the effects of various soil factors upon the degradation of a pesticide mixture varied greatly and were pesticide dependent. Of particular importance,

though, Winterlin et al. (1989) argue that the best approach for degrading contaminated soils involving various compounds may be to alternate between moist and flooded soil conditions.

Finally, for his master's project, Brian Vanderglas, a student of Dr. Brown's at Texas A&M, conducted a study to determine the fate of pesticides applied to their type of digestor (1988). Using a mixture of coarse sand and sewage sludge as the digestion media, five pesticides (simazine, lindane, malathion, captan, and 2,4-D) were applied either separately or as mixtures to separate digestors. On a daily basis, the digestion matrix was dosed with the contaminant solution. After 112 days, he reported that less than 1% of the pesticides remained in the liquid. Although the matrix did an excellent job of removing the chemicals from the liquid, little degradation was observed. In addition to design flaws, he atttibutes the pesticide persistence to the "inhibiting effects pesticide mixtures and/or high concentrations have on soil microflora." As a side note, in an additional water balance study, Vanderglas (1982) indicates that the digestor evaporation was only approximately 40% that of pan evaporation.

General remarks: Dwinell (1992) feels that these evaporation/degradation-type systems have the necessary characteristics for successful treatment of pesticide rinsates. Not only is the technology rather simple, requiring minimal operational skills, but he also indicates it is economically feasible. With the primary design/operational constraints being system capacity and evaporation rate, the capital costs constitute the major expenditure, ranging anywhere from $20,000 to $50,000 (Dwinell, 1992). However, the greatest

appeal to these evaporation/degradation-type systems lies in the fact that they are a "closed loop" system. If properly designed, constructed, and maintained, these soil digestors can sufficiently deal with both components of the waste (the water and the actual pesticide molecules). Additionally, the soil medium may remain undisturbed for the life of the system and, as Brown (1986) further indicates, the soil itself should be sufficiently decontaminated within a couple of years after use ceases. In this case the soil could then be simply land spread. Thus, there is no residual waste stream requiring further disposal.

The only documented problems associated with these soil bed systems appear to be regulatory issues. Although the lack of secondary containment was an issue with the initial systems, as Seiber (1988) advised and Brown (1985 and 1986) showed, this concern can easily be addressed. Now, however, several experts (Dwinell, 1992; Noyes, 1991, 1992) fear regulatory problems based upon a recent interpretation of the RCRA exemption clause pertaining to wastewater treatment facilities. This interpretation requires such facilities to obtain either a RCRA or NPDES permit. However, as Dwinell (1992) outlines, there are three ways for pesticide treatment systems to be exempt from RCRA treatment facility permit requirements:

1) There is no treatment of pesticides regulated as hazardous waste under RCRA.
2) A permit is obtained under the Clean Water Act (CWA) as a wastewater treatment unit.
3) The treatment system is designed to be part of a closed loop system.

In the case of soil disposal beds, if no pesticides listed as hazardous waste under RCRA are treated in the system, then RCRA facility permitting requirements are avoided. NPDES treatment facility permits are obtainable, and if so negate RCRA facility permits

even if RCRA-regulated pesticides are treated. However, since there is no effluent discharge from these systems, they are not subject to the CWA. Closed loop systems take advantage of RCRA permitting requirement exemptions designed for recycling operations (Dwinell, 1992).

Dwinell (1992) further states: "the systems (evaporator/degradator) currently in use either avoid treatment of pesticide rinsewater regulated as hazardous waste, or, in the case of the system at Iowa State University, have obtained a RCRA facility permit." Apparently, this is the only facility in the U.S. with a RCRA facility permit for the treatment of pesticide rinsate. Obtaining these permits is not only difficult but expensive. Application fees alone are reported to be in the thousands of dollars. Dwinell (1992) indicates that "additional large costs are associated with necessary engineering studies, environmental monitoring and consultant fees necessary to win permit approval."

Not only are these permits costly and difficult to obtain, but Iowa State officials revealed to Dwinell (1992) that they are also expensive to maintain. Personal communications between University of Tennessee Agricultural Engineering Department faculty and officials at Iowa State in 1996 revealed great problems in dealing with EPA regulators. Even after extensive system modifications to meet EPA standards for the RCRA facility permits, they were subjected to fines and threatened with additional violation penalties. Apparently, the EPA regional office responsible for Iowa was concerned about mixing production pesticide disposal with scientific research of an innovative technology. As Yoder (1996) discovered, these continual headaches eventually

forced Iowa State scientists to suspend and cancel all current and future research efforts in this area. For the disposal unit operating with the proper RCRA permit, this necessitated an official EPA facility shutdown process (Baker, 1996 and Huss, 1996). As the literature reveals, many experts agree that the EPA must loosen their reins a little if there is ever to be an acceptable treatment option for these waste solutions (Dwinell, 1992 and Craigmill and Winterlin, 1988).

SUMMARY OF BACKGROUND MATERIAL

Having reached a thorough understanding of all related background information with the above discussions, several general points can be made in summarizing the background material; points which will assist in narrowing our focus and deciding how to proceed. To begin with, evidence reveals that pesticide application rinsates constitute a voluminous amount of waste material. The manner in which an applicator chooses to handle these waste solutions will directly determine whether or not they are considered hazardous materials and fall under RCRA regulations.

As Junk and Richard (1984) outlined, there are three objectives for a proper pesticide rinsate disposal facility: 1) containment of the waste in order to minimize the risk of environmental pollution; 2) reduce the volume of waste requiring further disposal; and 3) maximize the amount of waste destruction. Of these, Yoder (1992) contends that meeting the first two goals provides the greatest risk reductions and cost savings, with any amount of degradation being a bonus. Although containment is the least complicated of

the disposal system objectives, degradation and volume reduction are more complex. From the previous discussions, a variety of waste detoxification and volume reduction schemes have been proposed. In general, three classes of approaches have been suggested. One approach involved completely ignoring the degradation process and concentrating efforts on reducing the volume of contaminated material. In the second, efforts were geared toward the complete destruction of the pesticide yielding a non-toxic effluent and thus negating the need for volume reduction. Yet another approach centered around a combination volume-reduction/degradation process.

All of the above-described methods possess varying degrees of positive qualities and, for the most part, appear to be somewhat viable options for the disposal of dilute pesticide waste solutions. Recall, however, that the originally stated goal of any realistic system was to execute the proper disposal of these wastewaters in a simple, inexpensive, and environmentally safe manner. Thus, upon further reflection, it is evident that the vast majority of these methods have drawbacks of some form which would preclude them from satisfying these outlined criteria. These objectionable qualities include being cost prohibitive, being extremely complex (technologically or management-wise), requiring further disposal of a residual wastestream, being environmentally unacceptable, being currently unavailable (in the research/development stage), containing uncertainties, or yielding questionable results.

For all practical purposes, it appears that the evaporation/degradation-type systems hold the most promise as a realistic approach for farmers and applicators looking for a

simple, safe rinsate disposal option. The concept behind these soil beds is not complex and is easily applicable to a wide variety of situations. The literature points to promising results from these original systems. Not only do these digestors provide excellent containment of the rinsate material, but they also exploit the characteristics of the waste solution for the ultimate disposal process. Within a single process, these systems employ both evaporation and biodegradation to achieve substantial reductions in the volume of waste and destruction of the pesticide molecules, respectively. Additionally, the process yields no residual wastestream requiring further disposal.

CHAPTER III:

SOIL BED VARIATION (OPTIMIZATION)

RESEARCH GOAL AND OBJECTIVES

Based upon knowledge gained from the extensive review of available technology options, a variation of the evaporation/degradation pits was proposed as the system holding the most promise and as the disposal option of choice for residual rinsate materials. Though there is a long history of using soil bed systems for pesticide waste reduction and degradation, none of the reports indicate that much background analysis went into their designs. The literature points to promising results from these original systems, but it seems as if little scientific consideration was given to the design, operation, and evaluation of these pits. Apparently, these initial efforts were mainly fueled by application needs and only as an afterthought were attempts made to scientifically evaluate their performance and applicability. As Yoder (1992) describes it: "They were set up specifically to meet evaporation requirements, with little attention given to optimizing either evaporation or degradation rates." Therein lies the goal of this research endeavor: to provide background information regarding the conditions and techniques which might optimize these rates.

More precisely, the objectives of this study can be broken down into four phases

as outlined below:

1) review and identify the factors/variables which influence the evaporative and degradative processes of a soil bed system;
2) design and construct an apparatus for the controlled evaluation of these variables within a laboratory setting;
3) determine the best combination of variables yielding optimal performance of a soil bed system;
4) based upon the research conclusions, provide recommendations for the logical design of an effective prototype pesticide rinsate reduction/degradation unit according to the soil evaporation bed concept.

INFLUENTIAL FACTORS

As previously acknowledged, the greatest economic advantage for the proposed pesticide disposal system lies not in its degradation capabilities, but in its volume reduction abilities, with degradation as a very desirable side effect. Pesticide degradation within the soil bed may be a secondary goal, but it is still very important to maximize its effect without significantly reducing evaporation. Thus, the desired system will give maximum or near-maximum evaporation, while at the same time keeping degradation relatively high. With this in mind, the parameters of interest are not those that specifically affect evaporation nor degradation, but rather those that affect both processes.

Evaporation

Given that the main objective of such a unit is to reduce the volume of waste via evaporation of the water constituent, careful examination of the factors controlling evaporation under this situation is a must. Evaporation of water from a soil surface is

basically controlled by a vapor-pressure gradient: the difference between vapor pressure at the soil surface and that of the atmosphere. This vapor-pressure gradient, in turn, is related to a variety of climatic and soil factors (Brady, 1990). According to Hillel (1982), three conditions are required for evaporation from a given body. Two of these conditions — supply of energy and removal of vapor — are influenced by meteorological factors such as air temperature, humidity, wind velocity, and radiation. Combined, these factors are what he terms the "atmospheric evaporativity" and determine the rate at which the atmosphere can vaporize water from a free-water surface.

The importance of these factors is clearly evident in the Penman equation. As most evapotranspiration and irrigation experts acknowledge, the work of H.L. Penman in 1948 resulted in the best known method for predicting evapotranspiration. Although there are a number of representations of the Penman method, this discussion will look at the FAO Modified Penman Method as described by Cuenca (1989). As he relates, this version of the Penman method was developed utilizing worldwide meteorological data in comparison to actual lysimeter data. This form of the Penman equation is given by:

$$ET_r = c\left[\frac{\Delta}{\Delta+\gamma}R_n + \frac{\gamma}{\Delta+\gamma}(0.27)(1.0 + 0.01U_{2m})(e_s - e_a)\right] \qquad \textbf{(1)}$$

where:

ET_r = reference evapotranspiration for grass, mm/d
c = calibration coefficient based on meteorological data
$\frac{\Delta}{\Delta + \gamma}$ = weighting function for elevation and temperature

Δ = slope of saturation vapor pressure versus temperature curve at T_{mean}
γ = psychrometric constant (relationship between vapor pressure deficit and wet bulb depression)
R_n = net radiation, equivalent mm/d
U_{2m} = wind run at 2 m height, km/d
Δe = vapor pressure deficit, mb
= $e_s - e_a$
e_s = saturation vapor pressure at T_{air}, mb
e_a = mean actual vapor pressure of air, mb

where:

$$\frac{\gamma}{\Delta + \gamma} = 1 - \frac{\Delta}{\Delta + \gamma} \qquad (2)$$

and:

c = $f(Rh_{max}, U_{day}/U_{night}, R_s, U_{2day})$
RH_{max} = maximum relative humidity, percent
R_s = solar radiation, mm/d
U_{2day} = daytime wind speed at 2 m height, m/s
U_{day}/U_{night} = day to night wind run ratio (daytime arbitrarily chosen as 0700-1900 hrs)

As the atmospheric evaporativity becomes more conducive to the evaporation process, a greater suction is placed upon the soil surface. The suction actually pulls water upward through the soil profile toward the surface. However, this rate of capillary rise is only partially dependent upon suction. As Hillel (1982) reveals, the ability of the soil to supply water to the surface is the third and final condition required for the evaporation process. Although the availability of water should not be overlooked, the rate of water movement through the soil profile is largely dependent upon the hydraulic conductivity of the soil in relation to the suction. Hydraulic conductivity basically describes the soil's ability to transmit water and is determined by the nature and size of pore spaces through

which the water moves (Foth, 1990). The rate of water flow is greater through larger pores than through smaller pores. Hence, soil texture plays a key role in the rate of evaporation since coarse-textured soils have higher hydraulic conductivity values than do finer-textured soils (Freeze and Cherry, 1979).

In examining these factors controlling evaporation, it is essential to keep in mind the ultimate goal of designing a practical system, which may limit the degree to which some of them can be manipulated. Thus, it is apparent that three influential factors are susceptible to manipulation with minimal effort. These include temperature, air flow (wind), and soil texture. These factors are readily controllable in a lab setting, in addition to being transferrable and easily manipulated in an actual field-scale disposal unit. Readily available soils of varying characteristics could be used in an actual unit. Simple use of fans and heaters can be employed to adjust not only air flow but temperature. Economics, in terms of energy costs, however, could limit the degree of heating and blowing air across the surface of the evaporation bed.

Since most experts agree on preventing precipitation from entering the unit, a roofing system is a must. With a little forethought this design criteria could be used to "kill two birds with one stone." Although Egg et al. (1980) reports reductions of evaporation rates of about 25% for most roofing materials, by careful design the disposal unit could be covered in such a manner as to create a greenhouse-type effect, thereby raising the temperature for enhanced evaporation due to radiation effects, in addition to providing protection from the elements.

Degradation

Pesticide degradation within a soil bed may be secondary to the goal of evaporation, but it is still important to maximize this effect. Again, it is important to realize that in this initial effort the main interest revolves around the general concept of an evaporation/degradation system. At this time no attempt will be made to investigate very specific processes such as separating chemical degradation from microbial degradation, since these are often strongly intertwined. Likewise, no effort will be spent concerning such topics as specific degradation pathways, actual microbial characteristics or nutrient enhancements, to name a few. Such issues, although important, warrant address in follow-up studies. Thus, only general environmental and soil factors pertaining to pesticide degradation in a soil environment are of concern at this time.

Omitted Factors

Because we are concerned with factors that contribute to both evaporation and degradation, we can narrow down the variables of interest which will help us achieve our desired goals. First, the factors that control pesticide degradation in the soil are more numerous than those that control evaporation. Several of the factors that contribute to degradation have no influence on evaporation whatsoever. For instance, soil pH can be eliminated for a couple of reasons. It appears that some pesticides degrade more readily in acidic soils while others quickly degrade in alkaline soils (Schoen and Winterlin, 1987; Stehunathan et al., 1982; Winterlin et al., 1989). Johnson and Hartman (1980) demonstrated that a soil-based degradation pit operated satisfactorily even though its pH

ranged from 6.6 to 8.2 over the course of their study. Since the goal of this project is to handle a wide variety of pesticides, we will select a soil with a fairly neutral pH. Also, the pH of the soil will have little or no effect on the evaporation rates of the unit.

Soil organic matter is another variable that can be eliminated. Although some research indicates that higher organic matter content leads to increased degradation of pesticides (Sethunathan et al., 1982; Ashton, 1982; Schoen and Winterlin, 1987; Mirsatari et al., 1987; Craigmill and Winterlin, 1988; Winterlin et al., 1989), it is not clear how much of this is due to its effect on the physical properties of the soil, and how much is due to the use of the organic matter by microbes as a food source. Work by Junk et al. (1984) shows that addition of a food source other than organic matter can inhibit pesticide degradation. Though this result is limited to specific conditions, it provides some indication that the effectiveness of organic matter is due to its physical properties rather than to its importance as a food source. Soil microorganisms will consume the organic matter within a soil environment, so maintaining it over time would require regular additions. Unless some form of soluble organic matter was used, this would be difficult in this type of digestor due to safety concerns, as the contaminated soil would need to be physically manipulated.

Still a third factor which influences pesticide degradation but can be eliminated from this study is the pesticide mixture and concentration. It has been shown that high pesticide concentrations inhibit degradation (Mirsatari et al., 1987), with Junk et al. (1984) seeing this effect for concentrations of 4000 ppm but not for concentrations of 200 ppm.

In our study, we should never reach concentrations high enough to inhibit degradation, since Seiber (1988) estimates the concentration of typical pesticide tank washwater to be 100 - 1000 ppm, and that of water used to rinse the exterior of the application equipment to be in the range of 10 - 100 ppm. Sethunathan et al. (1982) indicate that there may also be some inhibiting effect due to the overall concentration of the mixture rather than to some increased toxicity or resistance to degradation.

Temperature

Temperature, on the other hand, is a parameter worthy of a closer investigation. Higher temperatures led to both increased microbial and chemical activity, with Brady (1990) reporting a temperature range of between 21-38°C [70 - 100°F] as best for optimal microbial growth. Thus, the best temperature range for this design would be the highest that the system could maintain within this range. The importance of temperature led earlier scientists to place these initial systems below grade. However, this is no longer an acceptable practice; conditions dictate an above-ground unit. This being the case, without ready sources of waste heat, Yoder (1992) foresees practical use of this effect as probably being limited to tempering winter air by passage through below-ground tubes or through the use of passive solar technology. He goes on to say: "Any attempt to raise temperatures would also have to be balanced against the need for good airflow to maximize evaporation rates."

Soil Moisture

Soil moisture is another influential parameter in the soil biodegradation process. Research has shown that some pesticides degrade faster under aerobic conditions, while others degrade faster when conditions are anaerobic. Since it is desired to design a system capable of handling a broad spectrum of agricultural chemicals, the optimum degradation will occur in a unit providing opportunity for both modes. As Craigmill and Winterlin (1988) realized and expanded upon:

> ". . . there is no one factor that is best for all pesticides or even within a classification of pesticides. The conditions that may be optimum for one pesticide may not be for another. Therefore, the more degradation processes that can be incorporated into the dilute pesticide solution disposal process, the more effective it will be in degrading mixtures of pesticide."

Two such techniques have been suggested and used but never compared. The first is to introduce water to the bottom of the soil matrix at a rate which keeps the soil surface moist, providing a sufficient supply of water for evaporation (Hall, 1984; Winterlin et al., 1984; and Craigmill and Winterlin, 1988). In this technique, the rinsate is passed through an anaerobic section in the lower portion of the soil matrix, and through increasingly aerobic conditions as the wastewater rises through the soil. The other technique involves periodically flooding the soil surface with water, leading to anaerobic conditions throughout the majority of the matrix, and then increasingly aerobic conditions as the soil is drained and dries out (Sethanathan et al., 1982; Brown, 1986; Seiber, 1988; and Winterlin et al., 1989)

Soil Type

Although some limited work has been done on the effect of soil type on pesticide degradation (Schoen and Winterlin, 1987), there are two practical limits which make a medium-textured loam a desirable choice. Yoder (1992) points out that in addition to affecting the rate of water movement, soil properties also influence the number of sites available for chemical and microbial activity. Hence, the selection of a tight clay-rich soil can be excluded due to the need of maintaining reasonable evaporation rates and a supply of pesticides to the active chemical and microbial sites. Likewise, the necessity of maintaining a relatively large number of biologically and chemically active sites excludes the use of a loose sandy soil.

Time

One final variable deserving of attention is the effect of time. It is of interest to determine what effect, if any, the amount of time that the pesticides spend in the system will have on the degradation of the chemicals. Since a realistic soil digestor unit will be in operation for numerous years, will continual operation affect the performance of the system? Initial indications from early research points to successful operation with no pesticide build-up within the soil pits over time (Junk and Richard, 1984; Winterlin et al., 1984).

VARIABLES OF INTEREST

Given the information described above, the variables that influence both degradation and evaporation and are of interest in this study can be narrowed down to include:

1) temperature
2) soil texture
3) evaporation rate
4) mode of application
5) time

EVALUATION OF VARIABLES

In order to test the methods and optimize the variables, individual soil columns were built to simulate the conditions of a soil disposal bed. Each soil column was built out of PVC pipe and equipped with individual bottles for the supply of pesticide solution. These soil columns were then placed inside constructed air chambers where the temperature and evaporation rates could be controlled.

Temperature

In general, higher temperatures induce both higher evaporation rates and increased microbial activity. The effect of temperature was studied by using the ambient air temperature as a lower value, and heating this air to provide a higher temperature. This provided an indication of the effectiveness of placing the evaporation beds in a greenhouse or otherwise heating the bed and ventilation air.

Soil type

Soil texture, the second variable, not only affects the rate of water movement through the soil profile, but also the quantity of sites available for chemical and biological activity. Two soil types were used in this study, a medium fine (silty-loam) soil and a medium coarse (sandy-loam) soil. Since a realistic system would use a readily available soil, by choosing these two soil types an indication of the performance of relatively normal soil characteristics may be gained.

Evaporation rates

Next, the evaporation of water from the soil surface affects the rate of water movement through the soil, which has an impact on both volume reduction and degradation. By blowing air across the soil surface at different velocities, the evaporation rates can be changed. Two air velocities were used in this study, thus creating a high and a low evaporation rate.

Application modes

The mode of application of the pesticide solution to the soil was also considered. How the contaminated solution is applied to the soil impacts both the evaporation and degradation rates, since it controls both the availability of water at the soil surface and the relative sizes of aerobic and anaerobic regions within the soil columns. Based upon techniques proposed in the literature, two general approaches of applying the wastewater

were examined. The first was the flooding approach, in which the entire soil column was placed under alternating aerobic and anaerobic conditions. Since some pesticides are better degraded by aerobic microbes while others are more likely to be digested by anaerobic microbes, this approach forced the pesticides through first one form of degradation and then the other. This was accomplished by repeatedly saturating the soil and then letting it dry through evaporation.

For these flooding-type columns, the alteration between aerobic/anaerobic conditions was further explored by varying the cycle durations under each condition: a short cycle (termed short flood or SF columns) and a long cycle (termed long flood or LF columns). The columns underwent either a 5-day or 10-day saturation cycle to reflect performance differences, if any, regarding the amount of time spent under the various conditions. In order to accomplish this, the columns were first saturated with pesticide solution (i.e., anaerobic conditions) for either five or 10 continuous days. They were then allowed to dry out via evaporation (i.e., increasingly aerobic conditions) for the same respective length of time, after which they were re-flooded and the process begun again. This cycling continued throughout the study period, every five or 10 days.

The wicking approach is based on introducing water to the bottom of the soil column and allowing it to rise to the surface through capillary action. The concept of this approach is that the pesticides in the water will first undergo anaerobic degradation in the saturated area in the bottom of the soil column and in the capillary fringe, and then aerobic degradation in the unsaturated capillary rise portion of the column. The amount of time

that the pesticide solution spends in the aerobic zone is controlled by the soil characteristics and the rate of evaporation from the surface, but the amount of time that the solution spends in the anaerobic zone can be changed. By altering the depth of the soil below the free water surface, this goal was accomplished, subsequently having two different anaerobic zones. Thus, by simply changing the column length, the depth of the anaerobic zone was changed.

There were two different wicking-type columns based upon differing anaerobic zones: a deep column (long wicking - LW) and a shallow column (short wicking - SW). The columns with larger anaerobic zones were simply longer than the columns with smaller anaerobic zones. This additional length was added to the lower portion of the columns, thus maintaining the size of the upper aerobic zones for all columns.

Time

In order to test the effects of time in regard to the performance of the system, columns were continually operated for various amounts of time. Analysis of soil contamination levels were performed at day 0 and after the water had been evaporating for 30, 60, 120, and 180 days. This provided indications not only as to the amount of pesticide degradation occurring, but also the degree, if any, to which pesticides appeared to be building up within the soil.

Statistical design

The statistical design of the study was completed after defining the variables of interest and after discussions with the University of Tennessee Experiment Station statistical consultants. A partial factorial design would only yield information regarding the main effects and specific interactions. The main effects were already known and were of only minor interest to us, since we were concerned with the interactions of the variables. Thus, by using a complete factorial design, all possible combinations could be tested. A single replication of this design required $4*2^3*4 = 128$ treatment combinations (i.e., 4 application modes, 2 soil types, 2 temperatures, 2 air flow rates, and 4 times). However, having only a single replication provides no information on within-treatment variability. By the nature of the processes, this variability was expected to be high, requiring a large number of replications. Going beyond four replications becomes unrealistic because of the number of samples needed for each incremental increase in the quality of the results. Thus, with four replications, 512 soil columns were needed to properly conduct this study.

Contaminant mixture

The majority of farmers rely on limited equipment for a variety of application needs and hence produce rinsates consisting of various compounds. Therefore, any realistic soil/evaporation bed unit must be capable of handling a wide variety of mixed pesticide-containing solutions. Thus, the initial phases of this research effort looked at a limited mixture of pesticide compounds. Two herbicides, atrazine and fluometuron, were

mixed at low concentrations. These two chemicals were picked for a variety of reasons. To begin with, both compounds are widely used throughout the region. Atrazine is the most heavily used herbicide in corn across not only Tennessee, but also nationally. Likewise, fluometuron is one of the most widely used cotton herbicides in the state. Of additional concern was mixing the chemicals at concentrations equivalent to those reported of rinsate materials and being able to handle them within a laboratory setting. Thus, the chemical's properties dictated to some extent the compounds finally chosen.

Atrazine

Atrazine [6-chloro-N-ethyl-N^1-(1-methylethyl)-1, 3, 5-triazine-2, 4-diamine] (Figure 13) first became commercially available for use in corn in 1958.

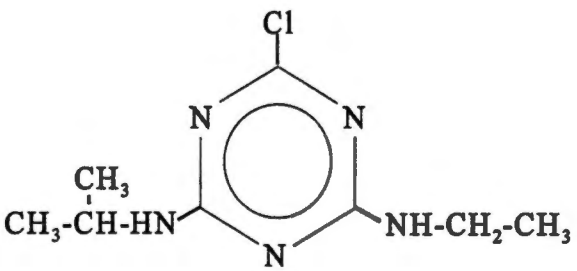


Figure 13. Structural formula of atrazine.

Principally registered and manufactured by Ciba Plant Protection Company, this triazine herbicide is regarded as the most heavily used pesticide in the United States. According to EPA estimates, Ware (1994) reports that about 36 million kilograms [80 million pounds] of atrazine active ingredient was used throughout the U.S. in 1991, primarily on

corn. With normal application rates of 1.1-2.2 kg ai/ha [1-2 lb ai/A], this restricted use herbicide provides season-long control of many broadleaf weeds as well as certain grasses, mainly in corn and sorghum. Either readily absorbed through roots from soil application and translocated to shoots or readily absorbed into leaves from postemergence applications, as its mode of action atrazine inhibits photosynthetic electron transport (Ahrens, 1994; and Ware, 1994). The Herbicide Handbook, 1994 edition, characterizes atrazine as being moderately adsorbed to soil, with increasing adsorption at lower pH's, and having relatively low losses due to volatilization. In terms of persistence, Ahrens (1994) reports an average field half-life of 60 days. He further indicates that, except in fairly arid climates, most rotational crops may be planted one year after atrazine application. Transformation properties applicable to this research study surround its biological and non-biological degradation. Biologically, the Herbicide Handbook reports a half-life of 146 days for aerobic and 159 for anaerobic microbial metabolism in a loam soil at 25°C [77°F] under laboratory conditions. In terms of non-biological degradation, the same reference indicates slow soil hydrolysis rates at high pH (pH 7.5 - 8) with hydrolysis becoming the major contributor to degradation at lower pH (pH 5.5 - 6.5), forming the hydroxy atrazine metabolite (Ahrens, 1994). Other important physical and chemical properties of this herbicide are listed in Table 5.

Table 5. Important physical and chemical properties of analytical atrazine and fluometuron.

PROPERTIES	ATRAZINE	FLUOMETURON
Chemical family	Triazine or s-Triazine	Phenylurea, substituted urea , or urea
CAS #	1912-24-9	2164-17-2
Molecular formula	$C_8H_{14}ClN_5$	$C_{10}H_{11}F_3N_2O$
Physical description	White, crystalline	White crystalline solid, odorless
Density	0.363 g/mL @ 20°C	0.408 g/mL @ 20°C
Melting point	175-177°C	163-164.5°C
Boiling point	Unknown	~280°C @ 760 mm Hg
Vapor pressure	2.9 x 10^{-7} mm Hg @ 25°C	5 x 10^{-7} mm hG @ 20°C
Stability	Decomposed by UV light; weak hydrolysis in water at pH 7, rates increasing at lower and higher pH	Hydrolizes slowly at pH 1 (half-life is 580 d @ 20°C)
Solubility	Water: 33mg/L @ 22°C & pH 7	Water: 110 mg/L @ 22°C
Acute toxicity (of technical grade chemical):		
1) oral LD_{50} (rat)	3090 mg/kg	6416 mg/kg
2) dermal LD_{50} (rabbit)	>3100 mg/kg	>10,000 mg/kg

Source: Ahrens (1994)

Fluometuron

Fluometuron [N, N-dimethyl-N^1-[3-(trifluoromethyl)phenyl] urea] (Figure 14) was first reportedly used in 1964 (Ahrens,1994). With Ciba Plant Protection Company being the primary industry source, Mueller and Moorman (1991) and Brown (1994) indicate that fluometuron is a widely used herbicide for weed control in cotton. At normal application

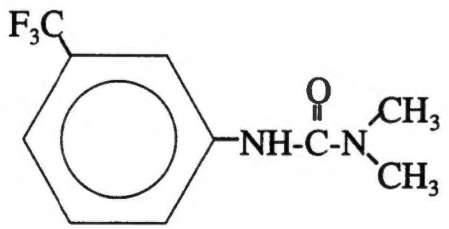


Figure 14. Structural formula of fluometuron.

rates of 1.1-2.2 kg ai/ha [1-2 lb ai/A], this general use herbicide provides pre- and postemergence control of many broadleaf and grass species in cotton. Readily absorbed by roots after soil application and translocated to the shoots, as its mechanism of action fluometuron inhibits photosynthesis by blocking electron transport (Ahrens, 1994). The Herbicide Handbook, 1994 edition, characterizes fluometuron as being moderately adsorbed to soil and having negligible volatility losses. In terms of persistence, Ahrens (1994) reports the average half-life of fluometuron to be 85 days. He further indicates that fluometuron residues often dissipate to nondetectable levels by four months after application at recommended label rates. Although transformation properties applicable to this research effort center around biological-based degradation, fluometuron is apparently highly photodegradable. Even though microbial metabolism is the most important contributor to field dissipation, the Herbicide Handbook reports the rates as being moderate. For aerobic and anaerobic microbial metabolism in a sandy loam soil at 25°C

[77°C], the half-life of fluometuron is reported at 189 days and 378 days, respectively. Under these conditions, the major degradation metabolite was mono-N-dimethylated fluometuron (Ahrens, 1994). Mueller and Moorman (1991) further indicate that the three major soil metabolites of this herbicide include: desmethyl fluometuron, 3-(trifluoromethyl)phenyl urea, and 3-(trifluoromethyl) aniline. Non-biologically, degradation is negligible at pH 5, 7, and 9 (Ahrens, 1994). Other important chemical and physical properties of this pesticide are listed in Table 5.

CHAPTER IV:

MATERIALS AND METHODS

THEORY, CONCEPTS, AND CRITERIA

Understanding the reasoning behind the construction of the various components of the laboratory apparatus requires a general grasp of the overall concept. As was briefly alluded to earlier, in order to test the methods and optimize the variables, individual soil columns were prepared to simulate the conditions of the actual soil disposal bed. Each soil column had associated with it an individual solution bottle supplying pesticide-laden water to the soil. The desire was to design the column/bottle system such that the soil uptake of the solution would be a continual process, driven by evaporation rates. The design criteria also mandated that the solution be introduced at the bottom of each column, thus relying on capillary rise for movement of the solution through the soil matrix. In order to accommodate the various modes of rinsate application, the columns had to be designed such that the correct anaerobic and aerobic zone lengths were provided. Provisions had to be made for simple and fairly periodic refilling of the solution bottles with minimal interruption to the system.

Once the column was packed with the appropriate soil type, control of the climatic variables required the column's placement in an environment where the airflow and

temperature could be accurately measured and adjusted. Four such environmental chambers (hereafter simply referred to as "air chambers" or "chambers") were used, two with low airflow and two with high airflow. For one from each set, the airflow was at ambient temperature, while for the others heat was added to the airflow. The soil columns were placed in such a way as to heat both the column itself and the air flowing over it. Although intake air was pulled from inside the building, the exhaust air was vented outside to remove any possibility of indoor air contamination. As the earlier cited results indicate, there is little danger to the environment from such venting. In addition to the chambers being sealed and relatively air tight, they also incorporated provisions to accommodate the required draining of the respective flood-type columns.

The initial contaminant solution (a mixture of both herbicides in water) was mixed at a known concentration and stored in a large container. From this mixing tank, the pesticide mixture was supplied to each solution bottle (and thus each soil column). The solution bottles needed to be replenished with mixture as dictated by the column's rate of evaporation. Keeping a continuous record of the quantity of pesticide solution supplied to each column provided not only an indication of its evaporation requirements, but also of the mass of pesticide added to the soil. At the end of each of the four time periods, the soils from the associated columns were analyzed for pesticide contamination levels. Thus, a simple mass balance procedure yielded the amount of degradation which occurred within each individual column. An indication of the most desirable treatment combination was then obtained from statistical analysis of the evaporation and degradation data.

SET-UP

Given this general grasp of the basic ideas behind this research effort, how could these concepts be developed into a workable system? This entailed the design and construction of all the necessary apparatus components such that they performed in an acceptable manner. Before any actual tests could be run or data collected from this research project, several initial steps were involved. These included:

- development, design, and construction of the soil column/solution bottle system;
- obtaining and preparing all soil (both types),and additional placement of soil into the columns;
- design, construction, and calibration of the air chambers, including airflow, temperature, and electrical considerations, etc.;
- development and construction of the rinsate systems, including both the mixing and the distributions systems.

The remainder of this section will address each of these areas in more detail.

Soil columns/solution bottles

Theory of Operation

Each soil column was built out of PVC pipe and equipped with two fittings (plastic elbows) in the side of the column. These were connected by vinyl tubing to a pesticide solution container, which consisted of a plastic bottle, a rubber stopper, and four glass tubes coming out of the top of the bottle through the rubber stopper. Two of these glass tubes were connected to the soil column via the vinyl tubing. The siphon tube was connected to the column's bottom fitting and to the glass siphon tube, which extended down to the bottom of the solution container. This connection supplied the pesticide

solution from the container to the bottom of the column. Another glass tube was connected to the column's top fitting. This glass tube and the remaining two extended a short distance into the solution container, stopping short of the surface of the solution. This connection acted like a vacuum line by allowing air to escape from the column, through the tubing and back into the solution container, thus allowing more solution out of the bottle and into the bottom of the soil column.

The solution containers were placed higher than the soil columns. This allowed the solution level in the containers to be kept above the level in the soil column. Once the soil column filled up with solution to the top fitting, the vacuum tube (the one leaving the column) filled with solution until it reached the elevation of the solution level in the container. The portion of the column from the lower fitting to the upper fitting was saturated with the pesticide solution, thus creating an anaerobic environment. The upper portion of the column, from the top fitting to the top of the column, was only moist with pesticide solution, thus creating an aerobic environment. With this set-up, the wicking columns possessed both aerobic and anaerobic zones within the same column. For the flood-type columns the fitting was placed very high on the column, so the whole column was saturated (i.e., anaerobic). To achieve aerobic conditions, the column was drained and allowed to air dry. See Figure 15 for a conceptual view of the various zones of saturated/unsaturated (i.e., anaerobic/aerobic) conditions within the columns.

The remaining two glass tubes in the solution containers (together termed access tubes) were used to refill the container with pesticide solution. In order to refill the

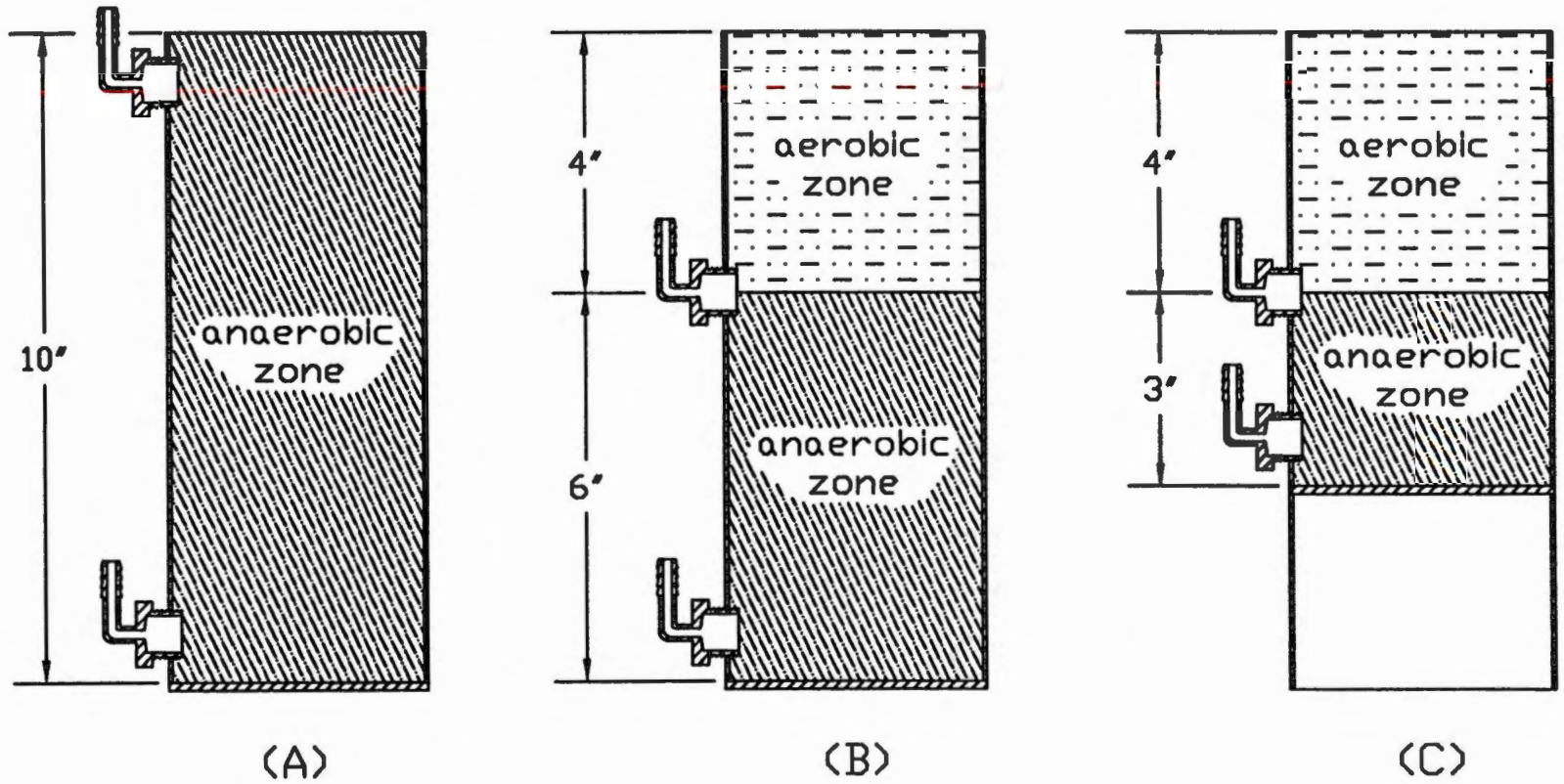


Figure 15. Conceptual drawing of soil columns showing the various saturated/unsaturated zones (i.e., anaerobic/aerobic conditions). Column (A) is a flood/dry column; column (B) is a 10"-wicking column; and column (C) is a 7"-wicking column.

containers, both the siphon and the vacuum tubes were clamped shut and the funnel and vent tubes opened (at all other times the funnel and vent tubes remained shut). This allowed more solution to be pumped through the funnel tube into the container, with the container vented through the vent tube.

Preliminary Experiments

Column design

Because the ultimate goal of this project was to build a fairly large soil disposal bed, the easiest way to conduct research on this type of problem was by using small soil columns to represent the soil bed. Large soil beds could have been used in this study, but complications would arise due to the sampling required. Therefore, enough soil columns with each treatment combination were set up so that the soil from an entire column could be mixed and tested for pesticide concentrations, thereby bypassing sampling complications. As dictated by the statistical analysis, 512 soil columns were needed. Using small columns was the only way of satisfying the requirements.

The soil columns were made out of ten centimeter [four inch] diameter thin-walled polyvinyl chloride (PVC) sewer pipe. It was originally thought that a two inch diameter pipe would be used, but upon further consideration, a larger diameter pipe was chosen for two basic reasons. First, by using a larger pipe diameter, the soil surface area was greater, facilitating better evaporation. Secondly, by increasing the pipe diameter, the edge effects associated with the soil/pipe interface were reduced. A ten centimeter [four inch] diameter pipe was chosen because it was the next larger nominal pipe size, and because anything

larger would cause problems due to space limitations and difficulty of construction.

Column design required answers to a few more questions. The first involved varying the time that the rinsate spent in the anaerobic zone during the wicking process. This goal was accomplished by varying the depth of the soil below the free water surface, creating two different anaerobic depths. This was done by changing the column length. It was found through experimentation that by setting the fittings at a distance of ten centimeters [four inches] from the top of the column for the aerobic zone, sufficient capillary rise occurred to keep the soil surface moist. Initially, it was thought that this distance might vary with varying soil textures. However, by experimenting with a 2:1 soil/sand mixture, it was found that the difference in the height of capillary rise was not sufficient enough to warrant a change. Further experiments with a range of varying soil/sand ratios showed little differences in capillary rise, so a ten centimeter [four inch] aerobic zone was used for all cases in the wicking process. The saturated zones were set at 15 cm [6 in.] and 8 cm [3 in.] so as to satisfy the need for two different lengths of time which the solution spent in the saturated zone.

The flood/drain type columns were a little different. For them, the entire column was first placed under anaerobic conditions when saturated, and was allowed to become increasingly more aerobic as it dried out. Thus, for all of these columns the top fitting was placed near the top rim of the PVC pipe. As such, the entire length of the column (25 cm [10 in.]) was saturated during the flood cycle, placing most of the column under anaerobic conditions. In order to achieve aerobic conditions, the supply of solution to the column

was interrupted by moving the associated solution supply bottle from above to below the column and the supply tubes were clamped off. The process of evaporation then dried the soil. Over this drying cycle time period, the soil conditions would become increasingly aerobic. The columns were altered between these two cycles for different durations of time. One set of these columns was operated on a 5-day cycle (5 days wet followed by 5 days dry), and the remaining were run on a 10-day cycle.

Applicator and container design

It was decided that using individual solution containers for each soil column would be best. Other methods were considered, but they seriously complicated the overall system design. For instance, one large tank could have been used to contain all of the pesticide solution. However, some type of piping system would have to have been designed to supply every column with waste solution. This type of pipe and valving system would not have been simple, and would also have complicated the air-chamber design. In addition, measuring the evaporation from each individual column would have been more difficult. By using a single solution container for each column, no pumps or valves were needed, and the evaporation could be monitored fairly easily.

A simple experiment was performed to help determine the size of bottles needed to contain the pesticide solution by estimating the porosity of the two soil textures. The soil itself was determined to have a porosity of approximately 40%, while the porosity of a soil/sand mix was approximately 34%. Therefore, the bottles needed to hold at least 40% of the soil column volume. Based on the column being made of four inch diameter pipe

with a maximum height of 25 cm [10 in.], a 1000 ml [0.264 gal.] bottle was found adequate to contain the pesticide solution for each column.

Column/Bottle Equipment and Supply Considerations

Although pricing played a large part in the decision of one type of item over another in the column and container construction, the main consideration was the type of material used in each item and the possibility of the chemicals affecting it or vice-versa. By utilizing the following materials, there should have been no problems with the atrazine and fluometuron use in this phase: PVC pipe and sheets for the columns; low density polyethylene bottles for the solution containers; high-density polyethylene elbows for the fittings; and glass and vinyl tubing for the piping.

Soil Column Construction

This step involved the actual construction of the soil columns. Because of the large number of columns to be built (512), the construction was done in stages.

Column assembly

This involved cutting the PVC pipe to the desired lengths (384 @ 25 cm [10 in.] and 128 @ 18 cm [7 in.]), and cutting and attaching the PVC bottom plates to the columns. An additional 7.62 cm [3"] PVC pipe base was added to the bottom of all the short 17.78 cm [7"] wicking columns. This was done in order to raise the top surface of the columns even with all of the tall 25.4 cm [10"] ones. By doing so, all 512 columns were at the same height, and were thus exposed to similar airflow conditions across the soil surface. Further column assembly details may be found in Appendix B.

Fitting installation

There were two polypropylene barbed pipe adapter elbow fittings (1.27 cm [½"]-NPT x 0.635 cm [¼"]-ID]) installed into each soil column. The first one was placed in the side of the column, near the bottom, in order to connect the siphon line to the columns. The second fitting was placed higher up on the columns, the location depending upon the type of column (i.e., flooded, short 18 cm [7 in.] wicking, or long 25 cm [10 in.] wicking), in order to connect the vacuum line. For the 256 flooded columns, the top fitting was placed at a distance of 15.9 mm [⅝ in.] below the top edge of the column. The critical factor in this location was the need to keep the soil surface very moist, almost ponded with water, but not overflowing. For the 128 short 18 cm [7 in.] wicking columns, the second fitting was placed eight centimeters [3 in.] above the bottom edge. For the 128 long 25cm [10 in.] wicking columns the fittings were placed 15 cm [6 in.] above the bottom edge. A mesh screen was used to cover the openings of each fitting so as to decrease clogging of the fittings. More column fitting installation details may be found in Appendix B.

Solution bottle assembly

The pesticide solution containers consist of 1000 mL [0.264 gal.] LDPE bottles, rubber stoppers (size 11½), and glass and vinyl tubing (0.635 cm [¼"] I.D.). Each solution container had four glass tubes coming out of the top, through the rubber stopper. Two of the glass tubes were connected to the soil column via vinyl tubing. To eliminate confusion, these tubes were referred to as the siphon and the vacuum tubes. The other two glass tubes were used in the refilling process of the bottles, and were referred to as

the vent and funnel tubes. To each of these access tubes were attached short pieces of vinyl tubing. The glass siphon tube extended from very near the bottom of the bottle, and to about four centimeters [1½ in.] above the rubber stopper. This tube provided the pesticide solution to the soil column from the bottle. The three other glass tubes all extended to about 4 cm [1.5 in.] above the stopper, and only extended inside the bottle about 25 mm [1"] below the bottom of the stopper. These three glass tubes should never come in contact with the solution, hence their short length.

The vinyl access tubes were clamped shut by folding the ends of the tubing over, thus pinching the tube closed. A small capacity 9.5 mm [⅜ in.] paper binder clip (used in office supplies) was placed over the bend in the tube. This clip tightly secured the folded tube, thus providing a sufficient seal against air leakage into the bottle. At initial glance, this seems fairly unimportant, but actually it was critical to the proper operation of the bottle/column system. Any air leakage into the bottle would allow the solution to leave the bottle and enter the column, and the system would free-flow and flood the column. Further solution bottle assembly details may be found in Appendix B. Additionally, a photograph showing examples of all four column types (column/bottle systems) may be seen in Figure 16.

Soil physical characteristics

The soils chosen for this experiment were agricultural-type soils typical of the area. Although the soils chosen were not extremely fine nor coarse, they were sufficiently

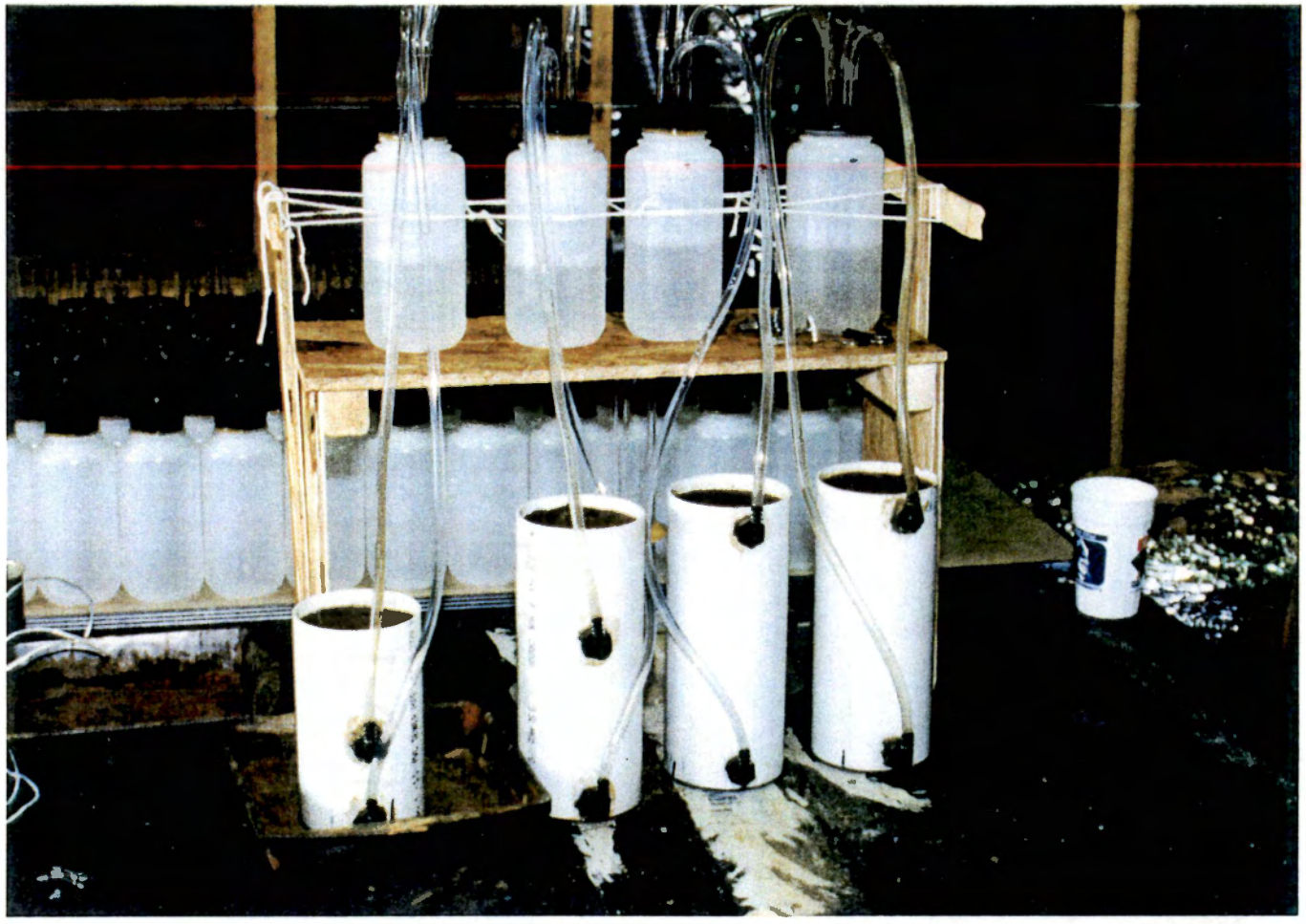


Figure 16. Photograph of the preliminary soil column system set-up. Note the various locations of the fittings. Columns (L to R) include: 7"-wicking (SW), 10"-wicking (LW), 5-day flood/dry (SF), and 10-day flood/dry (LF).

different so as to provide a good comparison of evaporation and degradation. The medium-fine textured soil was collected from The University of Tennessee Plant Science Farm located near Knoxville, Tennessee. Since this farm did not contain a soil of coarse enough texture for our purposes, the other soil type (i.e., medium-coarse texture) was purchased from a local distributor of top soil. Once obtained, the soils were taken to the lab, air dried, and screened before being placed into the columns.

The finer-textured soil was collected from an upper flood plain of the Tennessee River. This soil had previously been removed from a field and stockpiled for research purposes as needed. As can be seen in Table 6, particle size analysis revealed that this soil contained 40.8% sand, 38.8% silt, and 20.4% clay, thus classifying it as a loam (Brady, 1990). From a soil survey map this particular soil was determined to be a Whitwell Loam. In the context of this study, however, this medium-fine textured soil will be referred to as a "silty soil," for simplicity reasons. Other relevant properties of this soil are depicted in Table 7.

The coarser soil was obtained from a local supplier of top soil. This soil, termed by the supplier as a "Black Sandy" soil, supposedly consisted of a top soil/sand mix they collected locally. From our particle size analysis, this soil contained 80.9% sand, 9.1% silt, and 10.0% clay, classifying it as a sandy loam or loamy sand. From Brady's textural triangle, this soil falls along the borderline distinguishing both soil types. For the sake of simplicity, the coarse-textured soil will simply be referred to as a "sandy soil" in the context of this report.

Table 6. Soil particle size classification.

Soil Type	% Sand	% Silt	% Clay
Silty soil	41	39	20
Sandy soil	81	9	10

Table 7. Soil property characteristics.

Soil Type	% Organic Carbon	pH in H_2O	pH in 0.02 M Ca Cl_2
Silty soil			
rep #1	1.20	4.90	4.50
rep #2	1.17	5.00	4.60
average	1.19	4.95	4.55
Sandy soil			
rep #1	0.03	5.00	3.90
rep #2	0.01	5.20	3.90
average	0.02	5.10	3.90

Another preliminary test of the soils involved a background check to ensure that neither had traces of either fluometuron or atrazine. From HPLC pesticide residue analysis, both soils were determined to be free of any atrazine or fluometuron contamination.

Once obtained and transported to the lab, the soils were spread out in thin layers across the plastic lined floor and allowed to completely air dry. Upon drying, the soil was sieved to remove any gravel, organic material, clods, or other foreign matter, and to make the soil aggregate sizes more uniform. Because of the quantity of soil to be sieved, two large box screens (91 cm [36"] x 91 cm [36"]) were built out of lumber and were covered

with 6.35 mm [¼ in.] or 3.175 mm [⅛ in.] hardware cloth. The 3.175 mm [⅛ in.] opening screen was chosen because it was the size closest to the standard 2 mm [0.0787 in.] mesh (No. 10 US Standard Testing) soil sieve. All soil was first passed through the 6.35 mm [¼ in.] screen and then through the 3.175 mm [⅛ in.] screen. Any material not passing through both screens was discarded. The prepared soil was then placed in holding containers (new 121-L [32 gal.] trash cans with lids) and stored until needed for column packing. Refer to S.O.P. #BKC-1 (Appendix A) for actual soil preparation procedures.

The soil packed into the columns was actually only air-dried, and was not oven-dried. However, to perform an exact moisture mass balance on the soil for evaporation purposes required that the soil masses be converted to an oven-dry basis. Since it was unrealistic to oven-dry all 512 soil columns, several samples of each soil type were analyzed for gravimetric moisture content. It was then assumed that all soil columns had the same respective soil moistures since they were all handled in the same manner. From these preliminary tests, it was determined that the initial average moisture content was 1.18% and 3.33% for the sandy soil and the silty soil, respectively.

Column packing

In packing the columns with soil, it was desired that it be accomplished in such a manner so as to assure uniformity and to minimize both within-column and between-column variations. Thus, all similar columns needed to have nearly equivalent soil bulk densities. The column dimensions were known (from their construction), so by weighing them when full of soil the bulk densities could be calculated. All 512 columns were

required to have bulk densities falling within a specified range. A column study reported by Mueller and Banks (1991), achieved bulk densities with a maximum ±2% variation. This was felt to be a realistic goal for our purposes.

Another concern centered around how to add the soil to the columns. From conversations with Dr. Ron Yoder (1994), it was learned that there were several problems associated with packing columns which needed to be addressed. As reported by both Weber et al. (1986) and Mueller and Banks (1991), a standard method used in column studies involves adding small amounts of soil to the column while being agitated on a vortex-type shaker. However, Yoder (1994) pointed out that a common problem associated with this method is that larger particles will tend to move toward the outside edge of the column, while the finer particles tend to remain near the center of the pile. This will change the pore size distribution throughout the column and greatly influence (or have the potential to do so) the movement of water through the column matrix.

According to Yoder (1994), there are several ways to address this problem. The first is by doing nothing. Since all of the columns will be packed in the same manner, they will all have this problem. Therefore, it can be assumed that there will be no column-to-column variations. Additionally, since this is not a major aspect of the study, the effects can be assumed to be negligible. The second approach involves packing the columns by adding soil in small uniform increments, pouring it through a funnel while the funnel is being continuously moved around the inside of the column. After adding a couple of inches of soil to the column in this manner the column is lightly tamped. More soil is

added in the same manner and tamped again, repeating this process until the column is full. In this manner, the soil particles will not tend to separate and will be more uniformly distributed throughout the column matrix (Yoder, 1994).

Based upon this information and the fact that our columns are relatively small in size (diameter-wise), a protocol was developed to assure proper and accurate soil packing of all 512 columns. This standard operating procedure, S.O.P. #BKC-1, may be viewed in Appendix A. Based upon preliminary experiments, the following weight ranges were deemed to yield bulk densities within ±2% for all columns:

- 25 cm columns: 2.766 - 2.877 kg ⇒ Db = 1.397 - 1.343 g/cm^3
  [10 in. columns: 6.07 - 6.34 lb. ⇒ Db = 0.0505 - 0.0485 lb./in.^{3}]
- 18 cm columns: 1.957 - 2.037 kg ⇒ Db = 1.357 - 1.413 g/cm^3
  [7 in. columns: 4.32 - 4.49 lb. ⇒ Db = 0.049 - 0.0511 lb./in.^{3}]

Design considerations for the air-flow chambers

Control of temperature and evaporation rate required placement of the soil columns in environmental chambers. Within these chambers we needed to control the air movement across the column surfaces, thus controlling the evaporation rates. Also, in order to control the temperature within these air chambers, the air blown across the columns needed to be heated to the desired temperature. Four of these air-flow chambers were required, each with a unique combination of air flow rate and air temperature. Each chamber contained a total of 128 soil columns: 64 flooded, 32 - 25 cm [10 in.] wicking, and 32 - 18 cm [7 in.] wicking.

Other design criteria to be incorporated into the air chambers included:

- provide a structure to house the columns and hold their respective bottles;
- move air across the surface of the soil columns;
- provide heat not only to the air flowing above the columns, but also to the columns themselves;
- be able to seal the columns inside the chambers to allow for minimal heat and air losses, while still providing access for the tubing connections to the bottles;
- be able to drain the flood-type columns (i.e., move the bottle from above the columns to below) without disconnecting the associated tubing;
- provide for easy access to the bottles for replenishing the solution;
- incorporate all necessary safety considerations.

One important design consideration involved the positioning of the soil columns and the routing of the air within the chambers. The chambers needed to provide some form of support for the soil columns so as to keep them in position and upright. Additionally, consideration was given to whether or not the chambers should be designed such that the air flowed both around the soil columns themselves and evenly across the surface of the columns, or only across the soil surfaces. It was originally thought that the chambers would need to include some type of covering to be placed even with the tops of the columns. This covering would keep the air flowing evenly across the surface of the columns, and not flowing down the edges and sides of the columns, thus interfering with the maximum evaporation potential.

After considerable thought, it was decided that the best approach was to omit any baffles within the chamber directing air flow. Without directing the airflow, more turbulent patterns resulted, reducing any potential water saturation of the air (Yoder, 1994). An additional plus associated with this air mixing is that the air circulated all around the columns themselves. By doing so, the temperatures of the columns were very close to the air temperatures. This was very desirable, since temperature plays such a vital

role in microbial activity. Recall that temperature needed to be controlled from both the evaporation and degradation viewpoints.

Due to the placement of the columns within a confined area and the large amount of evaporation occurring, as mentioned above, there was some concern associated with the air becoming increasingly saturated with water as it moved from the inlet of the chambers toward the exit. What effect, if any, would this have upon the performance of the columns placed toward the rear of the chamber versus those located closer to the inlet? The mixing effect of the turbulent air flow helped reduce any drastic difference in the water content of the air from one end of the chamber to the other. More importantly, though, it was decided that the soil columns should be placed randomly within the air chambers, so that any differences which might occur could be treated statistically. In the same respect, any temperature differences between the inlet and exit air may be accounted for. Additionally, in terms of temperature, once the chamber systems were started up, they were expected to reach a state of equilibrium within a short time.

Another design consideration centered around sealing the chambers in order to minimize both air and heat losses. All seams and cracks were sealed, in addition to any access hatches being tightly shut and sealing around all tubing access. Additionally, all air supply conduit required appropriate sealing. In order to maintain the temperature integrity of the chambers, all necessary components were appropriately insulated.

A third design consideration involved the actual placement of the solution bottles which supply the mixture to the columns. Since these bottles had to be placed at a higher

elevation than the columns, they were placed on the top of the chambers. The vinyl tubing then ran from the columns, up through the top of the chamber and to the bottles. Placing the bottles outside of the chambers in this manner met several objectives. First, it was much easier to monitor the bottles for evaporation and for refilling. Also, by not being inside of the chambers, they did not obstruct the air flow inside the chambers. Finally, the top and bottom of the chambers were designed so that the bottles could be lowered below the columns in order to drain the flooded columns. Again, the sealing integrity of the chambers (in terms of air flow and heat losses) had to be maintained in the process of moving the bottles from one location to the other.

Yet other design considerations revolved around incorporating all necessary safety features into the chamber design and set-up. One concern was the potential hazard of the exhaust air from these chambers. Upon consulting with Deb Gingrich, University of Tennessee Institute of Agriculture Safety Officer (1994), it was decided to exhaust the air outside at a position at least 4.5-6 meters [15-20 feet] above ground. There were no problems in accomplishing this goal, as the laboratories in the Agricultural Engineering building are equipped with exhaust fans in the ceiling. As the literature pointed out, it was also felt that our laboratory facility should provide for secondary containment in case of spills, leaks, etc. And finally, because pesticides are involved, access to the area needed to be restricted, to some extent, from unauthorized personnel.

The construction process of the environmental chamber apparatus was broken up into stages. This was necessary due to the system size and allowed for more

customization. Following the design and construction of the structural framing portion of the chambers, the airflow system and the heat system were added. After this, all electrical considerations were addressed and components wired accordingly. Only after complete fabrication were the systems calibrated.

Chamber structure design

After a lot of deliberation on several preliminary design approaches, it was decided that the basic structural design of the chambers be in the form of vertical, upright, two-sided cabinets. In concept they resemble an enclosed bookshelf with six shelves. Three shelves were needed per bottle/column combination. The top shelf held all of the solution bottles. The soil columns rested on the middle shelf, and the bottom shelf provided a place for the solution bottles of the flooded-type columns during their draining cycle; the bottles could simply be lowered from directly above the columns and placed directly beneath them with relative ease. Thus, with six shelves, two sets of column/bottle systems would fit within a bookshelf. Additionally, enough shelf depth was provided so that columns could be placed on both sides of the cabinet (see Figure 17 for schematic design).

The only shelves requiring enclosure, though, were those actually holding the soil columns themselves. By utilizing the shelf above the columns and the one on which the columns actually rest, enclosure was accomplished by installing a door to cover the face of the shelf. Provisions were made, however, to seal the top and bottom shelves and the doors to the shelves. Thus, air (under the appropriate conditions) could then be easily

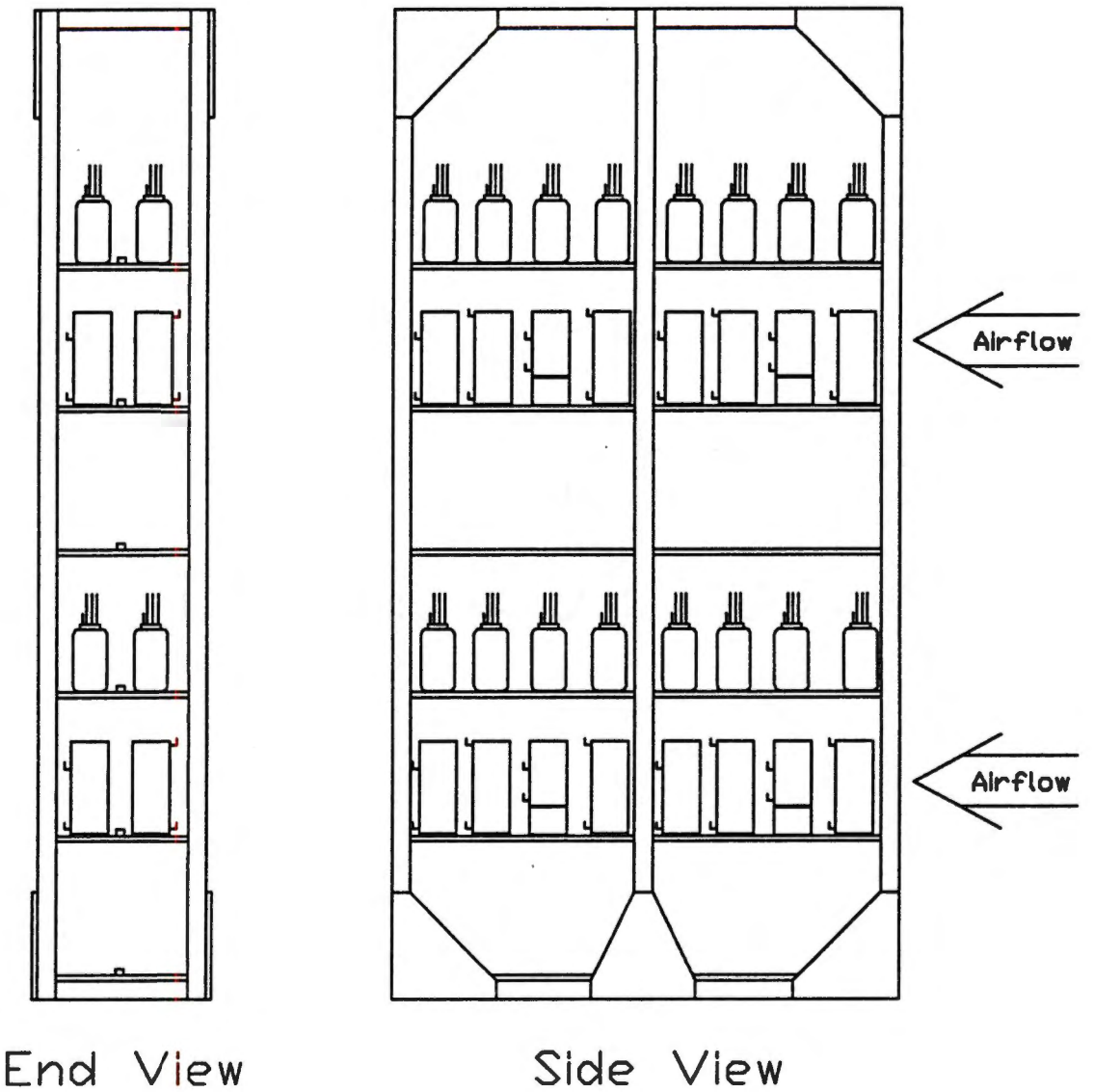


Figure 17. Schematic design of double-sided air chamber sections. Each chamber was assembled from four such 1.2 m [4 ft.] sections bolted together lengthwise. The doors were fastened onto the frame to enclose and seal the sections containing the columns. Air was only pulled through the enclosed sections housing the columns.

introduced at one end of the enclosed shelf and exit through the other. Finally, four such chambers were needed of sufficient length to hold 128 soil columns apiece (i.e., 64 per shelf, front and back). Construction of the structural frame involved simple lumber materials. Each chamber was built in four complete, identical sections. These sections, measuring 1.2 m [4 ft.] in length, were bolted together to give a total chamber length of 4.88 m [16 ft.]. Further details of the chamber construction may be found in Appendix B.

Chamber layout, containment and identification

Safety Considerations

As the literature pointed out, it was felt that our laboratory facility should provide for secondary containment in case of spills, leaks, etc. After consultation with University of Tennessee Institute of Agriculture Safety Officer Deb Gingrich (1994), a simple containment structure was built. Designed to accommodate the pesticide mixture of all 512 full solution bottles if spilled at once, it consisted of a wooden frame (two 2 x 4's stacked together), doubled lined with 5 mil black plastic sheets. Also, to minimize rips and tears and for safety purposes, scrap pieces of carpet were laid over the top of the plastic along the aisles between the chambers. As an additional safety precaution, the area around the laboratory set-up was roped off to deter entrance of unauthorized personnel. Finally, signs were posted warning of a pesticide usage area, along with all chemical label, Material Safety Data Sheets (MSDS), and safety information sheets.

Layout

The four 4.88 meter [16 feet.] long assembled chambers were arranged and positioned inside the containment facility such that they were parallel to one another. They were spaced approximately 76.2 cm [30in.] apart to allow for an aisle between each and along both ends. In order to prevent the possibility of the chambers being overturned, they were fastened together and anchored to the cinder block wall of the building. To accomplish this, 5.08 cm x 15.24 cm [2" x 6"] lumber braces were bolted across the tops of the chambers connecting them together. These braces were then attached to angle iron brackets and bolted to the concrete wall.

Identification

Two forms of identification were used for easy reference and to distinguish the chambers. To begin with, each chamber was labeled based upon its geographic orientation within the containment facility. Thus, the four chambers were labeled: North (N), North-Central (NC), South-Central (SC), and South (S). These labels were then used as an easy reference for their individual climatic conditions. Their layout was as follows:

NORTH ⇒ low air flow and high temperature
NORTH-CENTRAL ⇒ low air flow and low temperature
SOUTH-CENTRAL ⇒ high air flow and high temperature
SOUTH ⇒ high air flow and low temperature

The second numbering scheme involved the 128 individual column locations within each chamber, details of which may be seen in Appendix A.

Airflow system design

Although the routing of the air within the chambers has been discussed, the manner in which the chambers are actually supplied with this air has not. As previously alluded to, the main objective, in terms of air flow, was to provide two distinctive rates; essentially, a fairly low air flow rate and an elevated one. These rates, however, needed to be fairly reasonable; on the order of 11.26-16.09 $^{km}/_{hr}$ [7-10 mph] for the high rate and ⅓ - ½ of that for the low one. Two out of the four chambers needed each of these rates. The air flow system additionally provided a means of adjusting, controlling, and calibrating the rate of air movement within each chamber and between chambers. Also mentioned earlier was the need to exhaust the air outdoors via the building's ceiling exhaust fans. Thus, utilization of these exhaust fans also provided a boost to the air flow rates.

After much consideration, it was decided that blowers would pull air through the length of the chamber (and thus across the enclosed columns) and exhaust it via the ceiling exhaust fan's duct work. Second, it was felt that two blowers, each controlling two chambers, could generate a sufficient quantity of air movement. Basically, a smaller-sized blower provided the lower air flow rate and a larger-sized blower supplied the higher air flow rate. Also, recall that each chamber actually contained two separate enclosed sections, an upper level and a lower level. Connecting to each fan, two enclosure sections from each of two separate chambers required the design and construction of simple intake and exhaust manifold systems.

Airflow system assembly

Blowers

After considerable preliminary calculations, testing and evaluation of several blowers, two particular blowers were purchased and installed. To generate the higher air flow rate, a 3.73 KW [5 Hp] high pressure direct drive blower was purchased. For generation of the lower air flows, a 0.56 KW [¾ Hp] high volume direct drive blower was acquired. Each blower was required to supply two chambers (four shelves), so each fan controlled side-by-side chambers. Thus, it was arbitrarily decided that the South and South-Central chambers be the high air flow chambers and be supplied by the 3.73 KW [5 Hp] blower. This left the North and North-Central chambers as the lower air flow rates chambers supplied by the 0.56 KW [¾ Hp] blower. Fan mounting platforms were constructed out of lumber and placed on top of the chambers, so that the blowers were set above and directly between their associated chambers. Further details concerning the airflow system assembly may be found in Appendix B.

Manifold System Overview

There are basically three components comprising the overall air flow manifold system. The first component is the chamber intake manifold. It is connected to the air inlet end of each individual chamber and directs air into the chambers. The second is the chamber exhaust manifold. Located at the air outlet end of the chambers, it connects the inlets of the blowers to the outlets of each of their two respective chambers. The third and final component is the fan exhaust conduit. It serves as a connection between the

outlet of the blowers and the building's ceiling exhaust fans.

Chamber Intake Manifold

There were actually four separate chamber intake manifolds, one for each of the chambers. Although two chambers were supplied by each blower, the temperature provisions were accomplished by heating the intake air of two of the chambers (discussed in depth in a later section). To achieve the unique combinations of temperature (high and low) and airflow (high and low) required that one chamber of each blower set be heated while the other one was not; this required separate chamber intake manifolds.

There were only slight variations between the two chamber intake manifold systems to which heat was applied and the ones without. The manifold itself was assembled from 15.24 cm [6"] diameter flexible aluminum air duct and a collection of various expansions, tees, and collared flanges (all galvanized steel ductwork grade materials). The benefit of the flexible duct was that it could easily be bent, molded, and shaped to conform to any necessary configuration, thus eliminating the need for many of different duct-fitting accessory items. All duct components were connected and sealed together with 10.16 cm [4"] wide duct tape.

The flexible duct was attached directly to the chamber enclosure end cover plates. Depending upon the chamber, this intake duct was then either connected to a heat box (discussed in detail in a later section) or simply attached to an expansion fitting secured to the chamber tops. Thus, air was drawn into each chamber via separate intakes located along the top of the respective chambers. Figure 18 can be seen for a visual clarification

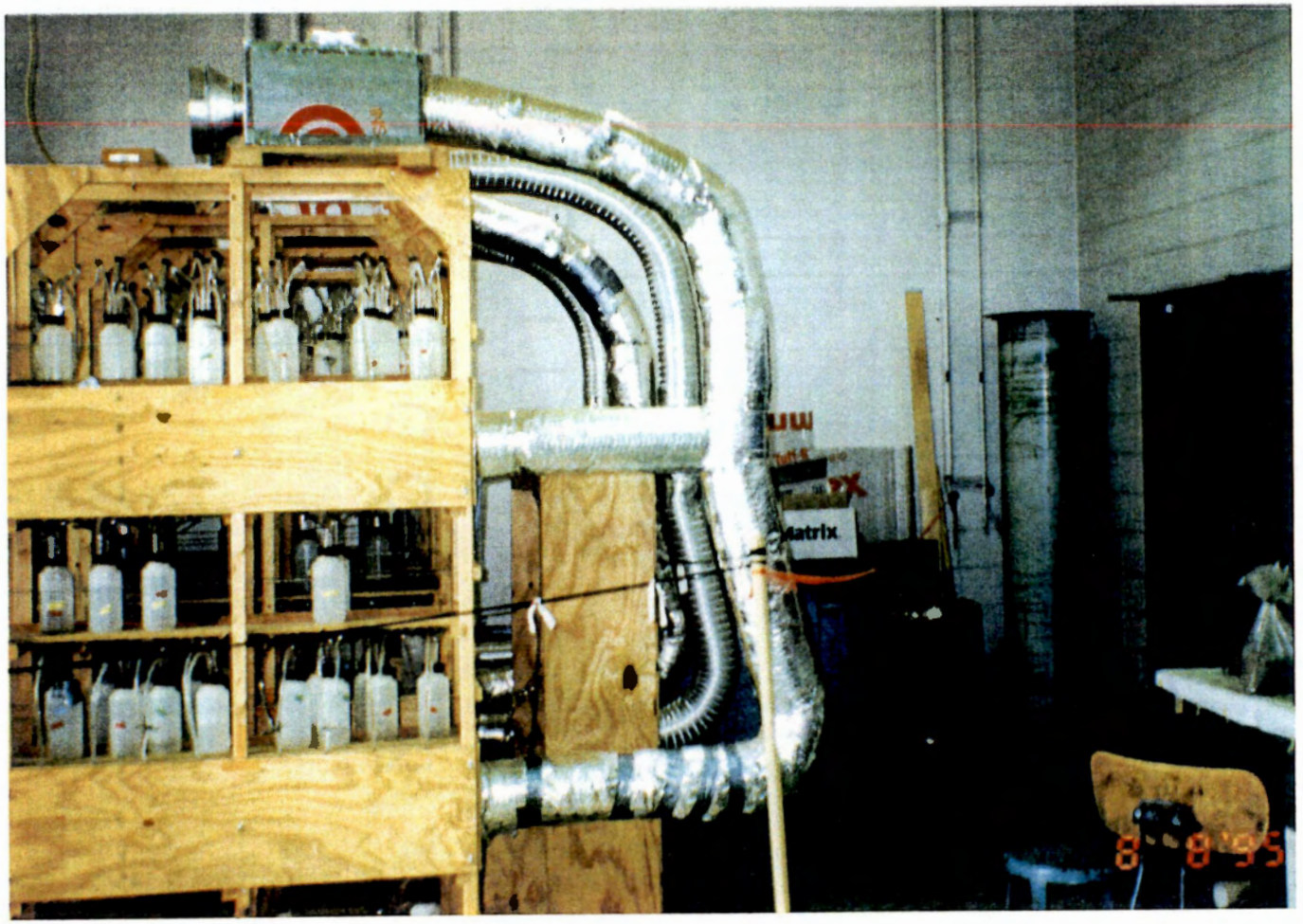


Figure 18. Photograph of the airflow entrance end of the chambers illustrating the intake manifold and the heat box (located on top of the chamber). Note the insulation around the duct and heat box.

of the chamber intake manifold systems. More details concerning the chamber intake manifold may be found in Appendix B.

Chamber Exhaust (Blower Intake) Manifold

The chamber exhaust manifold was assembled from the same general duct components and in a similar fashion to the chamber intake manifold. There were only two minor variations between the two. First, each collared flange attached directly to the chamber levels was equipped with an in-line butterfly valve. As seen in Figure 19 and discussed further later, these dampers could be easily adjusted, thus controlling the air flow in the duct of each separate chamber level. The second variation involved the manifold connection to the blowers. Recall that each blower controlled two side-by-side chambers. Thus, the exhaust ducts from these two chambers had to be connected together and attached to the blower inlet port. Further details about the chamber exhaust manifold may be found in Appendix B.

Blower Exhaust Conduit

It was desired that the chamber exhaust air be funneled outside via the building's ceiling exhaust fans. The particular laboratory housing the chambers contained two such exhaust fans. It was decided to utilize them both; one for each of the two blowers. Flexible duct was used to tie the blower outlet ports to the existing duct of each ceiling exhaust fan. Figure 20 may be seen for a photograph of the exit end of the chambers showing the exhaust maniflod and blowers. More blower exhaust manifold details may be seen in Appendix B.



Figure 20. Photograph of the airflow exit end of the chambers illustrating the exhaust manifold and the blower (located on top of the chamber). Note the removed chamber door revealing the columns enclosed in the chamber.

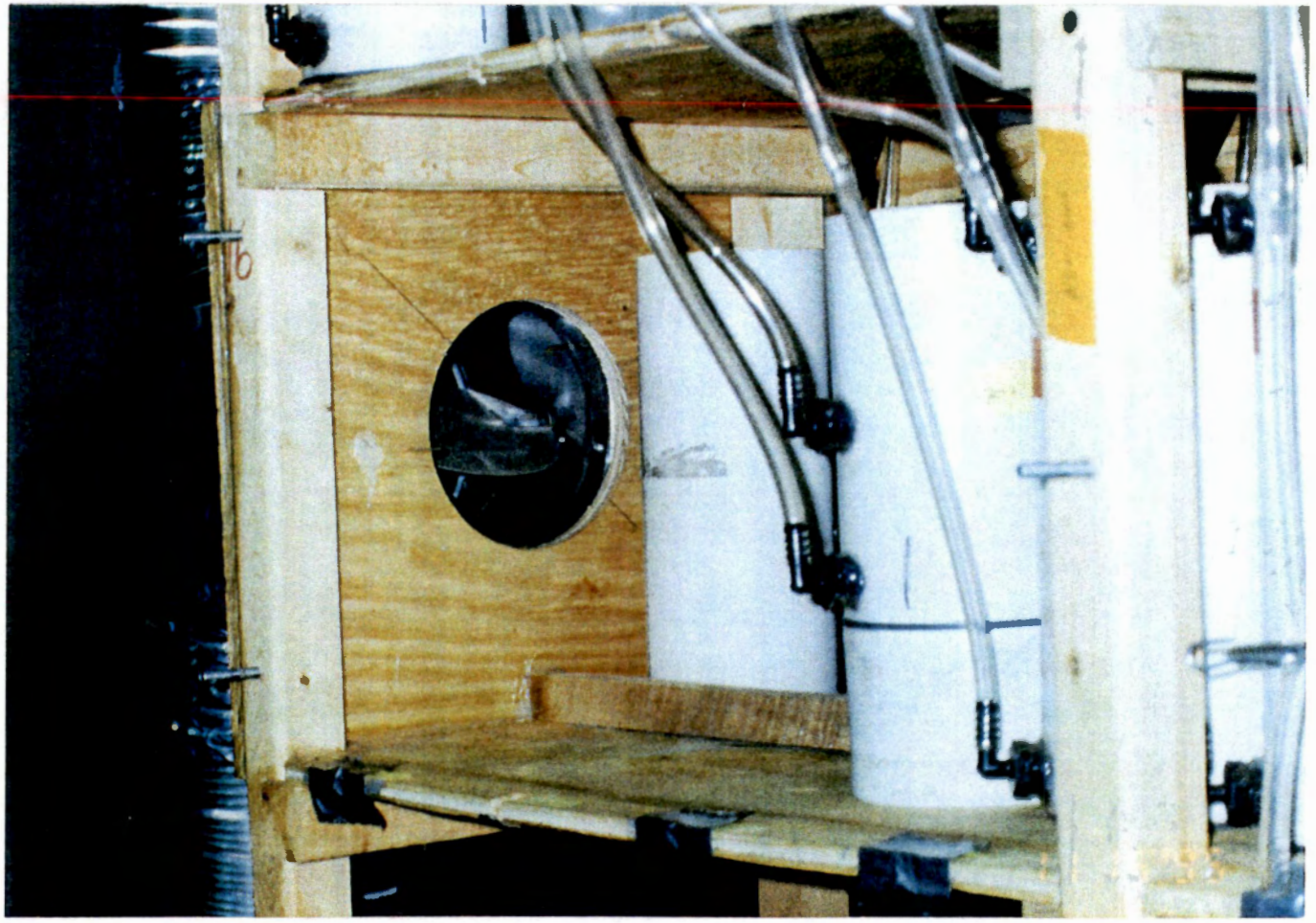


Figure 19. Photograph of the in-line butterfly valve located inside the exit manifold duct; used to control the airflow rate inside the enclosed chamber sections.

Temperature control design

As previously indicated, it was decided to control temperature by manipulating the air temperature as it entered the chambers. Only two distinctively different temperatures were desired, much like the soil differences and the air flow differences. The lower temperature was chosen to be that of the ambient condition and the higher temperature was set to be about 5.5°C [10°F] above that. The easiest approach to heating this air involved building heat boxes attached to the inlet duct of the chamber intake manifold. Within these boxes, the air could pass across heating elements designed to raise the temperature as required.

In order to accomplish this, through basic thermodynamic calculations one can determine the exact amount of energy which must be added to an air stream in order to raise the temperature a certain amount. According to the First Law of Thermodynamics (as stated by Lindeburg, 1992):

$$Q = \Delta U + W \qquad (3)$$

where:

Q = heat
U = internal energy
W = work

For our situation, however, we were interested in the thermal equilibrium application of the first law. In this case, Lindeburg (1992) noted that the work term, W, is zero since the drive toward thermal equilibrium requires no addition of external work when masses of different temperatures are mixed. He goes on to state: "The energy comes from the heat

given off by the cooling mass. Energy is stored by increasing the temperature of the warmed mass. These changes are equal and opposite, since the net change is zero." Thus equation 3 may be rewritten as:

$$Q_{net} = Q_{in} - Q_{out} = 0 \quad (4)$$

Heat, Q, depends upon the phases of the substances and the nature of the system. Thus:

$$(\dot{m} C_p \Delta T)_{in} = (\dot{m} C_p \Delta T)_{out} \quad (5)$$

where:

$\dot{m}$ = mass flow rate

C_p = specific heat

ΔT = change in temperature

However, we did not know the mass flow rate of the air moving through our system. Preliminary tests conducted on several blowers (similar to the ones actually used) revealed an expected maximum air flow rate of around 12 cfs at the blower inlet port. Knowing this volumetric air flow rate and applying some basic fluid mechanic principals, the mass flow rate can be determined. From White (1986), the volumetric flow rate of a fluid is given by:

$$Q' = VA \quad (6)$$

where:

Q' = volumetric flow rate of the fluid
V = velocity of the fluid
A = cross-sectional area of the conduit containing the fluid

It is further known by the continuity equation that mass flow rate is related to density and volumetric flow rate,

$$Q' = \rho VA \tag{7}$$

Substituting equation 6 yields,

$$m = \rho Q \tag{8}$$

where ρ = density of the fluid. For air,

$$m = \rho_{air} Q \tag{9}$$

where ρ_{air} = 0.0794 lbm/ft^3 @ 40°F (from Lindeburg, 1992). Thus,

$$m = (0.0794 \text{ lbm/ft}^3)(12 \text{ ft}^3\text{/sec}) = 0.9528 \text{ lbm/sec}.$$

Converting to SI units,

$$m = (0.9528 \text{ lbm/sec})(1 \text{ kg}/2.2 \text{ lbs}) = 0.433 \text{ kg/sec}.$$

Now, recalling $mC_p\Delta T$, where $C_{P\,air} = 1\ ^{KJ}/_{Kg\text{-}K}$ (from Lindeburg, 1992) and $\Delta T = 10°F$, and converting temperature to SI units:

$$\Delta T_{°C} = 5/9\ (\Delta T_{°F}) = 5.5°C. \tag{10}$$

Converting this temperature to absolute, it is realized that

$$\Delta T_{°k} = \Delta T_{°C} = 5.5°K$$

Thus,

$$mC_p\Delta T = (0.433 \text{ kg/sec})(1\ ^{KJ}/_{Kg\text{-}K})(5.5°k) = 2.38 \text{ KW}$$

The heat boxes thus needed to supply 2.38 KW to raise the temperature of the ambient air 5.5°C [10°F] under the maximum expected air flow rate.

The final design consideration regarding the temperature concerned to which actual

chamber to supply the heat. Recall that in order to achieve the unique combinations of air flow and temperature required that one chamber out of each blower-controlled set be heated. Therefore, the North and South-Central chambers were arbitrarily chosen to have heat boxes added to their intake manifold systems. So, the North chamber had high temperature and low air flow, while the South-Central chamber had high temperature and high air flow. The remaining two, North-Central and South, had low temperatures with low and high air flow rates, respectively.

Heat box

Construction and Installation

The heating elements decided upon were of the type used in typical space heaters. These stack heating elements consisted of a ceramic base and vertical stand, around which was coiled nichrome wire. A total of four such elements were purchased from a local electric supplier, two rated at 1000W and 240V and two rated at 1500W and 240V. Although either 120V or 240V elements were available, it was decided to go with the 240V elements due to the reduced amperage they would draw. Thus, a combination of one of each placed in a heat box would yield approximately 2.5KW, close to that required by the preliminary calculations. The heat boxes themselves were constructed from 20 ga. sheet metal with a funnel-shaped geometry to facilitate better air flow from the inlet to the exit of the box. Inlet and exit ports were included for easy connection of the flexible duct. Two such boxes were required, one each for the North and South-Central chambers. They

were placed above the necessary chambers in a fashion similar to the blowers. Further details concerning the heat boxes (including a close-up photograph showing the elements in the boxes) may be found in Appendix B.

Insulation

An important consideration to the heat boxes and, in general, to the temperature integrity of the entire system, centered around providing sufficient insulation to minimize heat loss. Two layers of insulation sheathing material (1.27 cm [½"] thick semi-rigid polyisocyanurate foam board with an aluminum foil face on both sides) were applied around the outside of the heat boxes. Another insulation consideration involved potential heat loss from the air flow manifold ducts. To minimize this, standard flexible duct insulation (with reinforced foil liner on one side) was wrapped around the ducts leading from the heat boxes to the chambers entrance. More detailed information concerning the insulation considerations may be found in Appendix B.

Element Wiring Notes

The air velocities inside the two heat boxes were different because one box supplied a high air flow chamber and the other a low air flow chamber. Because of this, the amount of heat supplied by each box needed to be different (i.e., the amount of power supplied to raise the temperature approximately 5.5°C [10°F]). This desired change in temperature was dependent upon two factors, the power output of the elements and the air flow. Thus, if the air flow was lower in one box, the actual change in temperature would be greater than that desired. Therefore, instead of being concerned with supplying

a certain quantity of power, we were actually interested in the power input per air flow (KW/cfs) so as to raise the temperature in each chamber 5.5°C [10°F] above ambient.

The preliminary heating element sizing was based upon the maximum expected air flow rate (i.e., conditions similar to the high air flow chambers). Thus, for the conditions of heat plus high air flow, both elements were wired as rated to give maximum power output of approximately 2.5 KW. However, for the condition of heat plus low air flow, the heat supply needed to be adjusted in order to compensate for the lower air flow. This was easily accomplished by changing the wiring scheme of the elements in this box. Numerous options and combinations were possible to achieve the desired power. For instance, the elements could be used separately or together, or the elements could be supplied various amounts of input voltage. As an example, by simply wiring the 1000W/240V element to 110V, the power was cut in half to 500W. This in turn decreased the temperature.

The wiring scheme of the low flow heat box was therefore manipulated as needed to achieve the proper temperature increase based upon the lower flow rate. However, these adjustments could not be made until the air flow in all chambers was calibrated and the actual temperature difference between the two high air flow chambers was measured. The actual wiring modifications may be seen in a later section of this chapter describing the calibration of the chambers. Additionally, all chamber electrical considerations may be seen in Appendix B.

Chamber calibration

Difficulties and Considerations

Air chamber calibration was required to ensure similar air flow rates in each chamber section supplied by each of the two blowers. By doing so, no errors could be attributed to air flow inconsistencies between like chambers. Accurate measurement of the air velocities within the chambers proved to be no easy task. Several methods and approaches were tried unsuccessfully. A couple of these tried to determine the static pressure drop across both the chambers and the fans, and employed various combinations of precision manometers, pitot-static tubes and pressure access fittings, to name a few. All of these attempts failed because precise measurements could not be obtained. Yet another approach utilized a hot wire anemometer probe inserted directly into the enclosed chamber sections. Although the hot wire anemometer provided very accurate velocity measurements, because of the fluctuating readings it became apparent that the air flow inside the chambers was very turbulent in nature. This was not completely unexpected due to the air moving around and across the soil columns as it flowed from one end of the chamber to the other. It was thus very difficult to get a stable "point" measurement.

Upon consultation with various sources, a combination of approaches was tried. To begin with, it was learned that "measurements of gas velocities below 0.3048 $^{m}/_{s}$ [300 ft per min. (5 ft/sec)] are difficult because the kinetic energy involved is insufficient to activate the gages used" (Henderson and Perry, 1976). Such was our case. However, these same authors feel that use of a hot-wire anemometer is one fairly reliable technique

for measuring such air velocities. Thus, we were on the right track. The actual hot wire anemometer used was a TRI-SENSE® combination temperature/humidity/air velocity sensor by Cole-Parmer (model #37000-00).

Two concepts were applied to address the turbulent flow patterns. Henderson and Perry (1976) suggest that velocity observations should be made in the middle of a long straight uniform section of pipe. For best results, they suggest the measurements be in a length of conduit at least 20 times the diameter. Additionally, any observations close to bends, outlets, blowers, grills, etc., will give erroneous results. Our manifold duct systems did not contain a fairly uniform long section of duct in which to measure the velocities accordingly. Thus, such a section of conduit had to be added to the air manifold system.

Finally, our measurement technique had to account for any inconsistent flow paths within the conduits and for any flow pattern variations between ducts. As both Wilhelm (1995) and Henderson and Perry (1976) suggest, several point measurements should be taken across the cross-section of the duct to get an average air flow velocity inside the conduit. In addition to taking measurements in this manner, a diffuser/stabilizer was also added to the long section of duct to reduce any turbulence and to give a more stable flow pattern (see Figure B-2 in Appendix B).

Manifold Modifications

For our manifold system, strict implementation of the "20 x diameter" rule of thumb would require an additional 12 ft of duct (for 6" diameter pipe). This was impossible due to the limited laboratory facility space. However, an additional 2 ft section

of rigid metal duct was placed along the inlet section to each chamber section. The rigid metal duct was used instead of the aluminum flex-duct because of its added strength and stability, along with having a smooth internal surface. Additionally, the diffusers/stabilizers could be more easily attachable to a rigid duct section. A few more details concerning this manifold modification are contained in Appendix B.

Final Airflow Calibration Measurements

As previously indicated, several measurements with the hot wire anemometer probe were taken across the cross-section of the duct. To accomplish this, two small probe insertion holes were drilled into each duct, fairly close to the chamber entrance. Velocity measurements were taken according to a grid system applied to the ducts circular cross-section. This sampling grid pattern may be seen in Figure 21. For each grid point, the probe tip was inserted an exact distance into the duct (see Figure 21). At each of the points, an air flow reading was taken after the sensor stabilized. These five measurements were then averaged to yield a representative air flow velocity through the duct. These modifications and sampling patterns greatly improved the flow stability and resulted in more accurate measurements.

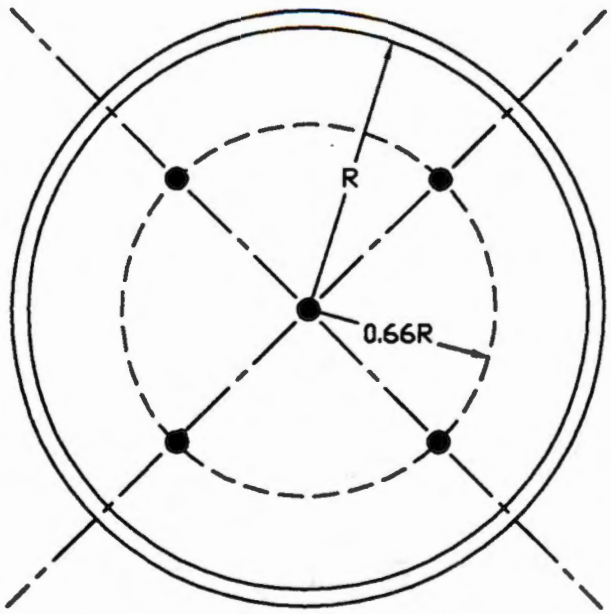


Figure 21. Hot wire anemometer traverse points in the 6"-diameter circular airflow duct.

The air flow of both chambers controlled by each blower had to be similar. Further, each chamber contained two enclosed sections. Thus, four enclosures per blower had to have fairly equal air flows within them. For the sake of simplicity, only one set of chambers (either the N and NC or the S and SC) were calibrated at a time. To begin with, all dampers were placed in the fully open position and the blower turned on. Velocity measurements (as described above) were taken in all four ducts. Their averages were compared to one another and any adjustments to the necessary butterfly valves could be

made. In order to decrease the flow rate in one duct, its damper was closed slightly; the opposite could be done to increase the air velocities. It was noted that any butterfly valve adjustment caused the exact opposite effect in the remaining three ducts. After any damper changes, the velocities in all four ducts were re-measured and compared again. This trial and error process was continued until all four ducts had very similar air flow velocities. This same procedure was then repeated for the second set of chambers. The final air flow calibration results can be seen in Table 8.

Table 8. Final chamber airflow rate calibration results.

Final Calibration Results	North		North-Central		South-Central		South	
	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom
avg. velocity (m/s)	1.46	1.47	1.49	1.46	3.82	3.77	3.82	3.77
avg. velocity (mph)	3.27	3.29	3.33	3.27	8.55	8.43	8.55	8.43
avg. flow rate (cfm)	56.33	56.72	57.49	56.33	147.39	145.46	147.39	145.46

These final air flow calibration results indicate that the two desired objectives were met. To begin with, two distinctive air flow velocities were achieved, thus supplying a good comparison base. The low air flow velocity averaged 5.29 $^{Km}/_{hr}$ [3.29 mph] while that of the high air flow chambers averaged 13.66 $^{Km}/_{hr}$ [8.49 mph]. Thus, the flow rate in the North and North-Central chambers were approximately ⅓ that in the South and South-Central chambers. Second, like chambers had very similar flow rates. Thus, when

comparing results from the various treatment combinations, no appreciable error should be attributable to air flow inconsistencies.

Final Temperature Calibration

After the air flows within each chamber had been established and measured, the final temperature measurements could be taken and heat boxes adjusted accordingly. The same hot wire anemometer probe was again used, since it had the capability of measuring air flow temperature. Since the South-Central chamber heat box was already wired to produce 2.5 KW, the temperatures were first determined for this set of chambers (i.e., both high air flow chambers, S and SC). After starting both the blower and heat box associated with these chambers, temperatures were measured inside the duct in the same manner as previously described for air flow measurements (i.e., the grid sampling pattern). From these observations, both sections of the South-Central chamber (high heat) had temperatures of 35.4°C [95.7°F], while both sections of the South chamber (ambient temperatures) yielded a reading of 22.4°C [72.3°F]. This is a temperature difference of exactly 13°C [23.4°F]. Although a little greater than originally anticipated, this range was acceptable.

Now, utilizing the calculation procedure outlined from equations 3-10, the amount of power necessary to raise the temperature inside the North chamber was determined. Knowing the average flow rate in the North chamber of 0.027 m^3/sec [56.82 cfm], it was calculated that 450 watts of power had to be supplied to each chamber section to achieve an increase in temperature of 13°C [23.4°F]. However, since the heat box supplies two

sections (upper and lower chamber sections) this power input was doubled to 900W. Thus, it was decided that only the 1KW heating element would be used in the North heat box; it was wired with the rated 240 volts. It was noted that this configuration provided slightly more power (by 100W) than required. This was deduced to be fairly negligible and thus acceptable for our purposes, as proved by the final calibration measurements. After modifying this heat box accordingly, final temperature measurements were taken from this set of chambers (i.e., the North and North-Central chambers). Measurements taken in the same manner as before yielded excellent results. The temperatures in the North chamber (high heat) were 36.6°C [97.9°F] while those in the North-Central chamber were 23.6°C [74.5°F]. This is the same temperature difference as observed in the other set of chambers, which was exactly what was wanted.

Rinsate solution

Herbicides

As previously indicated, two common herbicides were used in the study: atrazine and fluometuron. Ciba Plant Protection Company generously supplied technical grade atrazine and fluometuron for use in this research study. Due to the low water solubilities of these compounds (especially atrazine), it was decided to mix the rinsate solution at a concentration of 10 ppm. This is an acceptable level, since a realistic disposal system will only be required to handle dilute rinsate materials, generally on the order of 10-1000 ppm.

Mixing and Distribution Considerations

Because of their low water solubilities, there was considerable concern associated with being able to get the chemicals into solution at the desired concentrations. After much deliberation and preliminary experimentation, it was felt that a sufficient job could be obtained by utilizing hot tap water along with vigorous agitation. Additionally, it was felt that the easiest mixing strategy would be to only mix a given quantity of solution at a time (i.e., only mixing the amount needed for immediate use). Therefore, a fairly large batch of solution was mixed in a large container, and this solution was transferred to each individual solution bottle as dictated by its evaporation requirements. For this transfer, a distribution system was required to move the solution from the mixing tank to the bottles. A simple system was desired, requiring minimal valve and piping complications. An additional requirement was the need to know the exact amount of solution transferred to each bottle every time.

Pesticide Mixing System

The tank test stand designed, constructed and used by Davis (1992) was employed for our purposes. The components of his apparatus were easily incorporated to fill our needs, including providing a means of continual recirculation and agitation as desired. Although his apparatus was equipped with two separate pumps, only one of them was needed for our purposes. Thus, the 1.1 KW[1½ Hp] Teel centrifugal pump (model 1P837, with integral electric motor; rated @ 375 $^{L}/_{min}$ [99 $^{gal}/_{min}$] @0.0 Kpa [0.0psi]) was used as a recirculation pump. The pump pulled solution out of the tank and re-injected it back

through hydraulic tank agitators. Using this type of tank set up allowed for thorough and continual mixing of the rinsate. By doing so, the herbicides were easier to get into and maintain in solution. Refer to S.O.P. #BKC-2 (Appendix A) for the actual procedures and steps involved and followed for the mixture of each tank batch.

Tanks

The only major modification to Davis' apparatus involved the utilization of a different (size and shape) tank throughout the majority of our study. During the initial filling process for all 512 solution bottles, a 1136-L[300 gal.] capacity tank was used because of the sheer volume of rinsate needed for this process. This tank was slightly modified with the addition of hydraulic agitation nozzles. For this alteration, a tee riser tube installed in an underside tank port was used to position two in-line flow tank agitators several inches above the tank bottom.

After the initial filling process, a smaller 303-L [80 gal.] capacity conical-shaped tank was used for all subsequent batch mixes. Purchased from a local agricultural supplier, the tapered shape of this polyethylene "Mix-N-Fil" container helped facilitate and insure complete drainage of the mixture. Due to the fact that this particular tank was of a size and shape not conducive to Davis' (1992) test apparatus set-up, a new stand was built to hold it. The tank lids initially modified by Davis (1992) permitted vertical centering and adjustment of agitation and rinse nozzles within the tanks. Through one of the main lid ports, a PVC drop tube was extended down into the tank and positioned several inches above the bottom. To the end of this drop tube was attached a brass jet stream agitator

nozzle (TeeJet #6290 SC-2). A photograph of the mixing system (Figure B-5) and construction details of the tank stand are located in Appendix B.

Plumbing components

The plumbing hardware incorporated into the fluid recirculation system consisted of components to 1) supply the pump from the centrally located bottom tank outlet, and 2) deliver fluid to the tank agitation nozzle. Whenever possible, the components used were manufactured from non-corrodible materials. The pump housing and internal mechanical components were the only corrodible material which came into direct contact with fluids. Non-corrodible components were selected to limit possible contamination of test solutions. Rigid tubing, tees, nipples, elbows, reducers, hose barb fittings, transitions and connectors were Schedule 80 PVC. In-line strainer housings, ball valves, pressure relief valves, bulk head fittings, and anti-vortex devices were polypropylene, while the quick disconnect couples were either aluminum or polypropylene (male ends - aluminum; female ends - polypropylene). Reinforced rubber hoses were used to link the pump to tanks. Further plumbing component considerations may be viewed in Appendix B.

Herbicide Solution Distribution System

A simple and accurate distribution system was required to transfer the mixed herbicide solution to the individual bottles. After considerable deliberation, it was decided that the easiest method of accurately achieving this goal was via a metering pump. When pumping at a known flow rate in this manner, simply timing how long it took to fill a bottle to a certain point yielded the exact quantity of solution added. Based upon the desire to

be able to fill the 1000 mL [0.264 gal.] bottles in about 30 seconds, a Cole-Parmer model #50000-083 high volume, single head diaphragm pump, with an adjustable flow rate (max @ 2081 $^{mL}/_{min}$[0.55 $^{gal}/_{min}$]), was obtained. This metering pump was attached directly to the tank support stand.

Although this would accurately dispense the solution, consideration also had to be given to controlling this flow, timing it, and being able to move freely among the chambers to all the solution bottles. Conceptually, this involved pumping the solution from the metering pump through tubing, which could be dragged among the chambers to any bottle location. At the end of this tubing a three-way valve diverted flow either into the bottles or through a return (recirculation) line back to the tank.

To achieve this, a wooden mobile podium was constructed to house the required valving/timer system (Figure 22). This podium was designed to move freely among and around the chambers to provide easy access to all 512 individual solution bottles. Tubing from the metering pump ran directly to a three-way solenoid valve mounted on the podium. This solenoid valve was plumbed such that the metering pump could run continuously. When not filling, the valve bypassed flow directly back to the tank (i.e., recirculation). However, upon activation, the valve diverted the flow to the other port, where tubing was inserted into a bottle access tube. The solenoid valve used was of a Dayton 3-way normally closed stainless steel valve body with a NEMA class B 120V coil. Rated at a maximum flow rate of 7.95 L/min [2.1 gpm], the valve had an operating pressure differential of 0-275.8 KPa[0-40 psi] (H_2O).



Figure 22. Photograph of the herbicide distribution system mobile podium used for the individual bottle filling process. Note the solenoid valve mounted on the inside wall, the foot switch (red) on the stand platform, and the elapsed time indicator (black) located on the upper right corner of the podium top.

An elapsed time indicator was also mounted on the podium. This timer, a Syrelec series 10506, had a range of up to 9999.99 sec, was equipped with a reset button, and was powered by an internal lithium battery. Finally, a foot switch was installed on the podium to activate both the solenoid valve and the timer simultaneously. A double-pole/double-throw (DPDT) momentary switch was assembled from electrical contact blocks and a panic button (push button) switch. An electrical supply cable was run, along with the tubing, to supply power to the podium (for the solenoid valve). Due to the laboratory environment (i.e., the presence of liquids) a GFCI (ground fault circuit interrupter) plug was attached to the electrical supply cord as a precaution against electrical shock. An electrical schematic of this set-up may be seen in Figure 23. The exact operational procedure for filling bottles with this distribution system may be seen in S.O.P. #BKC-3 (Appendix A).

Miscellaneous set-up notes

Air Pressure Manifold

As outlined in S.O.P. #BKC-4, (Appendix A), the soil columns were actually started by pressurizing the solution bottles. Done correctly, this pressurization initiated fluid flow into the soil columns. Once this flow had begun, the column would run continuously on its own as long as there was a sufficient supply of solution. This bottle pressurization process was accomplished via air blown into the bottles. The building is equipped with an in-house air compressor and air line outlets throughout the laboratories,

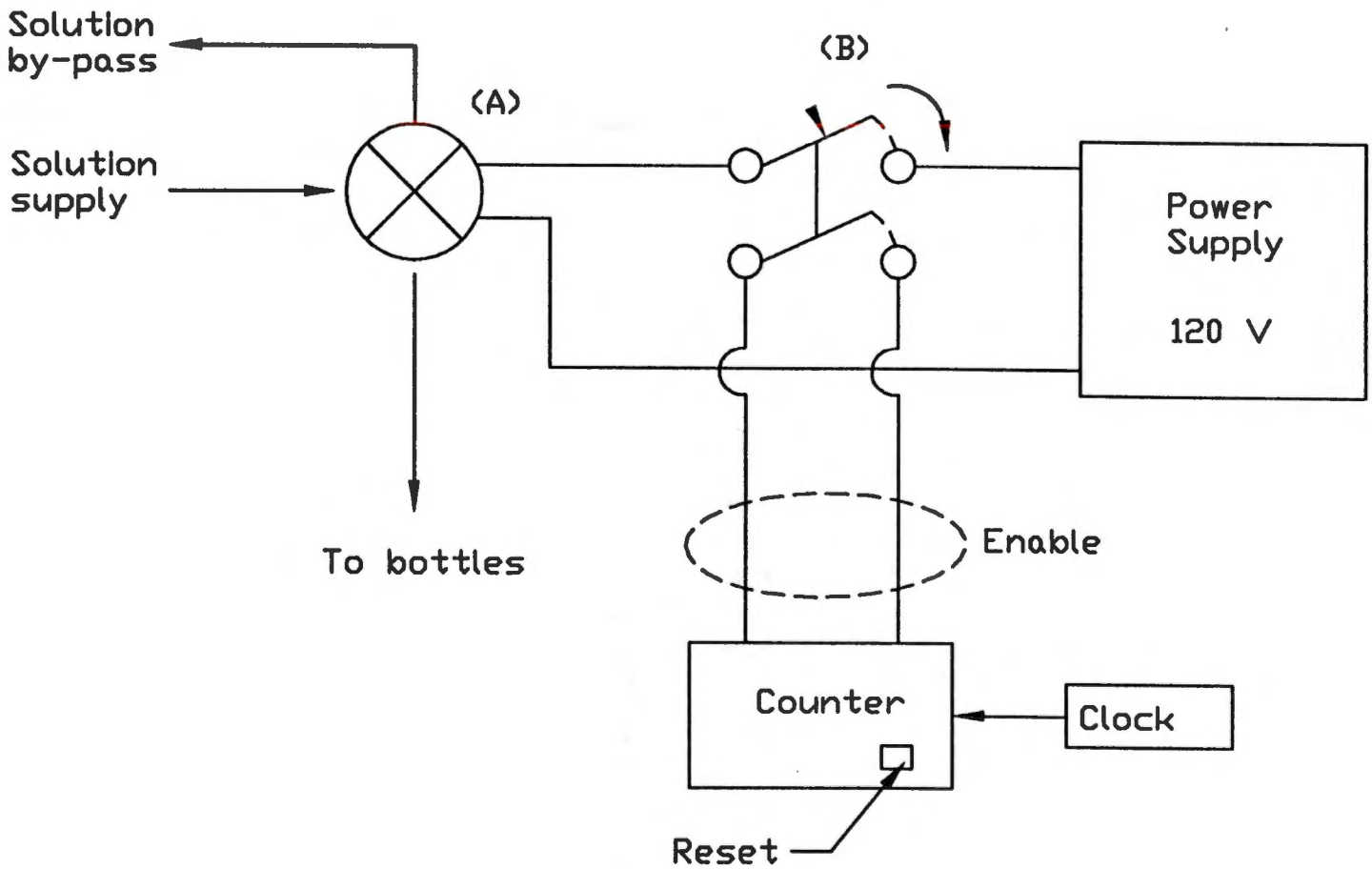


Figure 23. Electrical schematic of herbicide solution distribution system. (A) is the 3-way solenoid valve; and (B) is the foot switch: double-pole/double-throw (DPDT) momentary switch assembled from two electrical contact blocks.

so the approach took advantage of this. However, the normal pressure in these air lines is approximately 698.5-838.2 Kpa [100-120 psi]. This is much more than required for our needs. Bottle pressurization required ≤ 6.895 Kpa [≤ 1 psi], so a simple manifold system was assembled to control this pressure and provide for multiple hose attachments. Detailed notes of the air pressure manifold and related components are located in Appendix B.

Temperature Concerns

Some concern was expressed in regard to the manner in which the temperature inside the air chambers were controlled. As described earlier, only the temperature difference was controlled, with ambient conditions being the reference point. In actuality, this provides a "floating" reference point, since there were drastic ambient temperature fluctuations through the course of the study (i.e., from April when it was cooler, through the hotter summer months, and again into September as the cooler fall approached). This fluctuation greatly influenced the rate of evaporation, and thus the quantity of herbicides added to the soil, which in turn could affect the rates and amounts of microbial degradation. The concern was that "scientifically" the air temperature should remain constant inside the chambers throughout the duration of the study.

Not only would this have been nearly impossible to achieve in our laboratory building, but it would not have been representative of the conditions faced by a realistic disposal system. A realistic system utilized by a farmer or applicator would be located outside and would face these seasonal temperature fluctuations. Thus, our approach in

evaluating temperature difference upon the system is valid. However, data were also collected from a permanent weather station located on the Agricultural Engineering departmental grounds. This weather station was less than 91.5 m [100 yds.] from the entrance of the actual laboratory room used for this study. Also, the main garage door to the laboratory remained open as much as possible, such that the conditions within would be representative of those outdoors. This weather station data, collected for the duration of the study, was then used as necessary to address any concerns.

Safety and Worker Protection

Since this research study involved potentially dangerous chemicals, safety and worker protection considerations were of utmost importance. As already alluded to, a containment structure was built and the area was roped off and posted with all necessary safety information. Additionally, all workers involved with this project were provided access to protective clothing as warranted. These included: disposable Nitrile gloves, dust mask respirators, safety glasses or goggles, and a shop coat. The mandatory use of this equipment was incorporated in all protocols as necessary (see Appendix A).

DATA COLLECTION

Given this apparatus, how do we collect any useful information? The entire data collection phase of this project revolved around a mass balance approach. Conceptually, the first step involved recording both the volume of solution and the mass of active

ingredient added to each soil column over the prescribed period of time. Next, analysis of the soil in each column revealed the concentration of each chemical remaining within the soil. Thus, by simply calculating this difference, insight is gained into the evaporation rates and the amount of degradation. These three distinct steps are addressed in greater detail below.

Operational procedures

System Start-up and Day Zero

In order to have valid comparative data for all treatment combinations, it was imperative that all soil columns and air chamber systems be started in the same manner and at nearly the same time (i.e., at time zero). Thus, standard operating procedures were written to achieve this start-up in a timely and consistent manner (refer to S.O.P. #BKC-5 in Appendix A). The initial start-up process required approximately 969-L [250 gal.] of rinsate solution, enough to fill each solution bottle twice. After filling all 512 solution bottles, per S.O.P. #BKC-3 (Appendix A), the columns were started. Thus, on March 22, 1995, S.O.P. #BKC-4 (Appendix A) was employed in the start-up of the soil columns. By March 24, 1995, all 512 soil columns were successfully operating. Due to failure of the solution distribution system metering pump, the actual start-up of the air chambers (i.e., turning on the blowers and heat boxes) was delayed until the late afternoon of March 31, 1995. Although this delay was uncontrollable, it turned out to be a blessing in disguise. This allowed sufficient time to correct and fix all column leaks and allowed for all columns

to reach equilibrium and become stable. Additionally, since all columns were subjected to the same conditions, it can be argued that this delay had minimal (if any) effect on the relative performance of the columns. Official day zero was then recorded as April 1, 1995, thus allowing several hours for the airflow and the temperatures inside the chambers to stabilize and equilibrate.

Daily Operation of the System

After the initial start-up of the system, efforts were concentrated on the continual operation of the columns and the chambers. The majority of this effort involved keeping solution in all of the bottles, cycling the flood/drain columns according to schedule, and maintaining the integrity of the system. The filling of the solution bottles was entirely regulated by the rate of evaporation of the soil columns, the rate of fluid uptake by the columns and the rate of fluid depletion in the bottles. Batches of solution were mixed as needed. Through the course of this study (i.e., 180 days), a total of 23 batches of tank mix (about 5037.5-L [1300 gal.]) were prepared. Other than the initial batch, these tank mixes ranged on the order of 116.3-310-L [30-80 gal.] Each tank batch was mixed according to S.O.P. #BKC-2 (Appendix A).

The metering pump was always calibrated before filling bottles in any chamber. Since the time required to fill each bottle was recorded, this calibration flow rate could be used to calculate the volume of solution added to each bottle. In addition, solution samples were also obtained for each chamber. Three solution samples were collected per chamber (i.e., per filling of solution bottles associated with each chamber): one sample

prior to filling the first bottle, one sample after filling half the bottles, and one sample after filling the last bottle. These samples were analyzed via high performance liquid chromatography (HPLC) for exact herbicide concentrations. Thus, the quantity (i.e., mass) of active ingredient for each herbicide associated with the volume of solution added to the bottles could be determined.

The input data, in terms of quantity of solution and mass of active ingredient, were carefully recorded for each column throughout the duration of the study. In this manner, the first component of the mass balance concept (i.e., the amounts added to the system) was calculated. The steps outlined in S.O.P. #BKC-3 (Appendix A) were closely followed every time pesticide solution was metered from the large mixing tank to the individual solution bottles so as 1) to ensure that each soil column maintained an adequate supply of pesticide solution with minimal disturbance to the continual running of the soil column, and 2) to maintain quality control in the manner in which solution samples were collected.

The remaining miscellaneous operations included fixing problem columns and cycling flood/drain columns. Details of the procedures are outlined in S.O.P. #BKC-6 (Appendix A). Throughout the course of this study measures were undertaken to correct or repair the few minor problems associated with either the soil columns or solution bottles. Such problems threatened the integrity of the study and the quality of the data, and included such items as column leaks, column overflows, clogged tubing, blown stoppers on the bottles, and stopped column/bottle systems. Each of these problems and their corrective procedures are discussed and outlined in the afore-mentioned S.O.P.

The flood/drain type columns were alternated between aerobic/anaerobic conditions in either five-day or ten-day duration cycles. Thus, every five days after time-zero throughout the 180 day course of the study, various columns had to be either flooded, dried, or both. Again, the afore-mentioned S.O.P. outlines the exact steps involved in this process.

Column Sampling Procedures

At the end of each prescribed time period, one-fourth of the columns were pulled from the chambers in order to analyze the soil for herbicide concentrations. These 128 columns represented all possible treatment combinations (multiplied by four replications) for that time frame. Since day zero was established as April 1, 1995, the following dates corresponded to their respective time periods:

- May 1, 1995 ⇒ 30-day column samples;
- May 31, 1995 ⇒ 60-day column samples;
- July 30, 1995 ⇒ 120-day column samples;
- September 28, 1995 ⇒ 180-day column samples and system shut-down (end of the data collection phase of study).

At the end of each time period, the appropriate columns were removed from the chambers and the soil was prepared for analysis in accordance to the steps and procedures outlined in S.O.P. #BKC-8 (Appendix A). These procedures are discussed in a later section of this chapter.

After the soil columns had been pulled from the air chambers, it was necessary to determine the amount and concentration of the solution remaining in the solution bottles. This volume represented solution that was added to the system but not used by the

column. It was important to have both the volume of fluid remaining and the mass of each herbicide associated with this volume, so that it could be accounted for in the final mass balance equation. Likewise, any fluid remaining in the column (i.e., in the soil matrix) after it was pulled from the chamber represented solution added to the system but not actually evaporated. Thus, it too had to be accounted for in the final mass balance equation. The procedures for pulling the final solution bottle samples and determining the final solution bottle volumes are outlined in detail in S.O.P. #BKC-6 (Appendix A). Determination of the amount of fluid remaining within the soil matrix required weighing the "wet" columns as soon as they were pulled out of the chambers, as per S.O.P. #BKC-8 (Appendix A). By comparing this weight with the initial dry column weight, recorded during the column packing process, the amount of unevaporated solution could be accounted for.

Once the soil had been removed, the columns were returned to the system. This involved re-packing the columns with the same type of soil, placing them back into the chambers, re-connecting the bottles and re-starting them. By doing so, we could insure the integrity of the system and minimize any variations which might affect the remaining columns. The conditions within the system would thus remain virtually unchanged, and minimal variations would be caused by the column pulling process. Of special note, however, is that these replaced columns had water run through them rather than pesticide solution. Although data were no longer collected from these columns, they were treated just like the other columns for the remaining time duration, and they were also kept running on a continual basis.

System Shut-down

On September 28, 1995, after 180 days of continual operation, the system was shut off. This involved turning off both blowers, both heat boxes, and both ceiling exhaust fans. After this shut-down, the final set of soil columns were pulled from the air chambers and prepared for analysis. Also, the final set of corresponding solution bottles were sampled for both volume of fluid and concentration of herbicide active ingredient.

Sample chemical analysis

High Performance Liquid Chromatography (HPLC)

Analytical methodology was developed for the simultaneous determination of atrazine, fluometuron and fluometuron's initial soil metabolite desmethyl fluometuron at ppm to ppb levels in both soil extracts and water samples. This was accomplished via a reverse-phase high performance liquid chromatography (HPLC) method. This method consisted of a Waters (Melford, MA) LC system including a model 680 automated gradient control unit, a model 510 solvent delivery system, a model 717 auto-sampler injector, and a model 486 tunable UV absorbance detector. A Hewlett-Packard (San Fernando, CA) model 3396 integrator was used to interpret the detector response. The analytical column (Whatman partisil 10 ODS-2, Clifton, NJ) was packed with 10 μm C_{18} media and measured 250 mm x 4.6 mm [0.984 in. x 0.018 in.] ID. An in-line 1 cm x 1.5 mm [0.394 in. x 0.0059 cm] pellicular C_{18} guard column (Supelco #5-8232 pelliguard LC-18) was used to filter out contaminants and thus protect the analytical column. All

solvents were HPLC grade (Burdick and Jackson, Muskegon, MI).

Analytical parameters included a UV detector wavelength of 220 nm and a mobile phase flow rate of 1.0 mL/min [2.58×10^{-4} gal./min]. For the water samples the mobile phase consisted of a straight isocratic run of acetonitrite-water (60%/40%) at a 15 minute run time. However, for the soil extracts a system flush at 80:20 (v:v) acetonitrile-water for eight minutes was added. Injection volume was 20μL for all sample types. All standards were prepared from analytical and/or technical grade atrazine, fluometuron, and desmethyl fluometuron (Ciba Plant Protection Company), per S.O.P. #BKC-7 (Appendix A), and were >95% pure and each were used without purification. The retention times for the soil extracts were 5.5 minutes, 6.8 minutes and 8.1 minutes respectively for desmethyl fluometuron, fluometuron, and atrazine. All relevant chromatogram peaks, in general, were large and distinguishable, with no other evident similar peaks. Figure 24 may be seen for examples chromatograms. Standard Operating Procedure #BKC-8(Appendix A) may be referred to for additional HPLC analysis information and specific details.

Solution Sample Preparation

Basically, there were three types of solution samples which needed to be prepared for analysis on the HPLC:

- samples collected directly from the tank mixes at various times;
- samples collected during the bottle filling process;
- final samples collected from the individual solution bottles at the end of each of the four run times.

All solution samples were originally collected in 20 mL[0.005 gal.] screw cap scintillation vials. The only preparation for these samples was to transfer the solution to smaller 4 mL

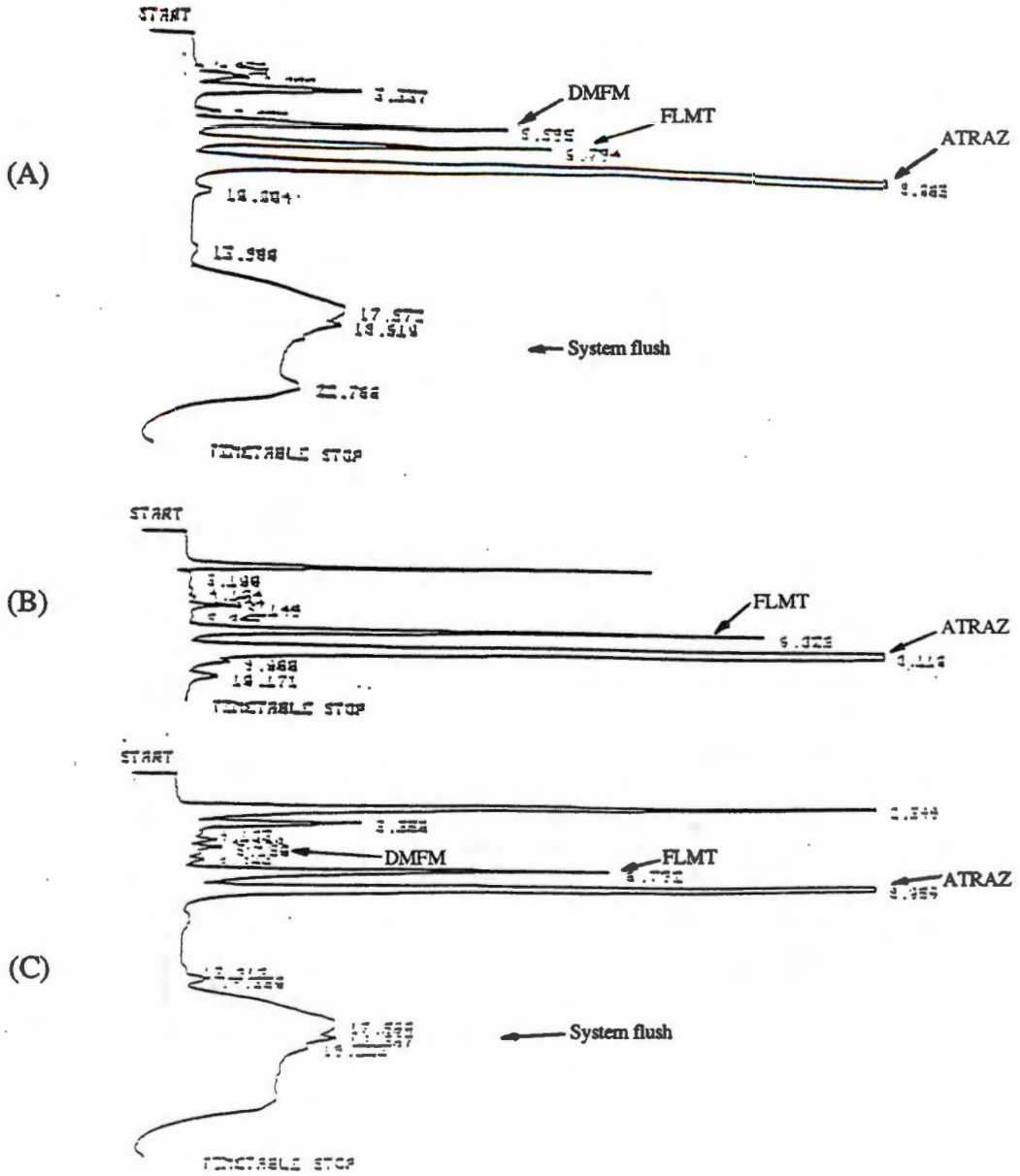


Figure 24. Example of HPLC chromatograms. (A): Analytical standards containing desmethyl fluometuron (DMFM), fluometuron (FLMT), and atrazine (ATRAZ), each at 6000 ng/g (ppb); (B): solution sample from tank mix #16 containing no desmethyl fluometuron, fluometuron at 10,168 ng/g (ppb), and atrazine at 7917 ng/g (ppb); (C): soil extract from column #491 containing desmethyl fluometuron at 910 ng/ g soil (ppb), fluometuron at 45,325 ng/g soil (ppb), and atrazine at 20,159 ng/g soil (ppb). Note the system flush at the end of runs (A) and (C).

[0.001 gal.] auto-sampler vials. All solution samples (both in 20 mL [0.005 gal.] vials and in 4 mL [0.001 gal.] vials) were stored and preserved via placement in the refrigerator (@4°C [39.4°F]) until no longer needed. In S.O.P. #BKC-8 (Appendix A), the actual steps are outlined for the analysis of these types of samples. The solution was fairly clean and free of particulates, and therefore needed no filtration before analysis.

Soil Sample Preparation and Extraction

Of major concern during the soil analysis was ensuring that a representative sample of soil was collected from each soil column. Thus, to maintain quality control throughout the sampling and analysis procedure, S.O.P. #BKC-8 (Appendix A) was carefully followed. The following description of the soil preparation procedures was observed for each soil column sample. After removal from the air chambers and careful column weighing, the soil was completely air dried and all of it was passed through a No. 10 USA Standard Testing Sieve with 2 mm [0.078 in.] openings. This required crushing the soil, utilizing plastic bags and a rolling pin. After sieving, the soil was thoroughly mixed to ensure that a representative sub-sample could be collected. This mixing was achieved by placing all of the soil in a plastic bag and vigorously shaking. Soil sub-samples were then collected and placed in 170g [6 oz.] whirl-pack bags. These sub-samples could then be stored in the freezer (at -10°C [14°F]) until needed for HPLC extraction and analysis (usually no longer than one week). By freezing, it was assumed that all herbicide degradation ceased. Gravimetric water content was also determined for each sample for later use in concentration calculations.

The HPLC analysis of soil samples from a given time period was performed on a block basis; the samples were analyzed in groups broken down on the basis of replication number per time period. Therefore, 32 samples were extracted and analyzed at a time (i.e., there were four sets of extractions and analyses per time period). To begin the extraction process, one set of soil samples was removed from the freezer. After allowing the soil to thaw, a 40 g [1.3 oz.] sample of soil was removed from the whirl-pack bag and placed into a 250 mL [0.065 gal.] low density polyethylene screw top bottle. (It should be noted, and is also pointed out in Chapter V, that the 30-day and 60-day soil sub-samples were 40 g. However, since the herbicide concentrations were increasing over time and approaching the upper limit of the linear range of quantitation of the system, ony 20g sub-samples were collected from the 120-day and 180-day columns.) To this bottle was added 80mL [0.021 gal.] of a methanol/water solution (i.e., 80% MeOH, 20% H_2O), and this sample mixture was placed on a reciprocating shaker (Eberbach, Ann Arbor, MI) operated at 180 oscillations per minute for 16 hours. The procedure was completed by filtering the extract through two pieces of qualitative filter paper (Whatman #1, Clinton, NJ) (to remove any particulates) directly into 4 mL [0.001 gal.] auto-sampler vials. Before filtering the extract, the bottles were allowed to statically equilibrate for two hours to allow soil particles to settle. Herbicide concentrations in the supernatant were determined by the HPLC method previously described. Also, all soil samples were archived. The soil remaining in each whirl-pack bag after the extraction process was preserved in the freezer. Thus, if any questions were raised about a particular sample or concentration number, that

sample could be recalled and subjected to further tests at a later date.

Data analysis procedures

Evaporation Data

As previously described, in addition to the metering pump calibration information, the solution bottle filling times were immediately recorded manually for each bottle filled. This information was later transferred to computer spreadsheet files for easy storage and manipulation. In these files the solution data could quickly be converted from a time basis to a volumetric basis. A separate spreadsheet "notebook page" was used for every filling day. At the end of the study these daily filling volumes were summed to yield the total amount of solution added to each solution bottle. These raw data are not shown in this manuscript.

Determination of the total amount of water evaporated from each soil column required accounting for the amount of water added to the system but not evaporated. This information was in two forms: 1) the solution remaining in each bottle at the end of the run time, and 2) the solution remaining within the soil matrix at the time of analysis. As already discussed, both pieces of information were collected during the column pulling procedures. The following calculations were performed to determine the quantity of water added to the system but not evaporated, and were compiled in a separate spreadsheet notebook.

Evaporation mass balance

Step 1: Calculate the initial weight of the moist soil packed into each column (data obtained from the soil column packing procedures):

$$Soil_{wet} = (Column_{full} - Column_{empty}) \quad (11)$$

where:

$Soil_{wet}$ = wet soil weight (kg)
$Column_{full}$ = full column weight (kg)
$Column_{empty}$ = empty column weight (kg)

Step 2: Convert this moist soil weight to a dry basis using the initial soil moisture information (i.e., 1.18% and 3.33% for the sandy and silty soil, respectively)

$$Soil_{dry} = Soil_{wet} * \left(1 - \frac{Soil_{\%moist}}{100}\right) \quad (12)$$

where:

$Soil_{dry}$ = dry soil weight (kg)
$Soil_{\%moist}$ = initial percent soil moisture

Step 3: Determine the volume of water remaining within the soil matrix upon column pulling at the end of the run times.

$$Column_{water} = (Column_{wet} - Soil_{dry} - Column_{empty})*1000 \quad (13)$$

where:

$Column_{water}$ = volume of water remaining in the soil matrix (mL)
$Column_{wet}$ = column weight at time of removal from chamber (kg)
1000 = conversion factor for units in mL

Step 4: Determine the volume of water remaining in the bottles which was added to the system but never actually entered the soil, and therefore was not evaporated.

$$Bottle_{water} = (Fill_{initial} - Fill_{final} + Bottle_{sample}) \quad (14)$$

where:

$Bottle_{water}$ = volume of solution remaining in the bottle (mL)
$Fill_{initial}$ = initial volume of solution added to bottle at start-up (mL)

$Fill_{final}$ = quantity of solution added to bottle at the end of the study to raise the fluid level to exactly that of the initial filling (mL)

$Bottle_{sample}$ = quantity of solution removed from bottle at end of study for concentration analysis (mL)

Step 5: Calculate the total amount of water added to the system but not evaporated

$$Nevap_{water} = Column_{water} + Bottle_{water} \quad (15)$$

where:

$Nevap_{water}$ = total water not evaporated (mL)

This information was used in conjunction with the daily bottle filling volumes for the final evaporation mass balance equation:

$$Evap_{water} = (\sum [Fill_{daily}] - Nevap_{water}) \quad (16)$$

where:

$Evap_{water}$ = total volume of water evaporated (mL)

$\sum[Fill_{daily}]$ = sum of the daily filling volumes added to bottles

The data may be seen in Appendix D.

Concentration Data

Management of the concentration analysis data for degradation purposes began with the interpretation of all HPLC chromatograms. As outlined in section VII of S.O.P. #BKC-8 (Appendix A), after initial observation and labeling, each chromatogram was interpreted with the pertinent information logged in the record book. This information included both the retention times and areas associated with the peaks of each sample, and was recorded for both atrazine and fluometuron, and for desmethyl fluometuron when detected. Like for the solution data, the HPLC data was then transferred to computer spreadsheets. The spreadsheet software was then employed to perform regression analysis

on the analytical standard results. Based upon these regression outputs, the actual sample concentrations were determined. For the solution samples, this simply entailed multiplying the sample peak area by the X-coefficient value generated from the regression analysis. This calculation yielded the concentration of that particular chemical in the sample in ng/mL (ppb).

For the soil samples, this process went one step further. The concentration result had to be amended for the extraction process, the soil moisture content of the sample, and the simple fact of dealing with soil samples instead of water samples. The following correction factor was employed (Mueller, 1993):

$$\left[\frac{ng}{mL} * \left(80 + \left(40 * \left(\frac{\%moisture}{100}\right)\right)\right)\right] \div \left[40 * \left(1 - \left(\frac{\%moisture}{100}\right)\right)\right] \qquad (17)$$

where:

80 = the amount (mL) of MeOH used in the soil extraction process
40 = the amount (g) of soil sub-sample extracted

The answer yielded from this equation represents the concentration of the chemical in the soil sample in units of ng/g soil (ppb). In some cases, only a 20 g soil sub-sample was extracted, and thus the proper correction to the above question was made. This raw form of the concentration data is not shown in this manuscript but is available from the author.

Degradation Calculations

All degradation calculations were performed on a mass (mg) basis. There were three types of concentration data needed for the degradation mass balance equation:

1) from solution samples collected during bottle filling, which represent the herbicide input;
2) from solution samples collected from the bottles during the column pulling procedure, which represent herbicides added to the system but not taken up by the soil;
3) from soil samples collected from the columns at the end of run times, which represent the quantity of herbicides remaining in the soil (and therefore, not degraded).

To determine the mass of each herbicide added to each bottle required data manipulation. Two pieces of information were known and used for this computation. First, the volume of rinsate solution added to each bottle was known. Additionally, solution samples were collected during the bottle filling process. The HPLC concentration analysis results of these samples could then be used to determine the mass of each chemical added to each bottle (i.e., simply multiplying volume by concentration yields mass). However, only three samples were collected over a multitude of bottles, instead of for every bottle (i.e., only three samples were collected per chamber during the filling process; only three samples were thus used to represent up to 128 different bottles). Thus, in order to get the best representation of the concentration of solution in every bottle, several numerical methods were employed.

A simple computer program was written in C language which linearly interpolated between the known concentrations (from the three samples), on a volume basis (i.e., total volume of solution dispensed between samples), to get the average concentrations for each bottle. This interpolation procedure was based upon the bottle filling order between samples. The program was written such that the necessary information was easily extracted as an ASCII file from the bottle filling spreadsheet files. After execution, the

program saved the output data as another ASCII file, which was then imported back into the bottle filling spreadsheet file. A copy of this program may be viewed in Appendix C. Now, with solution concentration values for every bottle filled, the spreadsheet software computed the respective mass of each herbicide added to each bottle. Simple summation of these individual bottle filling masses over the study duration yielded the total amount (mass) of each chemical added to each bottle.

Unlike for the bottle filling data, during the column pulling procedures solution samples were collected from every bottle. Since the volume of solution pulled during this sampling procedure was also recorded, simple arithmetic determined the actual mass of each herbicide remaining in the bottle. Multiplying the HPLC concentration values by the sample volume yielded the desired mass.

Degradation mass balance

The following calculations were performed to determine the actual amount of degradation occurring within each soil column:

Step 1: Calculate the total mass of each herbicide applied to the soil (on a mg basis)

$$FLMT_{soil}\ (mg) = (FLMT_{applied} - FLMT_{bottle}) \quad (18)$$

where:

$FLMT_{applied}$ = mass of fluometuron added to the column; summation of the daily filling data (mg);

$FLMT_{bottle}$ = mass of fluometuron remaining in the bottle at end of run time; collected from bottle samples (mg).

Step 2: Calculate the mass of each herbicide remaining within the soil (on a milligram basis)

$$FLMT_{remain}\ (mg) = \left[\frac{(FLMT_{fconc})(Soil_{dry})}{1000}\right] \qquad (19)$$

where:

$FLMT_{remain}$ = mass of fluometuron remaining in the soil at end of study time period (mg);
$FLMT_{fconc}$ = final soil fluometuron concentration from HPLC analysis (ng/g soil [ppb]);
$Soil_{dry}$ = as determined from step #2 in evaporation mass balance computation; take into account the initial soil moisture content (Kg);
1000 = conversion factor to get units on a mg basis.

Step 3: Now, knowing how much was added and how much remained, calculate the mass of herbicide degraded (on a mg basis)

$$FLMT_{degrad}\ (mg) = (FLMT_{soil} - FLMT_{remain}) \qquad (20)$$

Step 4: Convert the amount of degradation from a mass basis to a percent basis (i.e., of that applied, the percent of herbicide degraded)

$$FLMT_{degrad}\ (\%) = \left[1 - \left(\frac{FLMT_{remain}}{FLMT_{soil}}\right)\right] * 100 \qquad (21)$$

The same outlined steps were also used for the atrazine degradation mass balance computation by substituting the appropriate variables: $ATRAZ_{soil}$, $ATRAZ_{applied}$, $ATRAZ_{bottle}$, $ATRAZ_{remain}$, $Fconc_{atraz}$, $ATRAZ_{day}$. The data may be seen in Appendix D.

Both sets of herbicide data were analyzed in terms of percent degradation instead of total mass degraded. The percent degradation is based upon that which was added. In other words, of the amount of each herbicide applied to the columns, this percent was degraded. By only looking at the total mass degraded, the length of time it took to

degrade the chemicals would not be taken into account. Additionally, the columns were continually loaded with rinsate solution (i.e., masses of herbicide) over time, based upon their uptake of fluid due to evaporation. Since the columns were run for four different time durations, they were exposed to varying quantities of herbicide active ingredient. Thus, representing the data in terms of percent degradation allowed for the comparison of treatment combinations run for varying durations.

Preliminary Analysis

All previously described data, including results from all calculations and manipulations, were pooled into three separate spreadsheet notebooks — one comprising all evaporation data and one each containing the two herbicide degradation data. Pooling the data in such a manner provided a means for easy initial observation. Both the final evaporation results and the final two herbicide degradation percentages for each column were initially analyzed by calculation of the coefficients of variation (CV's) (i.e., the standard deviation divided by the mean) for the replications of each treatment. High CV's alerted us to potential erroneous data and/or extreme outliers. Corrective measures included double checking data entries and calculations, and, if necessary, re-analysis of soil moisture contents and re-analysis of archived soil samples on the HPLC. After all necessary data corrections, the final data set was exported to ASCII files to allow for easy import into SAS® for statistical analysis.

Statistical Analysis

As earlier mentioned, the study was conducted using a complete factorial design, testing all possible treatment combinations with four replications of each. Statistical analysis of the data (listed in Appendix D) consisted of running several tests utilizing SAS® software. Log transformations within the SAS® program were used where necessary to normalize the data. General Linear Modeling (GLM) procedures were performed on the data. A model was constructed using the fixed effects (five factors of interest) as independent variables, along with all possible interaction combinations. The dependent variables of the model were set as the evaporation and degradation data. This information provided an indication of which factors (and all possible interaction combinations thereof) contributed significantly to the model.

Since the data were from an unbalanced design (unequal numbers of levels for the different fixed effect variables), it was necessary to estimate the evaporation and degradation means. The least-squares means (LSMEANS) option in GLM produced estimates of what the evaporation and degradation means would be if factor levels were balanced. Additionally, the LSMEANS option provided an indication of the significance of the factor levels (and all possible interaction combinations thereof) on both evaporation and each herbicide degradation. All SAS® programs used for data statistical analysis may be viewed in Appendix C.

CHAPTER V:

RESULTS AND DISCUSSION

SYSTEM PERFORMANCE

Although preliminary testing of the system and system components revealed much about the performance of the apparatus, the true test of the concepts, designs, and components/equipment came during the actual 180 day-long study.

Soil columns

First, the soil column/solution bottle concept, although not without flaws, worked amazingly well. Even though all columns were tested with water for leaks immediately after construction, this posed a minor problem during the initial "wetting" of the columns upon system start-up. Numerous columns developed leaks in a variety of places such as around either of the two fittings or around the column bottoms (i.e., cemented interface of the PVC pipe and the PVC plate). These leaks were generally very minor, consisting of just beads or bubbles of water. As indicated in S.O.P. #BKC-6 (Appendix A), these were easily fixed with the application of silicone sealant around the leaky area, after which the columns performed as normal. Of all the leaks experienced, only one column could not be repaired as described and required replacement.

Leaks of some fashion occurred in roughly 10% of the columns during the initial start-up process. Several explanations may be theorized to account for this small inconvenience. First, the columns were constructed nearly a year and a half prior to their actual use. During this time span the silicon seal around the fittings may have deteriorated somewhat. Additionally, slight temperature fluctuations over the course of time may have had some impact on the glue, cement, and/or silicon. Finally, during the soil packing process, the columns were agitated quite vigorously and may have jarred or loosened the column parts.

Solution bottles

Likewise, minor problems associated with the solution bottles also occurred. Generally, these were of the form of popped (or blown) stoppers during the bottle pressurization process or during bottle movement for flood/dry cycles. Although the stoppers were sealed to the bottles during the bottle assembly process (using a bead of silicon) it was not sufficient in numerous instances. Actually, the problem centered around the stoppers being a half-size to one size too big for the bottle mouth. Thus, the stopper did not fit well enough down into the bottle to be secure and provide a quality seal. In essence, the silicon needed to serve a dual purpose: provide an air-tight seal and strongly hold the stoppers in place. Although the thin film of silicon originally applied did provide an air-tight seal, it was easy to accidentally rupture it and thus pop the stopper off during daily operational procedures. All popped stoppers were easily and quickly put back in

place and a liberal amount of silicon was applied to better hold them in place.

Another small inconvenience associated with the bottles had to do with their material and size. As described earlier in the theory section, the column/bottle system created a slight vacuum in supplying solution to the soil. In a few cases, the soil exerted such a suction on the bottles that they collapsed over the course of several days. Low density polyethylene (LDPE) bottles were used, and were probably not quite rigid enough in these few cases. High density polyethylene (HDPE) bottles probably should have been used. Also, the size of the bottles, although adequate, could have been a little larger. One liter bottles were used, and during the heat of the summer some of the columns evaporated this amount in only a few days. Frequent filling was thus required during these times. Solution management would have been easier if the bottles had been larger.

Column/bottle system

Clogged tubing had the potential to threaten the integrity of the continual operation of the columns and bottles working together as a system. In a few cases, soil particles tended to clog the top fitting of the column, which in turn stopped the movement of air into the bottle and the subsequent flow of solution to the soil. In essence, this caused the column to stop. Although this problem was foreseen in the design stages and an attempt was made to minimize its effect via the placement of screen over the fitting inlet, this was not sufficient in these few cases. In the majority of these cases, the fittings were easily unclogged, and once this was done the columns ran fine. However, one particular column,

#493, proved differently. This particular column experienced a clogged tube about two months into the study and was never successfully fixed and re-started. Thus, this column was omitted from the study, resulting in only three replications of that particular treatment combination. This column represented the only missing data point for the entire study.

One final performance note of the columns/bottles worthy of mention concerned the flood/dry cycling procedures. Originally, it was intended that the solution bottles would simply be moved and placed below the columns to facilitate gravity draining of the solution out of the soil columns and back into the bottles. However, an interesting observation was noted during the first cycling procedure. The necessary bottles were moved below the columns as intended. After several days, it was noted that these columns were still taking up solution (i.e., the fluid levels in the bottles were still decreasing). Thus, the soil columns were not actually draining, rather solution was still being supplied to the soil. Apparently, the environmental chambers (i.e., airflow and/or heat) accelerated the evaporation to such an extent that the suction potential of the soil was similarly increased. The soil suction was able to overcome the elevation/gravity difference and pull solution upward into the columns. This was unacceptable, since the intent was for the solution to drain out of the soil, and for the soil to become increasingly drier and thus more aerobic over the cycle duration time. To solve this problem, the bottles were not only lowered beneath the columns, but the supply tube connected to the bottom column fitting was clamped off. This ensured that the supply of solution to the column was indeed halted.

Although some of their problems and inadequacies have been elaborated on here,

they were very minor (even negligible), considering the number of columns and bottles and the sheer size and magnitude of this research effort. All in all, the soil bed simulation concept (i.e., soil column/solution bottle system) performed beautifully. One nice advantage the system possesses is its ability to be reused in subsequent studies with minimal maintenance.

Air chambers

The performance of the air chamber apparatus proved quite successful. The physical structure served its purpose as designed. Air flow and heat losses were minimized due to the diligent sealing and insulation of the chambers and duct work. The doors provided easy access to the columns with minimal disturbance to the system. Due to the extensive preliminary considerations and testing, the blowers and heat boxes operated flawlessly for 180 continuous days. Only twice was electrical supply interrupted to the chamber system. Once the building's panic button was accidentally pressed, shutting off all electrical supply to the entire lab. The breaker panels were quickly re-set and the system re-started fine. The second instance involved electric supply to the entire building being temporarily shut off for half an hour for building maintenance. Again, the system re-started with no problem.

Rinsate mixing and distribution systems

Following the outlined protocols for rinsate mixing, the tank mixing system performed more than adequately. No problems were incurred with Davis' (1992) equipment or their modifications. Although it was desired to mix the solution at a concentration of 10 ppm, and the ingredients were measured and added as such, the final tank mix concentrations were consistently slightly lower than expected. They generally ranged on the order of 8.2 to 9.2 $^{mg}/_{mL}$ [ppm] for atrazine and 8.9 to 9.9 $^{mg}/_{mL}$ [ppm] for fluometuron. This was fine for our purposes, since the actual concentrations were monitored, and only the total mass added was actually required for the final computations. A secondary note on the mixing system concerns the periodic cleaning of the tank and associated mixing components. After every other tank mix, the system was triple-rinsed via the incorporated tank lid rinse nozzle to prevent contamination and to help ensure quality control.

Other than for a few minor problems, the solution distribution system also performed very well. At the onset, during the initial start-up phases of the study, the metering pump failed. Although a replacement pump was acquired, the chamber start-up (i.e., turning on of blowers and heat boxes) was delayed for a week, as alluded to earlier. In addition to the replacement, a back-up metering pump was purchased and used for all clean water and wastewater delivery. Other than the original pump failure, the metering pumps worked well.

A second minor concern in the solution delivery system involved problems

experienced with the elapsed time indicator. At times, when the push button switch was depressed to engage the solenoid valve and start the timer, the timer would hesitate to start, or would not start at all. Other times, the indicator would start momentarily, only to temporarily stop in the middle of counting. Originally, 4-conductor shielded cable was used to wire both the solenoid valve and the elapsed time indicator to the push button switch. One hundred and ten volts of electricity was then supplied to the switch for the solenoid valve (the elapsed time indicator needed no external power supply since it was equipped with an internal lithium battery). Upon consultation with Wilkerson (1995), it was concluded that stray voltage/current from the solenoid valve wiring was being picked up by the timer wiring and was affecting the performance of the elapsed time indicator. This problem was addressed by re-wiring the elapsed time indicator with separate 2-conductor, shielded cable to the push button switch. This solution did an excellent job of deterring stray voltage from interfering with the timer.

Other than these two minor instances, the solution delivery system performed exceptionally well. An accurate account of the quantity of solution added to each bottle was determined and recorded. As an additional note, the delivery system was flushed with clean water periodically to prevent contamination and to help ensure quality control.

GENERAL OBSERVATIONS

Air chambers

From the daily operation and observations of the solution bottles and soil columns, early in the study it became apparent that the chambers were controlling the evaporation rates as designed. As shown later in this chapter, the evaporation data strongly backed these observations. The columns in the South-Central chamber (i.e., high temperature and high air flow) consistently used a greater amount of solution than the others, and thus required far more frequent bottle filling. The columns in the North-Central chamber, however, exhibited the extreme opposite conditions, and thus its bottles required far less frequent filling.

Noticeable changes in the evaporation rates, within all four chambers, was also observed with outside weather fluctuations. For example, during the heat of the summer, the bottles used more solution than during the spring and fall weeks. Consequently, at these times the bottles required constant attention, with batches of solution being constantly mixed and bottles being filled on a daily basis. This was different from the fall and spring weeks, which in many cases required only weekly mixing of a batch of solution, and bottle filling only periodically throughout the week. From these general observations, a greater appreciation was gained of the role of temperature and air flow in the evaporation process.

By comparing the plotted evaporation rates from Figure 25 to the weather station graphical information shown in Figure 26, one can see the climatic influence upon the

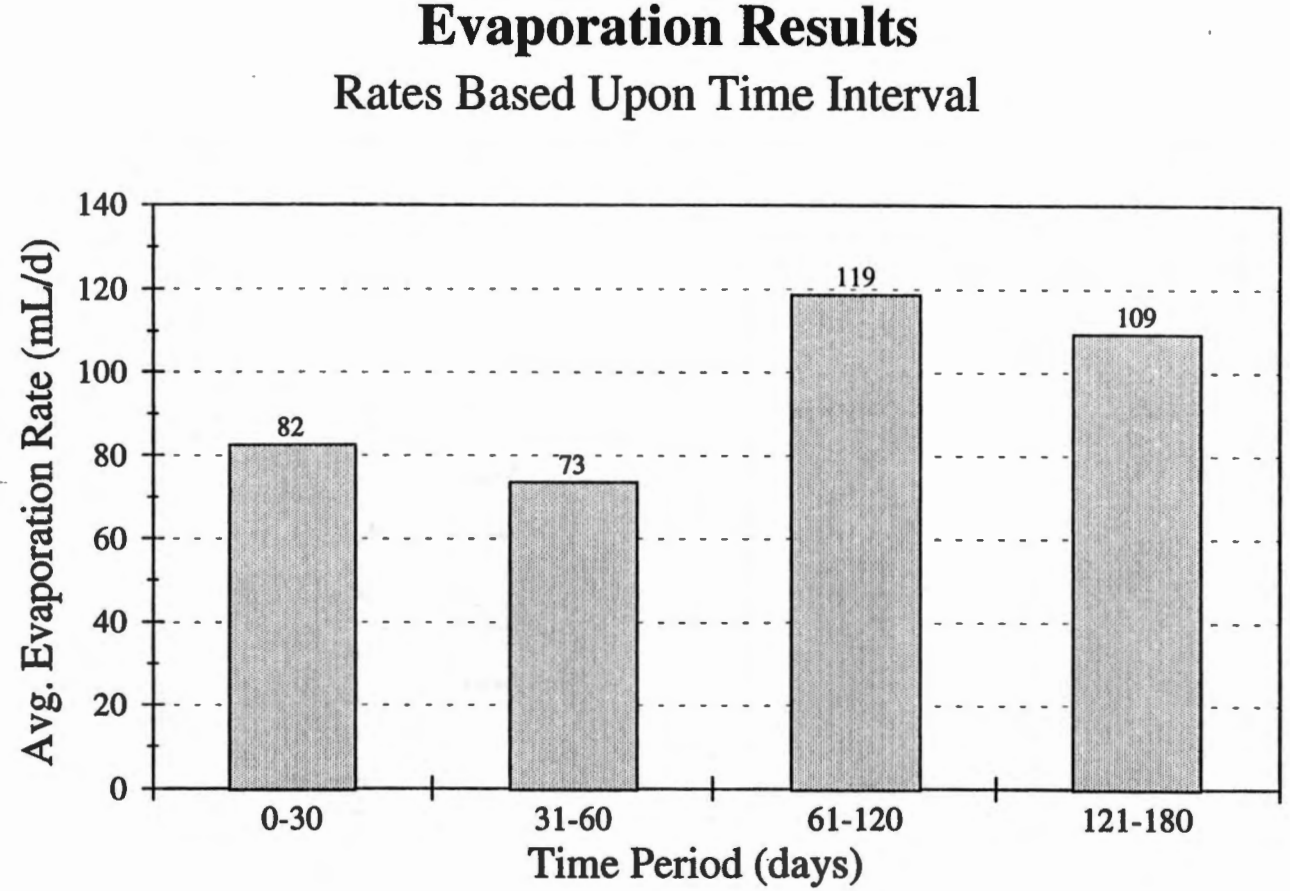


Figure 25. Evaporation rates during each time interval. Values are averaged for all columns per time period. Day zero corresponds to May 1, 1995 and day 180 corresponds to September 28, 1995.

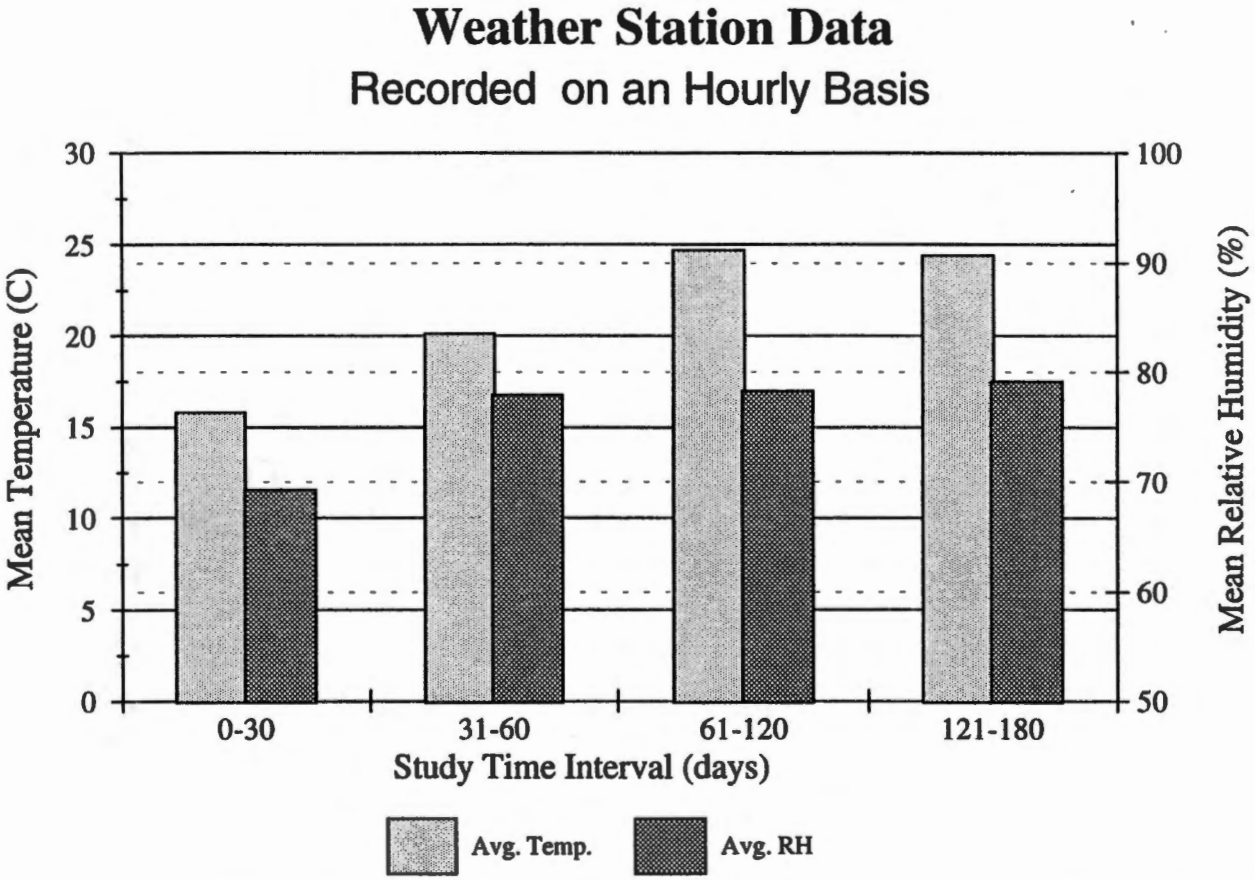


Figure 26: Temperature and relative humidity reported for each time interval. Data recorded hourly and collected from permanent weather station. Values are averaged over each specified time interval. 180-day time frame corresponds to Julian days 91-271. Day zero corresponds to May 1, 1995 and day 180 corresponds to September 28, 1995. Note: fifteen days of data are missing over the entire study duration.

evaporative process. Figure 25 depicts a graphical representation of the average evaporation rate (mL/day) of the active columns during the four prescribed time intervals. As expected, the time periods with the highest average rates of evaporation occurred during mid-to-late summer and early fall. Between study duration days 61-120 (i.e., June and July), the average rates of evaporation were at their highest, 119 mL/day and 109 mL/day, respectively. From the weather station data, one also notes that these particular time periods coincide with the combination of highest average temperature and moderate average relative humidity.

The lower rates of evaporation, 82 mL/day and 73 mL/day, occurred during the months of April (days 0-30) and May (days 31-60), respectively, when the temperature was lower. However, during days 31-60, the rates were the lowest, even though the weather data indicates that the temperature was greater than during the initial 30 days (i.e., in April). Although the average temperature was higher during the second thirty days of the study, so too was the relative humidity. The net result was a decrease in water evaporation due to the higher moisture content in the air.

One final general observation in regard to chamber performance concerns temperature and its role in degradation as opposed to evaporation rates. Recall that the literature points to elevated temperatures as enhancing microbial activity. Thus, the chambers were designed such that the air flow temperature not only influenced evaporation rates, but also the soil conditions. Once the chambers reached equilibrium, there were noticeable temperature differences between the heated and unheated chambers.

For instance, the components of the heated chambers (i.e., doors and duct) were noticeably warmer to the touch than those of the unheated chambers. Likewise, the PVC soil columns themselves were also warm to the touch, thus indicating that the soil conditions were being influenced similarly.

Soil columns

Throughout the duration of the study, notable differences were observed between the soil surfaces of the different column types. For instance, the soil surface of the wicking columns appeared only moist and damp with solution, whereas the soil at the surface of the flooding columns (during their flood cycle) appeared saturated and glistened with wetness. The majority were somewhat ponded with solution, with small pools of fluid around the PVC rim and the top fitting inlet. This provided strong visual proof of the proper performance of the columns and their achievement of various states of saturated versus unsaturated soil conditions. Additionally, upon drying of the flood/dry columns, the saturation quickly disappeared and the soil seemed to dry substantially during the cycle duration. Likewise, upon re-flooding the columns, the presence of saturated conditions returned to the soil surface.

Many of the columns exhibited some type of material formation on the soil surface and along the top PVC edges. In some instances, this material appeared white and crystalline-like in formation, similar in appearance to calcium-like deposits and scaling on water pipes. Since no specific samples were collected or analyzed, the exact makeup of

this material is unknown. Whether herbicide chemical crystals or mineral deposits from either the soil or water, it is believed that this material is the direct result of the upward flux of solution to the top soil surface due to evaporative processes. Recall that Winterlin et al. (1984) observed a similar chemical mass transport in their soil bed systems due, in theory, to the "wick effect."

Also, some of the columns exhibited a greyish, hazy growth across portions of the soil surface. This material was different from the crystal-like structures, and again its exact composition is unknown. It is theorized to be the result of some form of biological activity, perhaps fungal or microbial growth. Although only based on observations, both of these occurrences were interesting and lend themselves to a variety of speculation. Photographs showing examples of this material formation on the soil surface may be seen in Figure 27.

There were several other noteworthy observations associated with the soil preparation procedures prior to HPLC extraction and analysis. More specifically, during the process of removing the soil from the PVC columns, strong indications of column performance were noted. For instance, variations in soil moisture were very noticeable. In general, the columns containing sandy soil were either wetter or drier than their counterpart silty columns. This was as expected, due to the extreme differences in soil texture and the associated impact on water movement within the matrix. This observation proved a good indication of the chosen soil type achieving the desired goals.

Observable soil wetness differences between the various column types also gave

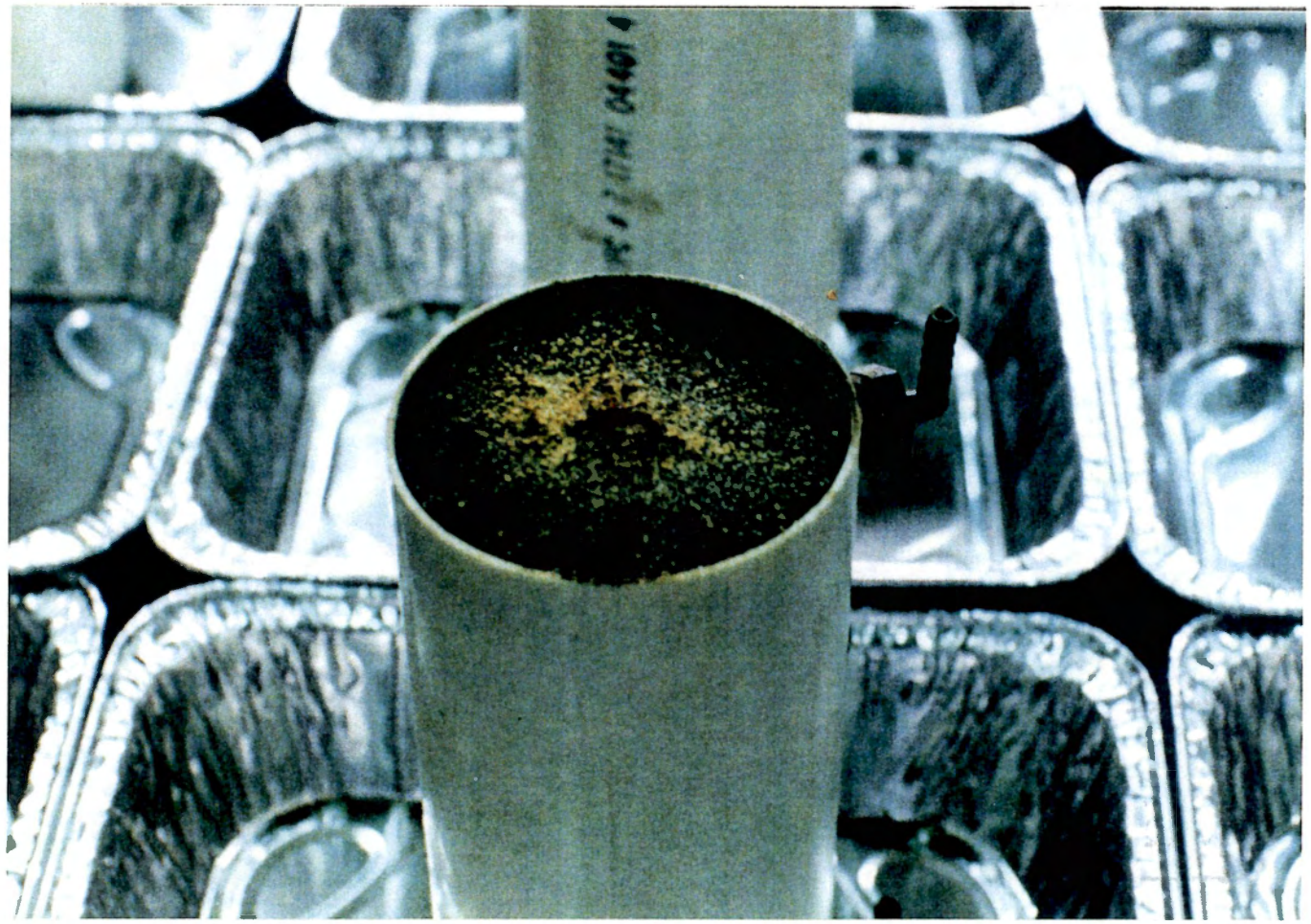


Figure 27. Close-up photograph of a column illustrating the material formed on the soil surface of many columns.

some indication of their performance. Of the flood/dry-type columns, those which had been in the drying cycle prior to being pulled were generally much drier than the remaining columns. In many instances, the soil was so dry that it had to be dug out of the columns. Thus, it appears that during this cycle those columns were indeed drying out sufficiently, probably becoming more aerobic in nature.

Similarly, the flood/dry-type columns pulled during their flood cycle exhibited the extreme opposite conditions. The soil from these columns was saturated with solution and appeared muddy and "soupy" or "gooey" in nature. This provided further positive indications that the flood/dry cycling approach of these columns was achieving the desired alternating aerobic/anaerobic conditions.

Observations of the soil within the wicking-type columns also provided positive indications about their performance. In terms of wetness, the soil in the lower half of the column was very wet, while that above appeared only moist. In addition to being saturated, the soil in the lower portion of the wicking columns generally exhibited a different coloration (this became more pronounced later in the course of the study). Particularly noticeable in the silty soil was its color, a distinctive greyish, similar to that of the mud or muck in pond or river bottoms. It was very distinctly that of a saturated-type anaerobic soil. On the other hand, the upper portion of soil in these columns had much more color, appearing reddish-to-brownish and with more structure associated with it. This color variation occurred along a very distinct line, usually if not always along or very near the saturated/non-saturated interface (i.e., at the location of the top fitting in the

columns). In many cases, this distinct interface left permanent stains on the insides of the PVC columns. In addition to these observations, the soil in lower portions of these columns, in many cases (particularly in the silty soil), seemed to have a stronger odor than normal, as one might expect under saturated anaerobic conditions. All of these indications point to successful performance of the columns as intended and designed.

DATA QUALITY

Solution input data (bottle filling)

The solution delivery system provided an accurate account of the quantity of solution added to each and every bottle. The metering pump, calibrated at the onset of each filling process, delivered a consistent volume of solution. Likewise, the elapsed time indicator provided precise timing of the dispensed solution, recording the data to the nearest tenth of a second. Utilization of spreadsheet software yielded accurate and reliable solution input data.

Within-column variability

One concern was whether the herbicide concentrations throughout the columns would vary spatially. This possibility may potentially result from several factors such as 1) introduction of the solution at the bottom of the column, 2) various zones of saturated/unsaturated conditions, and/or 3) the upward flux of solution toward the soil

surface ("wick" effect). The desire of this research effort was not to determine any individual degradation characteristics within the various soil column treatment combinations; rather, it was to determine their overall degradation performance. Thus, some concern was expressed concerning the preparation procedures of the soil prior to HPLC analysis. In particular, discussion centered on potential within-column concentration variability and the ability to obtain a single soil sub-sample truly representative of the entire soil column.

The soil preparation protocol (S.O.P. #BKC-8, section II, Appendix A) calls for not only screening the air dried soil, but also thoroughly mixing it via placement in a large plastic bag and shaking vigorously. To ensure that a single 40g sub-sample of this soil would accurately represent the entire 2-3 Kg of soil in the columns, a preliminary analysis was performed. The South chamber was randomly selected, and eight 30-day columns, representing the various soil types and application modes, were removed and the soil prepared per S.O.P. #BKC-8. From each of these, four soil sub-samples were collected, and their respective HPLC concentration results were compared. Except for a few outliers, the coefficients of variation for the multiple sub-samples for the columns were less than 5%. In actuality, the majority of the CV's were on the order of 1 - 3% (data may be seen in Table F-1, Appendix F). This provided an excellent indication that thorough mixing was achieved, and that a representative sub-sample was collected. It could thus be assumed with confidence that HPLC results were indicative of the total amount of herbicide remaining in the soil within each column.

HPLC analysis

Upward of 1500 samples were analyzed on the HPLC system previously described. These samples represented both rinsate solution samples and soil samples. Throughout nearly the entire study, this system yielded quality chromatograms with sharp peaks. Regression analysis of the various output consistently produced r^2-values on the order of 0.97 - 0.99 for all chemicals detected. The voluminous amount of hard copy data (both chromatograms and regression results) is not included in this manuscript, but is retained by the author. Regular maintenance of the system during the study period included such things as replacement of UV lamps, HPLC columns, the auto-sampler pressure transducer, and the periodic replacement of sample standards. All of these alterations had minimal impacts on the system.

One noteworthy alteration to the soil extraction technique involved the quantity of soil sub-samples collected. Initially, 40g of soil were extracted from each column sample for analysis. This was the case for both the 30- and 60-day samples, with good results. However, the herbicide concentrations were increasing over time and approaching the upper limit of the linear range of quantitation of the system. It was decided to reduce the sub-sample size for all future column analyses. So, for the 120- and 180-day samples, only 20g of soil was extracted. Analyzed in the same manner, these results were also extremely good.

One final note in regard to the HPLC concentration detection data concerns the first metabolite of fluometuron, desmethyl fluometuron. Although all samples (both

solution and soil) were analyzed for it in addition to the two main herbicides, the desmethyl fluometuron data was not used or reported in this manuscript. However, it is worth noting that desmethyl fluometuron was never detected in any of the solution samples. It was detected in about 84% of the soil samples, with concentration values ranging from 90 to 4950 $^{ng}/_{g\,soil}$ [ppb], although the majority were < 1000 $^{ng}/_{g\,soil}$ [ppb].

Data modifications

The final check of data quality prior to any actual analysis procedures (statistical or otherwise) involved coefficient of variation calculations for replications within the various treatment combinations. Performed on the evaporation data set as well as both herbicide degradation data sets, high CV's brought to attention questionable data and/or possible outliers. Special attention was given to any number more than two standard deviations (STD) away from the mean. Thus, the CV was calculated for all 128 different treatment combinations. From these, the overall average CV and its associated STD were determined for each data set (i.e., both fluometuron and atrazine degradation results). Any individual CV outside of the 2-STD range indicated a need to address that particular set of treatment combinations for questionable numbers. Corrective measures included correction of data entry errors, re-analysis of soil moisture content data, and re-analysis of archived soil samples on the HPLC. Through two rounds of re-analysis procedures, eight data entry errors were detected and corrected, 61 archived samples were re-extracted and re-analyzed on the HPLC (of those, all but 12 yielded more consistent results), and six

soil moisture samples were re-run and replaced. These re-analysis procedures improved the accuracy of the final data set. In terms of degradation, Table 9 depicts the levels of improvement.

Table 9. Data quality improvement from preliminary coefficient of variation analysis.

	FLUOMETURON		ATRAZINE	
	Mean CV*	**STD†**	**Mean CV***	**STD†**
Original data set	0.213	0.564	0.118	0.118
After first round of re-analysis	0.194	0.133	0.103	0.087
After second round of re-analysis	0.164	0.092	0.096	0.078

* average coefficient of variation between replications for entire data set
† standard deviation of the CV's for the entire data set

As Table 9 shows, the final data set had an average coefficient of variation between all 128 different treatment combinations of 0.164 for fluometuron degradation, with a standard deviation of 0.092. Likewise, the final atrazine degradation data set contained an average CV of 0.096 with a STD of 0.078. This tight grouping of the data is indicative of the quality and confidence in the correctness of the numbers. It is also a testimony to the performance and reliability of the system and its design. The degree of similarity between treatment replication data is a direct result of the attention to detail and the painstaking hours spent properly preparing the system.

DATA ANALYSIS

Procedures

After addressing all questionable numbers, the final data set appears as seen in Table D-1 (Appendix D). In addition to being analyzed graphically for any clearly observable trends or indications, the data sets were also subjected to statistical tests. The statistical analysis began by testing the data for normality and standard deviations. SAS® Univariate procedures were used to evaluate this important characteristic. The first attempt at this revealed non-normal distribution of the evaporation data set. As seen in Appendix C, a new variable (levap, equation 22) was defined in the SAS® program to help stabilize the evaporation value distribution. This new variable was defined as:

$$levap = \log (evap) \tag{22}$$

where:

levap = new variable
log = natural log
evap = original evaporation values

This minor manipulation corrected the data and, with the exception of only a couple of outliers per data set, all three then appeared normally distributed. Standard deviation values revealed the same results. Therefore, it was concluded that the transformed evaporation data and the two original degradation data sets could be assumed normal, and that standard statistical procedures would be valid.

Significant variables were determined with SAS® software utilizing the General Linear Model (GLM) procedures on all three data sets (i.e., evaporation, fluometuron degradation, and atrazine degradation), including the least-square means (LSMEANS)

option. Both sets of degradation values and the normalized evaporation values were modeled against the independent variables of airflow, temperature, application mode, soil type, and all possible interaction combinations thereof. At a 95% confidence level, this procedure indicated which factors contributed significantly to the model. The actual SAS® program may be seen in Appendix C.

Computation of the least significant difference (LSD) provided insight into the degree of significance among the levels of all influentially determined factors (main effects and interaction terms). Utilizing the standard error computed by SAS®, the LSD was calculated as follows:

$$LSD \approx 2*\sqrt{2(std.\ err.)^2} \tag{23}$$

The LSMEAN values reported from SAS® were then compared via the LSD. For factor levels to be significantly different from one another required that their LSMEAN values differ by at least the LSD value. If not, then the factor levels were considered to be statistically the same at a 95% confidence level.

It is also important to note that the LSMEANS reported in the various tables throughout this chapter are actually the back-transformations (i.e., e^x) of the values SAS® computed utilizing the normalized evaporation data set (i.e., the natural log [$ln(x)$] of the original raw evaporation data). These tabulated values vary from and should not be confused with the raw data values utilized for graphical figures. The raw data means depected in the various graphs have not been normalized and represent the actual

evaporation observed. The back-transformed LSMEAN values, however, were used for statistical determination and are only represtantative of the actual raw data values.

The statistical results from these analyses of variance tests are located in Tables E-1 – E-3 (Appendix E). P-values revealed that 11 variables and/or interactions were significant from the evaporation model, which had a computed $r^2 = 0.967$. Similarly, for the fluometuron degradation model, 12 variables and/or combination terms appeared to contribute significantly, with a lower computed $r^2 = 0.854$. At 18, the atrazine degradation model contained the highest number of significant variables (and/or combinations), and produced a computed $r^2 = 0.960$.

Since the full model indicated so many main effects and interaction terms as being statistically significant at $\alpha = 0.05$, it became difficult to achieve a realistic estimate of each variable's impact on either evaporation or herbicide degradation. Thus, before delving too deeply into the analysis and explanation of these significant factors, it was first necessary to narrow down the scope of interest. Although a change in the reference probability (α - level) is a generally accepted practice for limiting the range to which attained probability values (p-values) appear as significant (Elliott, 1981), this likely would not have made a dramatic impact upon the data set. Additionally, the intent of this study was to establish the influential factors controlling a disposal method, rather than intending to challenge any established principals. The assumptions made based upon the significance level are thus not quite so severe. Therefore, it was decided to let the confidence level remain at 95% and to explore other alternatives.

Basically, the statistical results reported in Tables E-1 – E-3 (Appendix E) were divided and analyzed as two separate sections. To begin with, it was felt that the variable of time was inherently different than the other main effect factors. The influence of time was of interest more in terms of general behavior of a realistic soil disposal system, as opposed to the design and management-related issues addressed by the other main variables. Although statistically speaking (Tables E1 – E-3, Appendix E) time is significant to all models tested, it is probably more importantly deemed as being practically significant (i.e., based upon common sense). This is especially the case in terms of evaporation. Also, the major reasons for even introducing time as a variable in the study were to address a couple of degradation issues--namely, in addition to gaging the extent of degradation which may be expected, concerns centered around the potential for herbicide accumulation within the soil over time.

Based upon this special attitude toward the time variable, result interpretations were divided along these lines. Thus, the significance of time and all time-related interactions are addressed separately from all remaining main effect variables and their respective interactions.

Time and time-related interactions

The sources listed in Table 10 represent only those related to time which contributed significantly to the full models. Here and in Tables E1 – E-3 (Appendix E), time itself is shown to be one of the most influential factors in terms of both rinsate

Table 10. Listing of time related variables (and combinations) statistically significant to the full models at a 95% confidence level.

Source	*Evaporation		Fluometuron		Atrazine	
	F Value	Pr > F	F Value	Pr > F	F Value	Pr > F
Time	2924.54	0.0001	630.46	0.0001	292.63	0.0001
Temp*Time	3.82	0.0101	3.94	0.0087	2.64	0.0492
Airflow*Temp*Time	†N/S	N/S	3.23	0.0224	N/S	N/S
Applic*Time	2.67	0.0051	5.79	0.0001	13.84	0.0001
Airflow*Applic*Time	2.12	0.0274	N/S	N/S	N/S	N/S
Airflow*Temp*Applic*Time	N/S	N/S	N/S	N/S	2.91	0.0024
Soil*Time	N/S	N/S	N/S	N/S	49.12	0.0001
Airflow*Soil*Time	3.74	0.0114	N/S	N/S	N/S	N/S
Temp*Soil*Time	N/S	N/S	3.69	0.0121	8.75	0.0001
Applic*Soil*Time	N/S	N/S	N/S	N/S	5.68	0.0001
Airflow*Applic*Soil*Time	N/S	N/S	2.01	0.0375	N/S	N/S
Temp*Applic*Soil*Time	N/S	N/S	N/S	N/S	2.45	0.0101

* Statistical results reported on the natural log transformed evaporation data set.
† N/S: Not statistically significant at $\alpha = 0.05$.

evaporation and soil metabolism for both herbicides. Looking more closely at the four individual time levels (Tables 11, 12, and 13) it is clearly shown that both average evaporation and average percent degradation (for each herbicide) significantly increase the longer the soil columns are allowed to operate.

Intuitively, the longer the columns were allowed to operate, the more solution they were able to evaporate (Figure 28). The evaporation appears to almost linearly increase with time. The columns operated for the longest duration of (i.e., 180 days), on the average, evaporated about 5½ times as much fluid as those operated for the shortest time (i.e., 30 days).

Table 11. Mean evaporation amounts obtained from columns operated over different time durations.

Time (days)	Normalized Evaporation (mL)	
	LSMEAN	Standard Error
30	2294.0[A*]	0.01411
60	4289.5[B]	0.01411
120	8706.4[C]	0.01418
180	12848.1[D]	0.01411

* Means with like letters are not significantly different at $\alpha = 0.05$

Table 12. Mean percent degradation of fluometuron from soil samples collected from columns operated over different time durations.

Time (days)	Fluometuron Degradation (% of that applied)	
	LSMEAN	Standard Error
30	23.67[A*]	0.6474
60	25.66[B]	0.6474
120	46.74[C]	0.6508
180	56.97[D]	0.6474

* Means with like letters are not significantly different at $\alpha = 0.05$

Table 13. Mean percent degradation of atrazine from soil samples collected from columns operated over different time durations.

Time (days)	Atrazine Degradation (% of that applied)	
	LSMEAN	Standard Error
30	45.07[A*]	0.4634
60	49.35[B]	0.4634
120	56.19[C]	0.4658
180	63.15[D]	0.4634

* Means with like letters are not significantly different at $\alpha = 0.05$

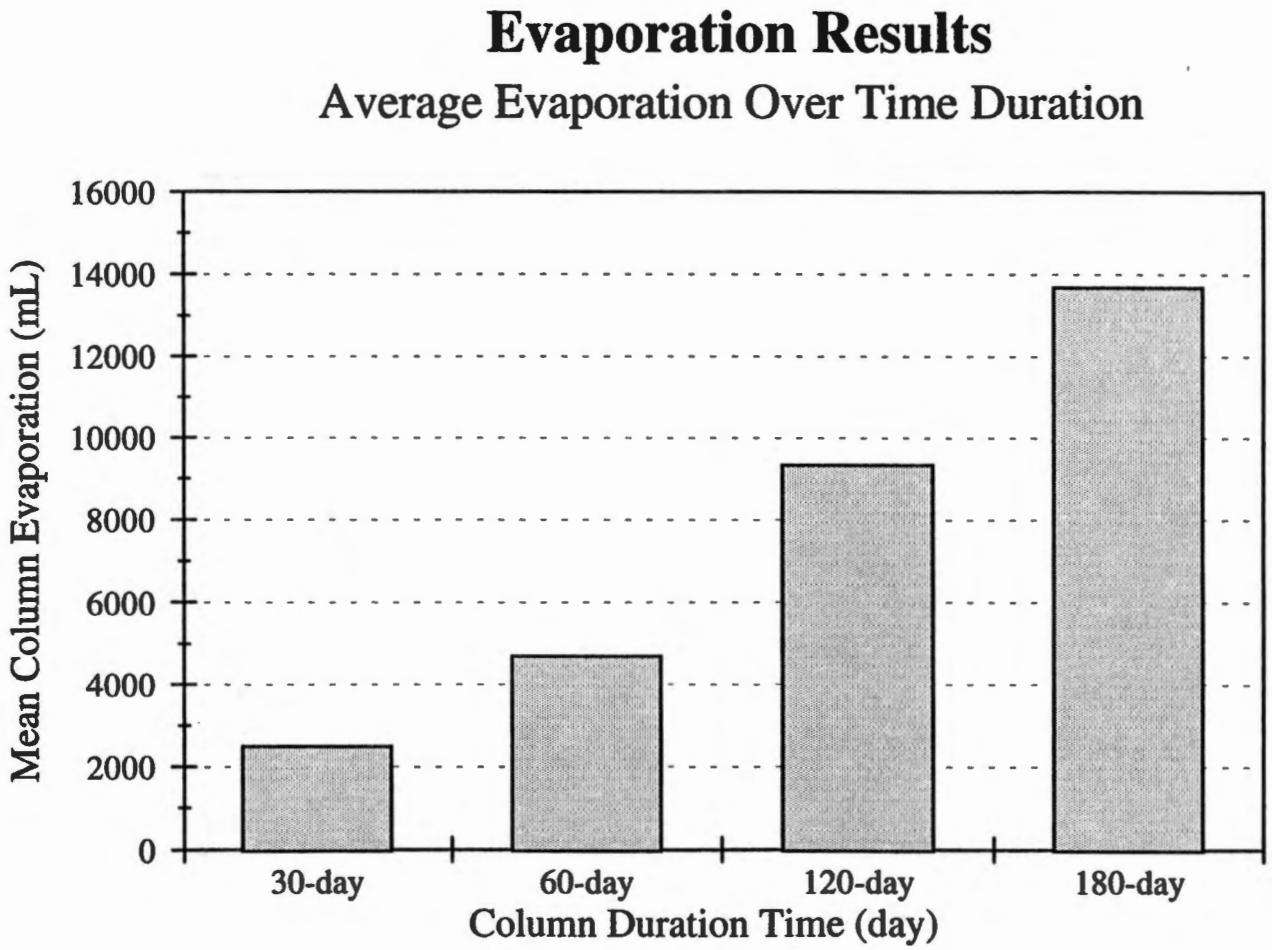


Figure 28. Time effect (statistically significant at $\alpha = 0.05$) on final evaporation. Values are averaged over all treatment combinations per time period.

As already stated, in terms of degradation, the concerns surrounded potential build-up of herbicides within the soil over time. In other words, under continual loading, would the herbicide concentrations increase, such that any degradation would be minimal? As illustrated in Figure 29, the chemical concentration within the soil did increase over time. This is as expected, since the soil was being continuously loaded. After the first thirty days, the average concentration of both fluometuron and atrazine within the soil columns sampled was 11.5 ppm and 7.3 ppm, respectively. Although the concentration within the samples collected over the next 150 days increased dramatically, the trend appears to be leveling off somewhat. By the end of 180 days, the soil samples revealed an average of 28.3 ppm of fluometuron and 22.3 ppm of atrazine. Another clearly observable note from this figure is that the fluometuron concentrations were consistently greater than the atrazine concentrations in samples analyzed from all time periods.

Although these herbicide concentrations indeed increased over time, so too did their apparent degradation. As seen from Figure 30, the actual percent degradation for both herbicides actually increased as they remained in the soil and were exposed to soil microbial activity. Over the first thirty days of exposure, 23% of the amount of fluometuron and 45% of the amount of atrazine applied during this time frame were degraded. Comparably, 81% of the amount of fluometuron and 77% of the amount of atrazine added during the final 60 days of the study were degraded. As each herbicide is spread throughout the column (over time), the column is better at breaking down the herbicides. As pointed out earlier, it was also warmer during the summer months and this

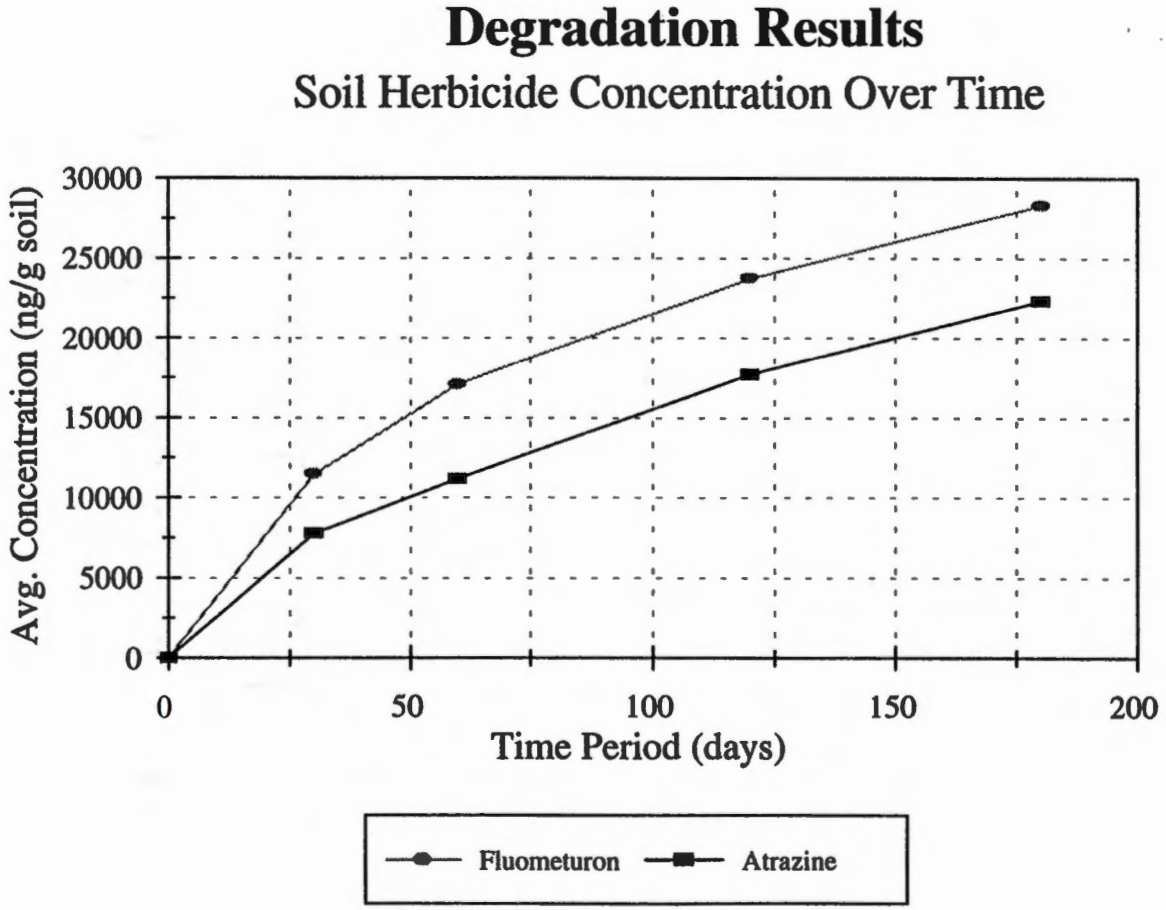


Figure 29. Soil herbicide concentrations from column samples collected at each of the four time periods. Values are averaged over all possible treatment combination samples collected per time period.

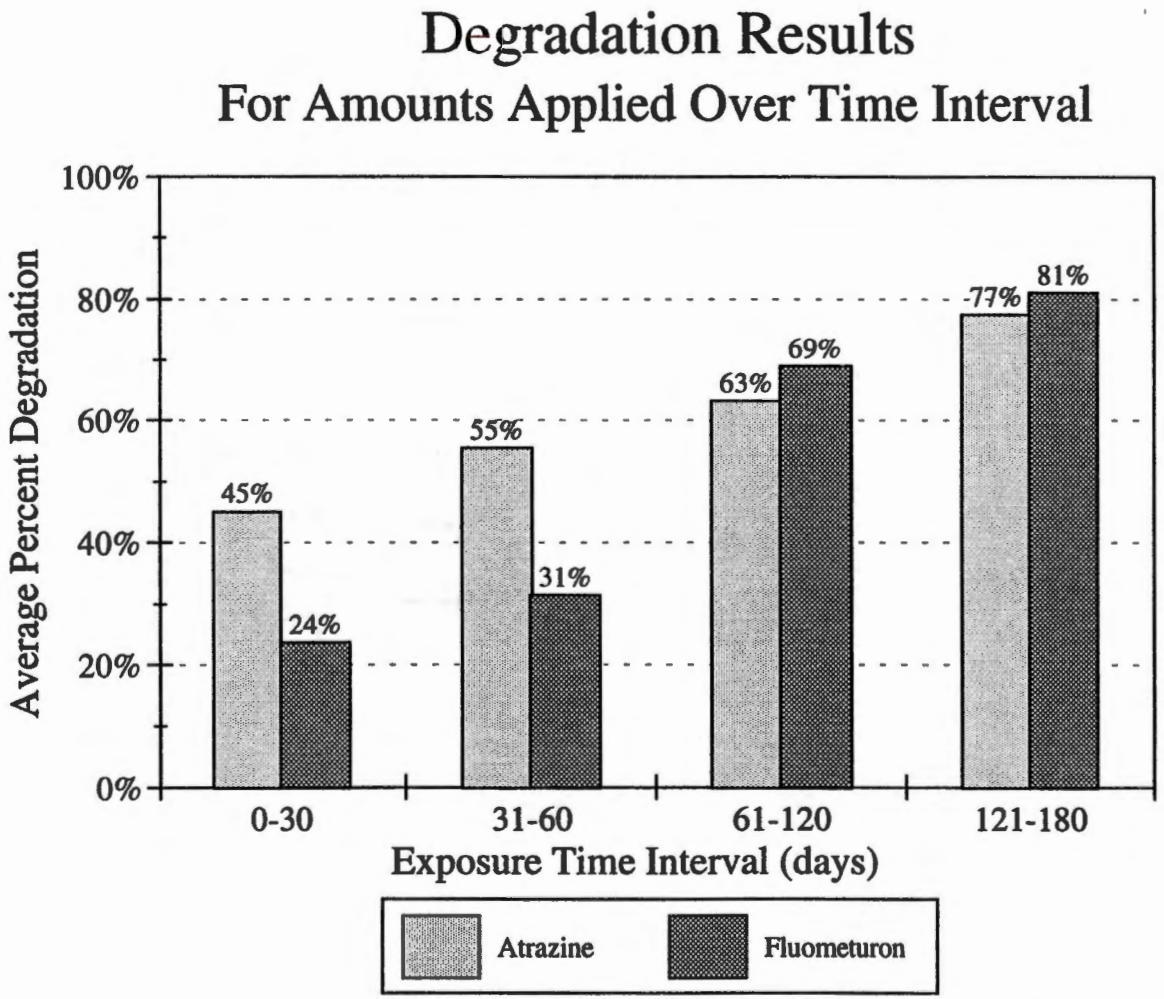


Figure 30. Quantity of herbicide degradation of that which was applied to the columns during each specific time interval. Values are averaged over all possible treatment combination samples collected per time period.

probably influenced the increased herbicide breakdown. The atrazine degradation numbers tended to steadily increase over the course of the study, whereas the fluometuron degradation started out more slowly and then increased dramatically somewhere between days 60 and 120. The fluometuron degradation rates during the last 60 days are actually greater than those of atrazine. A partial explanation of this may lie in the fact that the average half-life of fluometuron (85 days) is longer than that of atrazine (60 days) (Ahrens, 1994). In terms of microbial metabolism the same can be said, with half-lives under both aerobic and anaerobic conditions being 146 and 159 days for atrazine as compared to 189 and 378 days for fluometuron (Ahrens,1994).

Representing overall average degradation for all columns sampled during each noted time period, Figure 31 exhibits similar general traits; again, these degradation numbers represent the percent of the total applied chemical which has degraded. The plots in this figure are directly correlated with the concentration results plotted in Figure 29 shown earlier. A higher concentration in the soil indicates that less of the material which was applied has degraded. This figure again shows that the longer the soil columns are allowed to run, the more degradation occurs. An obvious point of interest, as also pointed out in the concentration data, is that the columns consistently degraded more atrazine than fluometuron.

The most important indication from these initial degradation discussions is that although the concentrations went up, their rate of increase over time is diminishing. As indicated by the substantial increase in herbicide dissipation over time, the degradation

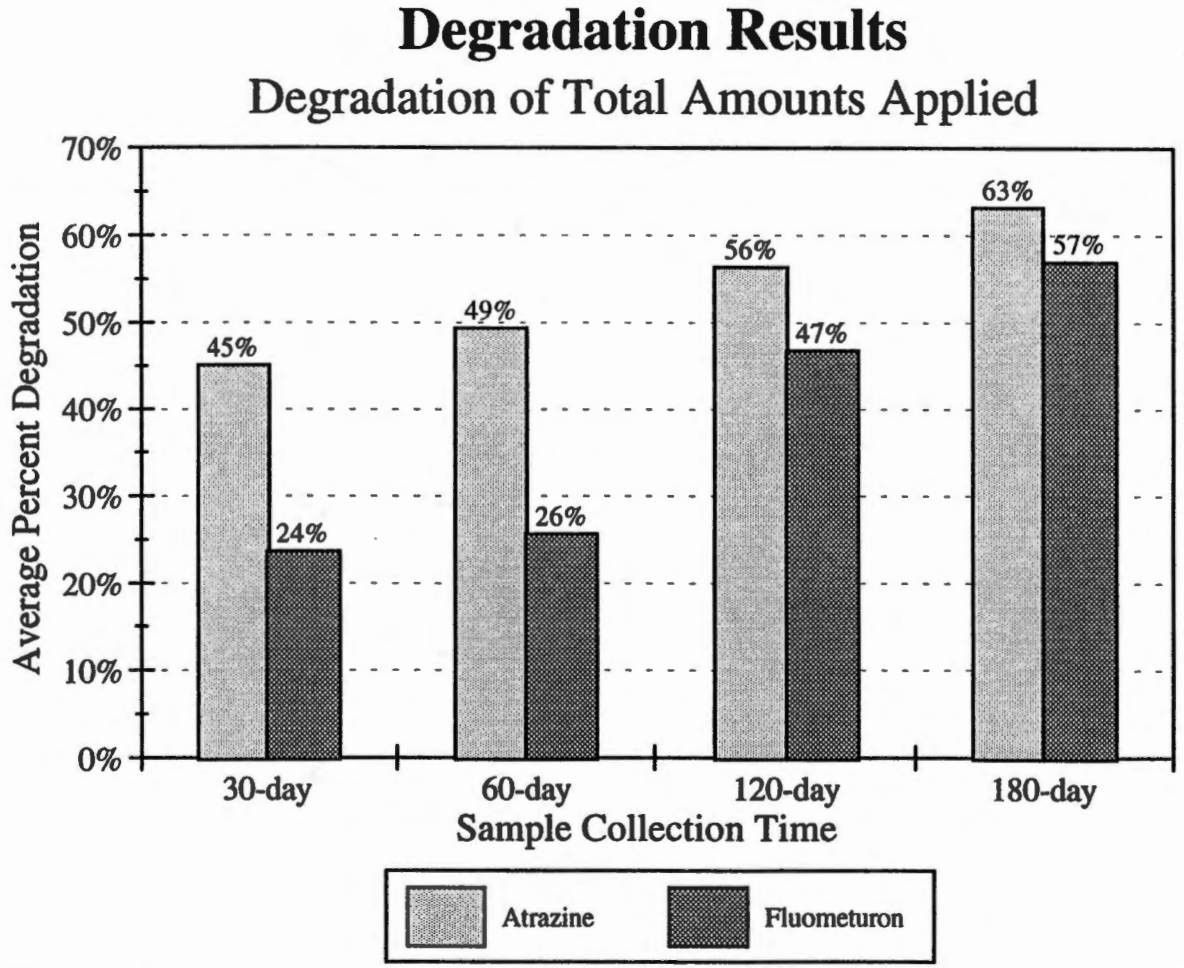


Figure 31. Overall herbicide degradation from all columns sampled during noted time period. Values represent average percent degradation of the total amounts applied to all possible treatment combination columns per time period.

process does not appear to be overwhelmed by the continual loading of the columns. This conclusion is similar to the reports from the soil disposal system used in Iowa and California. As the literature revealed, evaluations of both of these systems concluded that there was no chemical build-up within the soil over many years of operation.

The main questions surrounding the effect of time have thus been addressed. However, in addition to these obvious influences on the overall performance of the system, there were numerous time-related interaction model terms shown to be statistically significant (Table 10). Before dismissing time from the rest of the analysis, it is first necessary to briefly take a closer look at these interaction terms for any further trends or peculiarities.

temp*time:

- for the columns operated for similar lengths of time, performances were significantly different for the two temperature levels;
- in general, the vast majority of columns with similar run times achieved significantly better evaporation and degradation when exposed to elevated temperatures; the only exception to this was fluometuron degradation results over the first 30 days;
- this is overshadowed, however, by the distinction that regardless of temperature, longer exposure time always yielded significantly higher results (both evaporation and degradation); the amount of increase in both evaporation and degradation was slightly greater at higher temperatures than at lower temperatures.

airflow*temp*time:

- for the columns with the same run times and temperature exposures, airflow rates significantly impacted the amount of fluometuron degradation;
- regardless of airflow and/or temperature, the 180-day columns had significantly higher mean percentage of fluometuron degradation than all others;
- under all airflow/temperature combinations, the degradation of fluometuron started off slowly and was similar over the first 60 days; over the last 120 days, however, it increased dramatically;
- this amount of increase over time was either more or less pronounced under low airflow conditions, with the elevated temperature proving best.

applic*time:

- for the columns operated for similar lengths of time, their performances were significantly different based upon mode of application;
- in regard to evaporation, the only apparent trend is that within each application method, the mean evaporation significantly increased over longer run times;
- in terms of degradation (both for fluometuron and atrazine), the impact of time is much more pronounced for the flood/dry-type columns than for the wicking-type; mean percent degradation generally increases over longer times.

airflow*applic*time:

- although shown to be significant, no readily observable trends were noticed.

airflow*temp*applic*time:

- in general, indications are that for columns with like combinations of temperature, application, and time, increased airflow decreased the amount of atrazine degradation;
- however, no observable trends were apparent.

soil*time:

- for columns run for the same length of time, soil significantly impacted the amount of atrazine degradation;
- as acknowledged earlier, silty soil conditions degraded more atrazine than did sandy soil;
- the degradation increase over time was also more pronounced for silty soil columns than for those containing sand.

airflow*soil*time:

- for columns with like soil and run time, airflow rates influenced evaporation;
- evaporation consistently increased over time regardless of airflow/soil combinations;
- for similar soil columns, low air chamber velocities had a larger impact on the overall increase in evaporation over time than the higher air velocities; in other words, the climatic conditions (ambient temperature and relative humidity) changes over time had less effect upon the evaporation for those columns exposed to higher air velocities.

temp*soil*time:

- temperature significantly influences the degradation of both herbicides in columns of similar soil type and run time;
- for all soil/temperature combinations, the columns in general experienced increased degradation of both herbicides over time;
- for fluometuron, the rate of increase of degradation was enhanced through either high temperatures or silty soil conditions; a combination of these two yielded a

quicker increase in degradation;
- atrazine degradation, however, is overwhelmingly soil-influenced regardless of temperature; however, it is apparently temperature sensitive over time, with degradation rates increasing somewhat at higher temperatures for both soil types.

applic*soil*time:
- for sandy soil columns, those with wicking-type application methods produced lower atrazine degradation numbers and lower rates of degradation increase over time;
- for the silty soil columns, there appeared to be no similar link; all degradation seemed to increase over time with no obvious trend. For the silty soils, it thus appears that the increase in atrazine degradation over time is much less sensitive to application methods than it is for sandy soils.

airflow*applic*soil*time:
- for columns with sandy soils, regardless of application methods, those exposed to higher airflow rates consistently experienced lower amounts of fluometuron degradation; however, the rate of fluometuron degradation over time increased similarly regardless of airflow rate;
- under low airflow conditions, both the amount of fluometuron degradation and its associated rate of increase over time were similar; this observation holds true across all soil and application conditions.

temp*applic*soil*time:
- across all applicable treatment combinations, those with sandy soil had observably lower atrazine degradation (both in terms of amounts and the rate of degradation increase over time)
- also for those combinations with sandy soils, exposure to higher temperatures appeared to cause more atrazine degradation than under lower temperatures;
- again for the case with sandy soil conditions, the absolute amount of atrazine degradation increased over time, and was much higher for the flood-type columns than for the wick-type columns;
- for silty soils, however, the atrazine degradation values increased in a consistent manner across similar treatment conditions.

From all of these significant time-related interactions, a few general comments can be made in summation. To begin with, the most obvious indication is that both evaporation and average percent degradation (for each herbicide) significantly increase the longer the

columns were allowed to run. Although longer run times seemed to overshadow the influence of the other interaction terms on the overall increased performance of the columns, the rates of increase were a little more sensitive to these other individual terms. A few more specific trends (all regardless of time) may be summarized as follows:

- elevated temperatures yielded better column performances;
- although higher airflows increased evaporation, lower airflows enhanced degradation due to longer exposure to the soil microbial populations;
- the flood/dry type columns generally appeared to have increased amounts of degradation;
- atrazine degradation was overwhelmingly soil influenced, with much greater degradation in silt;
- the climatic condition (ambient temperature and relative humidity) changes over time had less effect upon the evaporation for those columns exposed to higher air velocities.

However, the most important indication from these time-related observations is that although the herbicide concentrations in the soil went up, so too did the average percent herbicide degradation. The rate of herbicide concentration increase over time diminished as the degradation process increased substantially under continual loading of the columns.

Main effects and interactions

The sources listed in Table 14 reflect those of interest which significantly impact each model and are not associated with the time variable. Several general observations from this table are noteworthy. The remaining four main effects (airflow, temperature, application mode, and soil) all contribute strongly to the three models, with the exception of airflow upon fluometuron degradation. This indicates that the main effects were appropriately chosen.

Table 14. Listing of variables and combinations (excluding time) statistically significant to the full models at a 95% confidence level.

Source	*Evaporation		Fluometuron		Atrazine	
	F Value	Pr > F	F Value	Pr > F	F Value	Pr > F
Airflow	1079.35	0.0001	N/S	N/S	15.51	0.0001
Temp	1187.20	0.0001	34.28	0.0001	80.72	0.0001
Airflow*Temp	18.54	0.0001	6.04	0.0144	N/S	N/S
Applic	11.10	0.0001	23.30	0.0001	72.25	0.0001
Airflow*Applic	N/S	N/S	2.92	0.0341	11.04	0.0001
Temp*Applic	3.08	0.0275	N/S	N/S	3.41	0.0176
Airflow*Temp*Applic	N/S	N/S	N/S	N/S	3.55	0.0147
Soil	45.17	0.0001	31.84	0.0001	7386.21	0.0001
Temp*Soil	N/S	N/S	N/S	N/S	28.16	0.0001
Applic*Soil	N/S	N/S	4.27	0.0055	21.77	0.0001
Temp*Applic*Soil	N/S	N/S	N/S	N/S	5.27	0.0014

* Statistical results reported on the natural log transformed evaporation data set.
† N/S: Not statistically significant at $\alpha = 0.05$.

Evaporation

Airflow and temperature

As expected even before analysis, the F-values (Table 14) show that, individually, the climatic conditions are clearly the most dominant factors in terms of evaporation. Both higher airflow rates and higher temperatures resulted in significantly higher amounts of evaporation than did their counterparts (Tables 15 and 16). Additionally, the interaction term of these two variables, airflow*temp, also proved to contribute significantly to the evaporation model. This interaction term basically reflects the four different chambers. As seen in Table 17 and shown graphically in Figure 32, for all possible treatment

Table 15. Mean evaporation data obtained from columns exposed to two levels of airflow.

Airflow	Normalized Evaporation (mL)	
	LSMEAN	Standard Error
H	7264.83[A*]	0.00998
L	4566.95[B]	0.01000

* Means with like letters are not significantly different at $\alpha = 0.05$

Table 16. Mean evaporation data obtained from columns exposed to two levels of temperature.

Temperature	Normalized Evaporation (mL)	
	LSMEAN	Standard Error
H	7347.39[A*]	0.01000
L	4515.63[B]	0.00998

* Means with like letters are not significantly different at $\alpha = 0.05$

Table 17. Mean evaporation data obtained from columns placed in the individual chambers (i.e., interaction term of airflow*temp).

			Normalized Evaporation (mL)	
Airflow	Temperature	Chamber	LSMEAN	Standard Error
H	H	SC	9552.90[A*]	0.01411
L	H	N	5651.07[B]	0.01418
H	L	S	5524.79[B]	0.01411
L	L	NC	3690.81[C]	0.01411

* Means with like letters are not significantly different at $\alpha = 0.05$

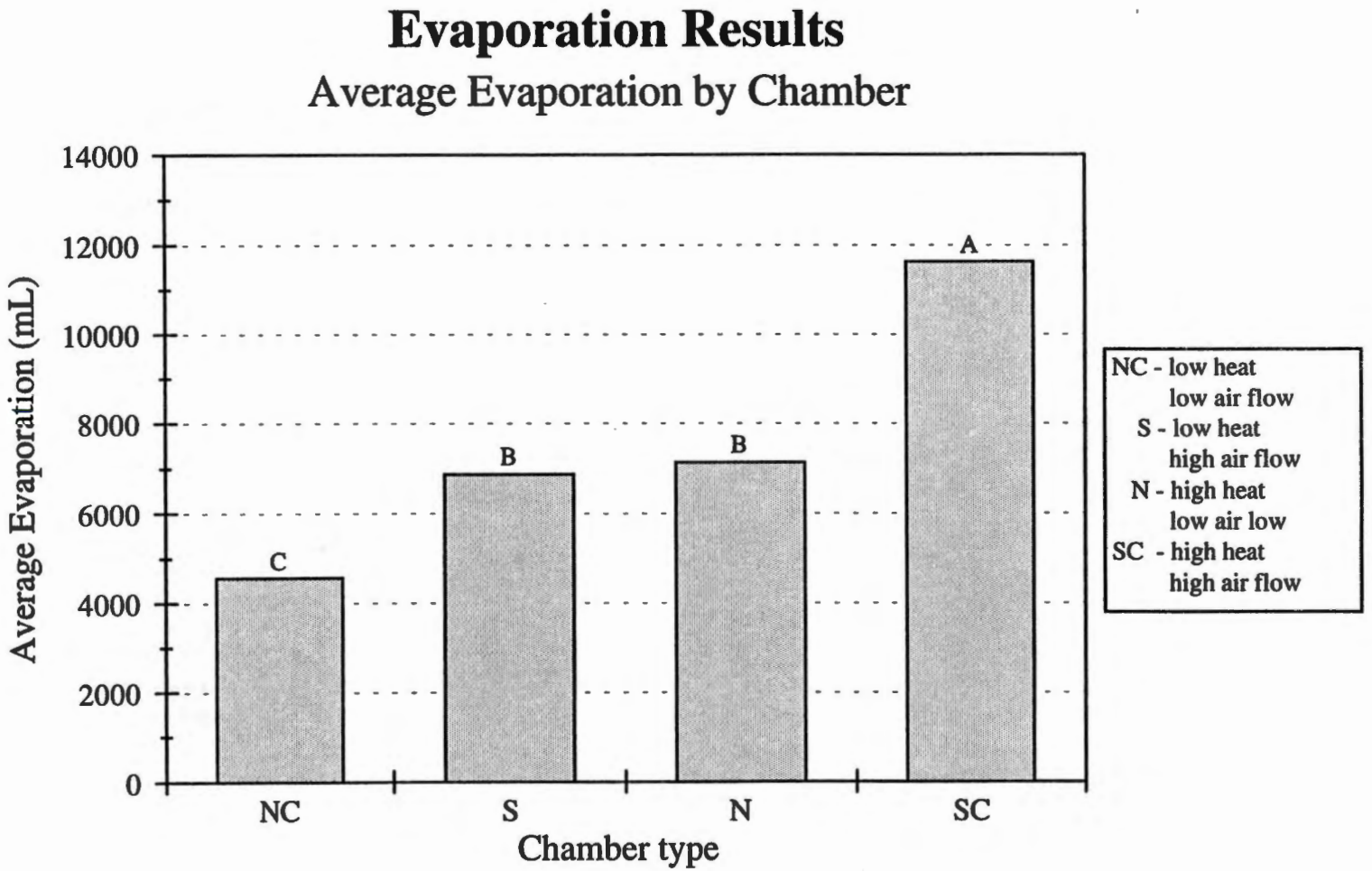


Figure 32. Climatic effects, as controlled by the chambers, on evaporation. Values averaged over all columns within each chamber. Bars with like letters are not significantly different at $\alpha = 0.05$.

combinations, the columns within the South-Central chamber (high airflow and high temperature) averaged significantly greater amounts of evaporation than did the columns in the other three chambers. On the other hand, the columns in the North-Central chamber (low airflow and low temperature) evaporated the least amount of solution. The evaporation within these two chambers was as expected, since they represent the extreme combinations of climatic conditions. The evaporation performance of the other two chambers fell about mid-way between these two extremes, and were not significantly different from one another. This too was as expected based upon the chamber design, with the combination of low airflow and high temperature having similar effects on evaporation as the combination of high airflow and low temperature. Thus, both individually and in conjunction with one another, higher air flow rates and higher temperatures greatly enhance the evaporation performance of the soil columns.

These particular evaporation results were not suprising. They strongly support the general observations noted during the ongoing bottle filling process, as were previously mentioned. These results provide an excellent indication of the performance of these chambers as intended, and are a testiment to the attention to detail in their design and construction phases.

Soil

The third most important factor influencing evaporation is that of soil type. The perception during the bottle filling process was that, in general, the sandy soils seemed to evaporate more solution than the columns containing silt. This, too, was as expected due

to the pore size differences between the two soil types and their relationship to fluid movement. As Figure 33 indicates, this in fact was the case. However, the differences were not as pronounced as expected. Although significantly different at the 95% confidence level (Table 18), the differences between the two amounts of evaporation averaged only abut 11¼%. For all 256 columns of each soil type, the sandy soil columns averaged about 8000 mL [2.11 gal.] of evaporation, while those containing silty soil averaged about 900 mL [0.24 gal.] less.

Table 18. Mean evaporation data obtained from columns containing two types of soil.

Soil Type	Normalized Evaporation (mL)	
	LSMEAN	Standard Error
Sandy	6040.25[A*]	0.00998
Silty	5492.84[B]	0.01000

* Means with like letters are not significantly different at $\alpha = 0.05$

Mode of application

The main effect contributing least to the evaporation test model was that of application mode. The method in which the rinsate was applied to the columns was hypothesized to affect the availability of water at the soil surface, which in turn may influence the evaporation. However, the 10-day flood/dry saturation cycle columns were the only ones significantly different from any of the others (Table 19 and Figure 34). They averaged the least amount of evaporation, which is not totally unexpected due to the extended drying cycle times. However, it is interesting to note that the column type with the highest mean evaporation is the other flood/dry-type (5-day cycle duration). One

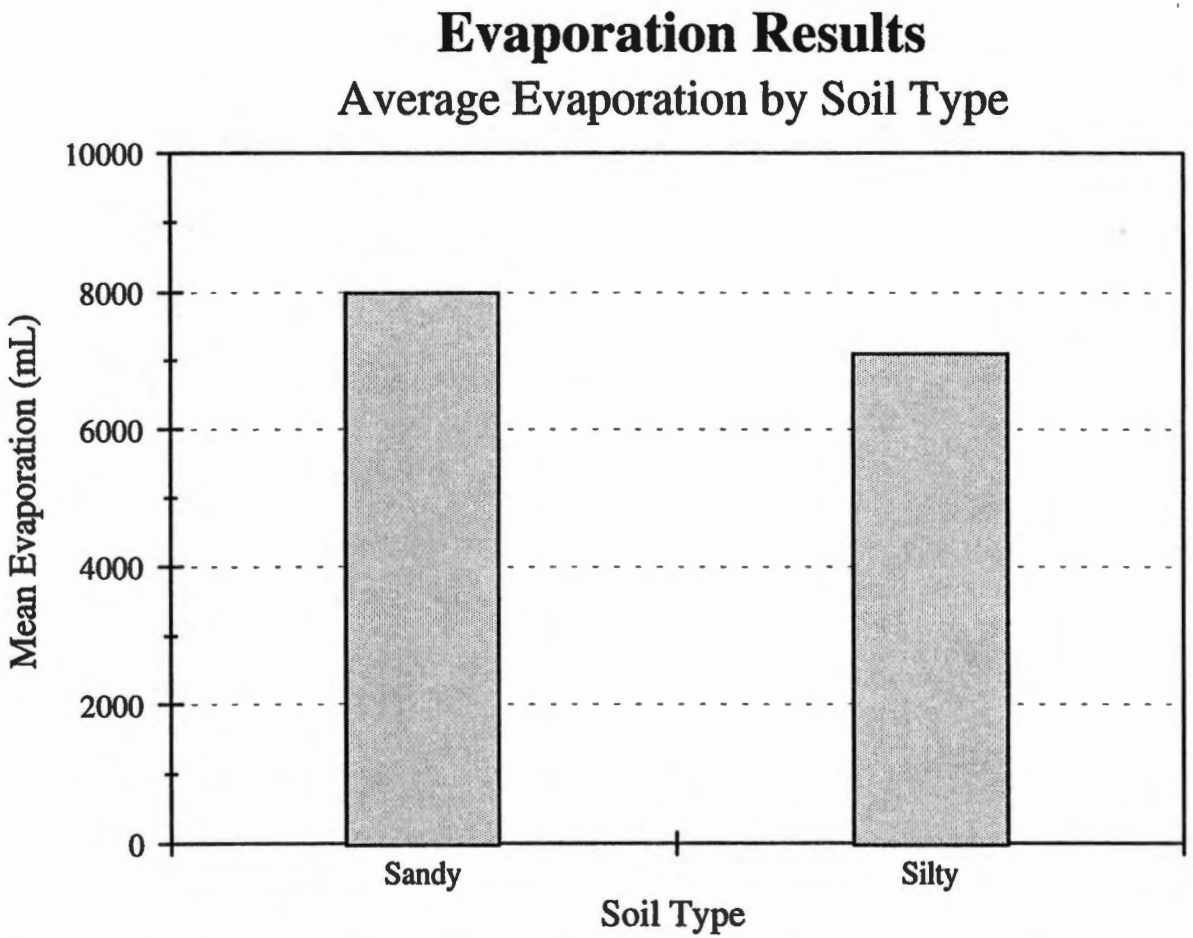


Figure 33. Relationship between evaporation and soil type. Values are averaged over all column treatment combinations per soil type. Soils are significantly different at $\alpha = 0.05$.

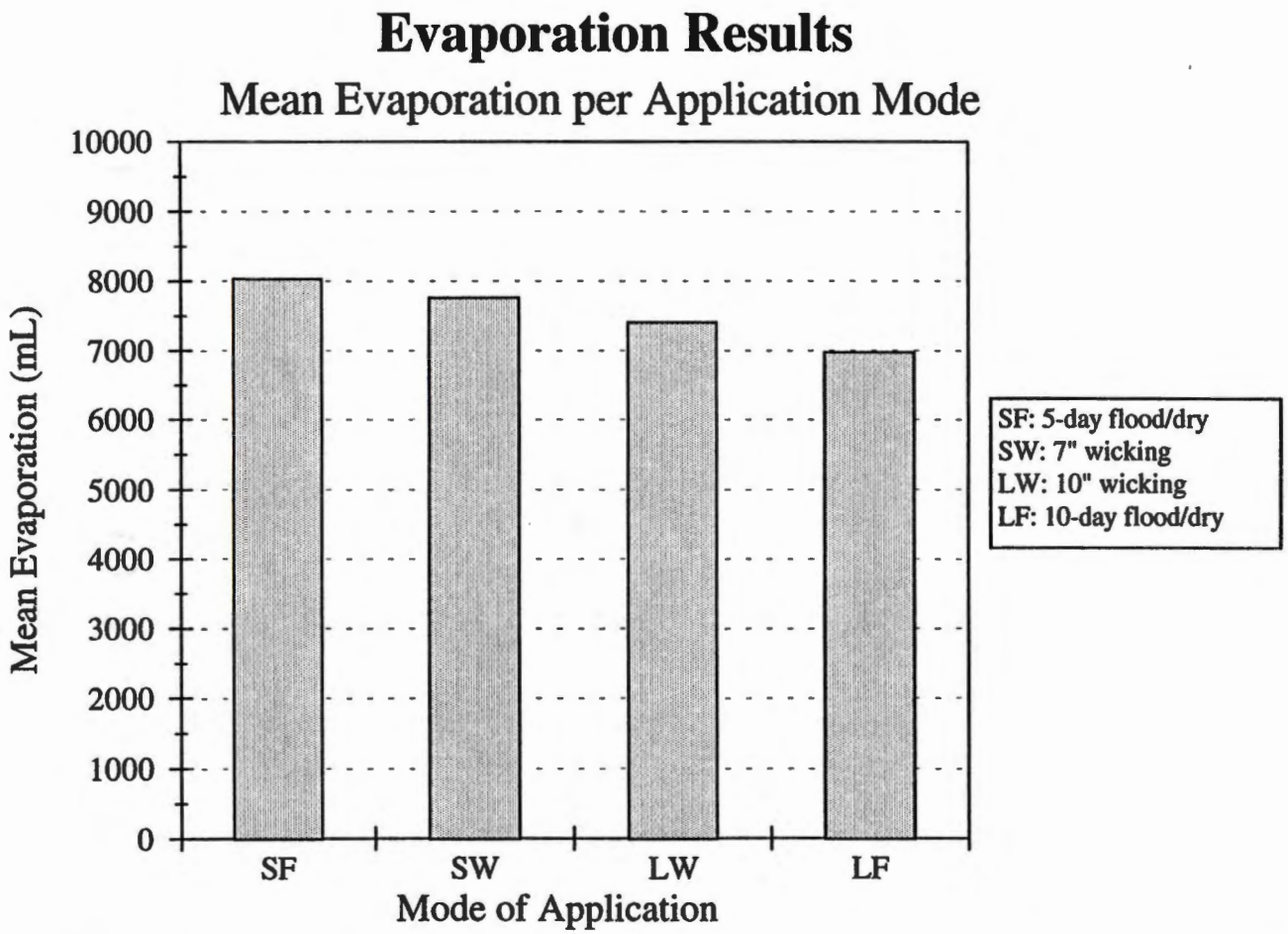


Figure 34. Relationship between evaporation and mode of rinsate application to soil columns. Ten-day cycle duration flood/dry-type columns produced significantly lower evaporation than the remaining others at $\alpha = 0.05$. Values are averaged over all column treatment combinations per application mode.

Table 19. Mean evaporation data collected from each column type with different methods of rinsate application.

Mode of application	Normalized Evaporation (mL)	
	LSMEAN	Standard Error
LF	5379.23[B*]	0.01411
LW	5807.47[A]	0.01411
SF	5974.17[A]	0.01411
SW	5898.19[A]	0.01418

* Means with like letters are not significantly different at $\alpha = 0.05$

would have expected that the wicking type columns might have the highest amounts of evaporation, since fluid was continually present at the soil surface throughout the entire 180 days. Conversely, the flood/dry type columns only had solution continually supplied to them half the time. One possible explanation of this may be that after the drying periods, the soil quickly soaked up a larger quantity of solution in order to become re-established. This rapid uptake of fluid would offset any differences due to the drying cycle.

Temperature*application interaction

The two-way interaction between temperature and application mode appears as the final factor of significance in terms of evaporation (Table 14). Although the F-value concedes that it has the lowest degree of significance, Table 20 and Figure 35 clearly show that temperature significantly impacts the amount of evaporation per column type (i.e., mode of application). At higher temperatures, the long-flood (LF: 10-day cycle) columns appear to dry out too much during the dry cycle and thus affect the rate of water uptake

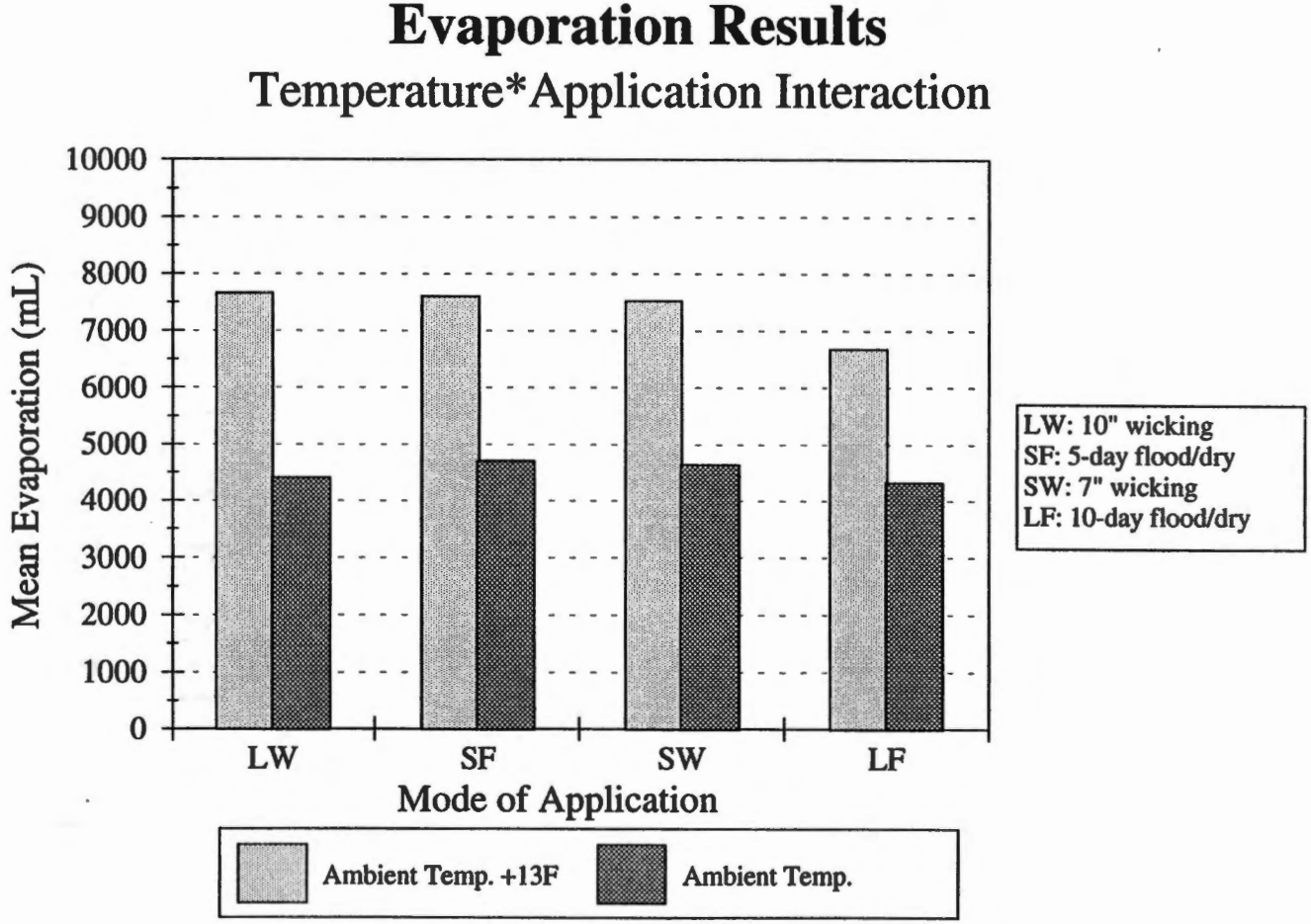


Figure 35. Relationship between evaporation and mode of rinsate application in terms of exposure to different temperatures. Values are averaged over similar column types with like temperatures. Temperatures significantly affected evaporation for each column type (at $\alpha = 0.05$).

Table 20. Mean evaporation data collected for each column type with different temperature exposures.

Temperature	Mode of Application	Normalized Evaporation (mL)	
		LSMEANS	Standard Error
H	LF	6677.33[C*]	0.01995
H	LW	7655.24[D]	0.01995
H	SF	7590.02[D]	0.01995
H	SW	7511.76[D]	0.02016
L	LF	4333.48[A]	0.01995
L	LW	4405.54[A]	0.01995
L	SF	4702.21[B]	0.01995
L	SW	4631.24[B]	0.01995

*Means with like letters are not significantly different at $\alpha = 0.05$

and amount of evaporation. These same columns also experienced similar evaporation trends under low temperature, though the trends were not as pronounced.

Degradation

From the list of effects and interactions deemed statistically significant to degradation by the SAS® output (Table 14), a couple of key general observations may be made. More terms are significant at the 0.05 alpha level for the atrazine degradation model as compared to that for fluometuron degradation. Additionally, the order of dominance of these significant variables was slightly altered for the two chemicals. Finally, although all the main effects were significant in the atrazine model, airflow by itself did not contribute significantly to the soil degradation of fluometuron. These early signs of varying individual degradation performance point out the role of different pesticides and

their individual characteristics as playing a part in the overall performance of the system. As previously noted, fluometuron was consistently detected at higher concentration levels in the soil samples than was atrazine, and thus had lower amounts of degradation. Clearly, varying herbicide properties and/or characteristics are playing a major part in this.

Soil

During the preliminary examinations of the final data set, it appeared obvious that soil type played a major role in degradation. Even earlier than this, some indications to this effect were also observed in trends noticed from the HPLC chromatograms. As it turns out, this was particularly the case for atrazine degradation, with the F-value (Table 14) indicating soil type to be the dominant factor. In terms of fluometuron degradation, soil type appeared as the second most significant contributing variable. Atrazine was particularly responsive in the silty soil (Table 21 and Figure 36), with the average degradation being more than double of that detected in the sandy soils. Although much lower percentage-wise, fluometuron degradation was significantly different (at $\alpha = 0.05$) between the silty and sandy soil columns (Table 21 and Figure 36).

Table 21. Mean percent herbicide degradation observed in columns containing two different soil types.

Soil Type	Percent degradation of that applied			
	Fluometuron		Atrazine	
	LSMEAN	Standard error	LSMEAN	Standard error
Silty	36.43^{A*}	0.4578	73.38^{A*}	0.3277
Sandy	40.09^{B}	0.4590	33.50^{B}	0.3285

*Means with like letters within the same herbicide are not significantly different at $\alpha = 0.05$

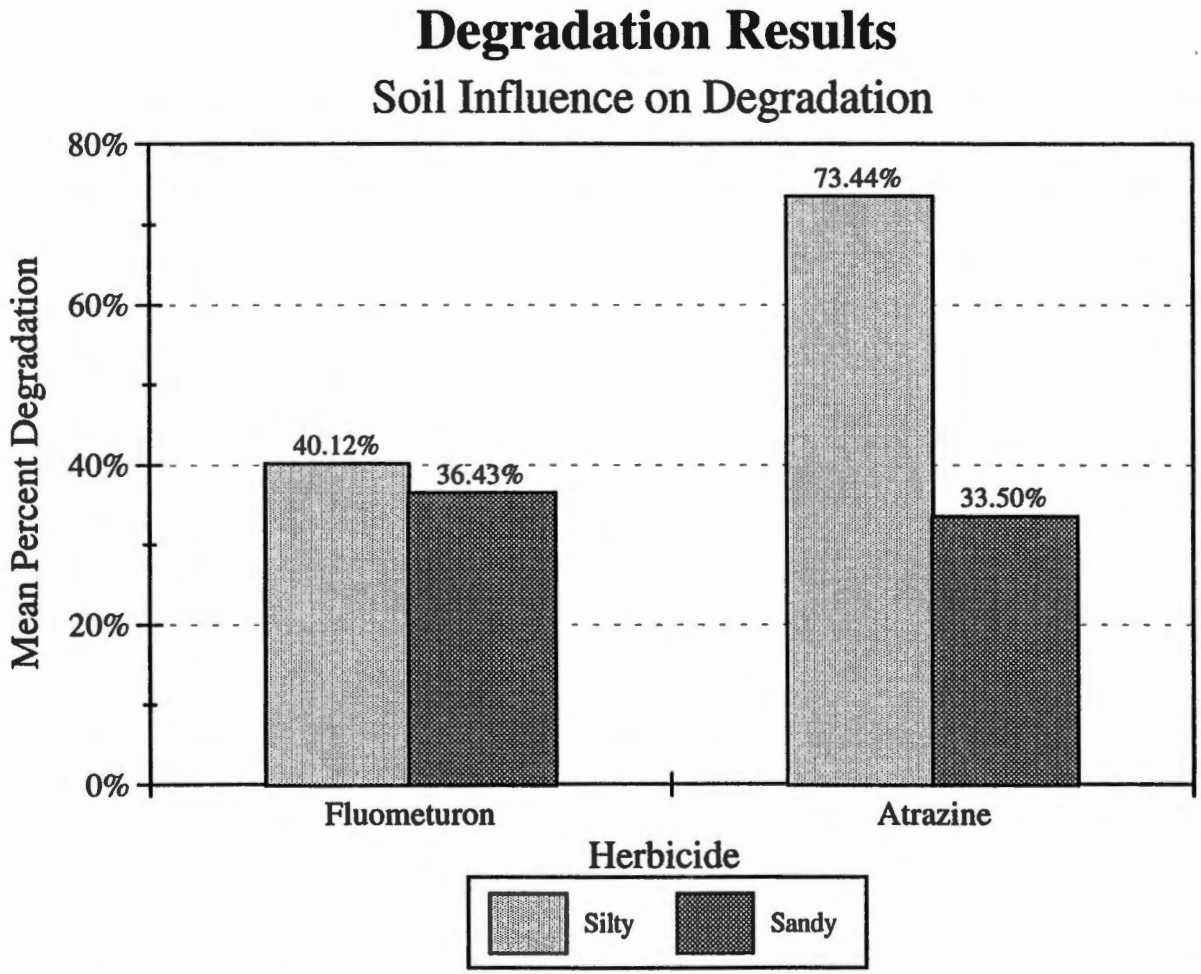


Figure 36. Soil type effect (all differences were statistically significant at $\alpha = 0.05$) on percent degradation of both herbicides. Values are averaged over all columns containing similar soil types and represent percent degradation of the total amount applied.

The significant difference in percent degradation due to soil type perhaps can be attributed to the organic matter content differences associated between the two. As reported in Chapter IV (Table 7), the silty soil contained 1.19% organic carbon, as opposed to 0.22% in the sandy soil. Higher organic matter can generally be related to higher soil micro-flora activity, and hence potentially more metabolism of the herbicides. As further reported in the review of literature, however, the exact role organic matter plays in pesticide degradation is unclear. There is speculation as to how much of this is due to its effect on the physical properties of the soil, or to the use of the organic matter by microbes as a food source.

Additionally, soil pH possibly influenced the degradation of atrazine. From preliminary analysis of the soils used in this study, the pH was determined to be 4.95 and 5.10 for the silty soil and the sandy soil, respectively (Chapter IV, Table 7). As reported by Ahrens (1994) and mentioned by Mueller (1993), at low pH (pH 5.5 - 6.5), hydrolsis becomes a mojor contributor to atrazine degradation (this can happen quite rapidly).

Temperature

Temperature simply swapped roles with soil type in terms of both atrazine and fluometuron degradation. As such, it exhibited the most pronounced effect on the degradation of fluometuron, and had the second most important effect on atrazine metabolism. Although not as influential upon herbicide degradation as upon evaporation, elevated temperatures did cause slightly higher mean percent degradations (Figure 37). Even though only about a 4-5% difference in average percent degradation was observed,

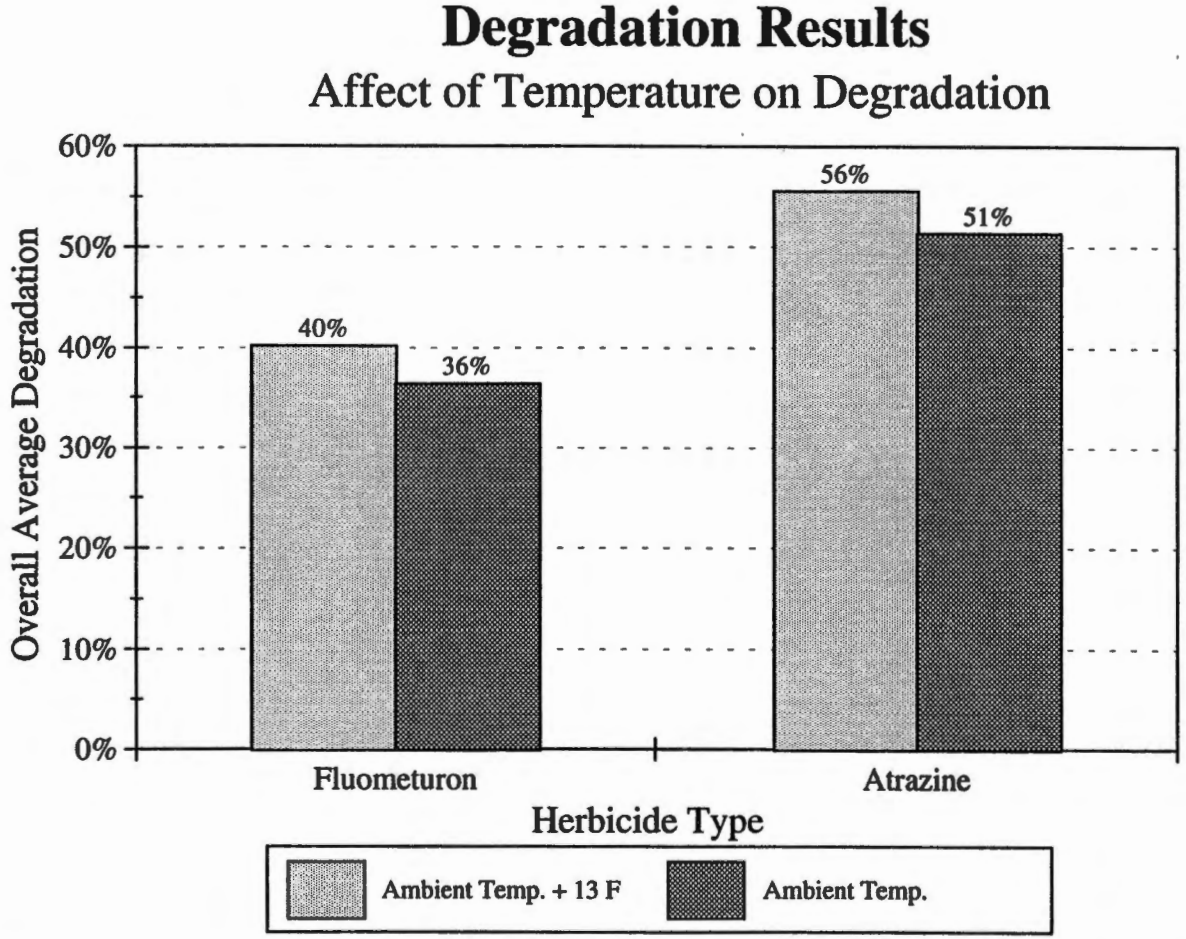


Figure 37. Temperature effect (statistically significant at $\alpha = 0.05$) on percent degradation of herbicide. Values are averaged over all columns exposed to similar temperatures and represent percent degradation of the total amount applied.

statistically significantly higher degradations were associated with higher temperatures (Table 22). Thus, solely relying on the graphical analysis might be misleading. Even though the literature indicates enhanced microbial activity at warmer temperatures, this range is only 21-38°C [70-100°F] for optimal microbial growth. One must realize that the 180-day duration of this study occurred during the warmer parts of the year. As previously seen from the weather data (Figure 25), the average ambient outside temperatures were generally ≥ 20°C [68°F], except during the first thirty days. Thus, even the lower observed temperature range was well within that reported for optimal microbial activity. Because of this, it is believed that the degradation differences based upon temperature, although statistically significant at $\alpha = 0.05$, were not very pronounced. If, however, the study had taken place during a cooler part of the year, the effect of temperature upon degradation might have shown up to a greater extent.

Table 22. Mean percent herbicide degradation observed in columns exposed to two levels of temperature.

Temperature	Percent degradation of that applied			
	Fluometuron		Atrazine	
	LSMEAN	Standard error	LSMEAN	Standard error
H	40.16[A*]	0.4590	55.52[A*]	0.3285
L	36.36[B]	0.4578	51.36[B]	0.3277

*Means with like letters within the same herbicide are not significantly different at $\alpha = 0.05$

Mode of application

In terms of degradation, one of the most important results concerned the modes of rinsate application to the columns. The various application modes directly controlled the amount of exposure of the herbicide to aerobic and anaerobic conditions (and hence, to their respective microbial populations). Although overshadowed by soil and temperature factors, application modes appeared as the third most influential main effect for degradation in both herbicide types. Closer inspection of the different application modes revealed several trends (Table 23). The flood/dry-type columns consistently outperformed (i.e., had higher degradation) the wicking-type columns regardless of herbicide type, with the long wicking (LW) columns producing the least degradation (Figure 38). Again, subtle discrepancies in the trends between herbicide types point to individual chemical characteristics as being influential. For fluometuron, the degradation within the long-wicking columns is the only one significantly different (at $\alpha = 0.05$) from the others. For atrazine, on the other hand, degradation within both types of wicking columns were not significantly different (at $\alpha = 0.05$) from one another, but were both lower than the two flood/dry-type columns. Of the flood/dry columns, those exposed to longer cycle durations significantly out-performed (i.e., higher average percent degradation) those with short cycle duration times (for atrazine only). Although somewhat inconclusive, it appears as if exposing the soil to alternating cycles of saturated/unsaturated conditions (i.e., anaerobic/aerobic conditions) may hold more promise for enhanced microbial degradation than other methods of rinsate application.

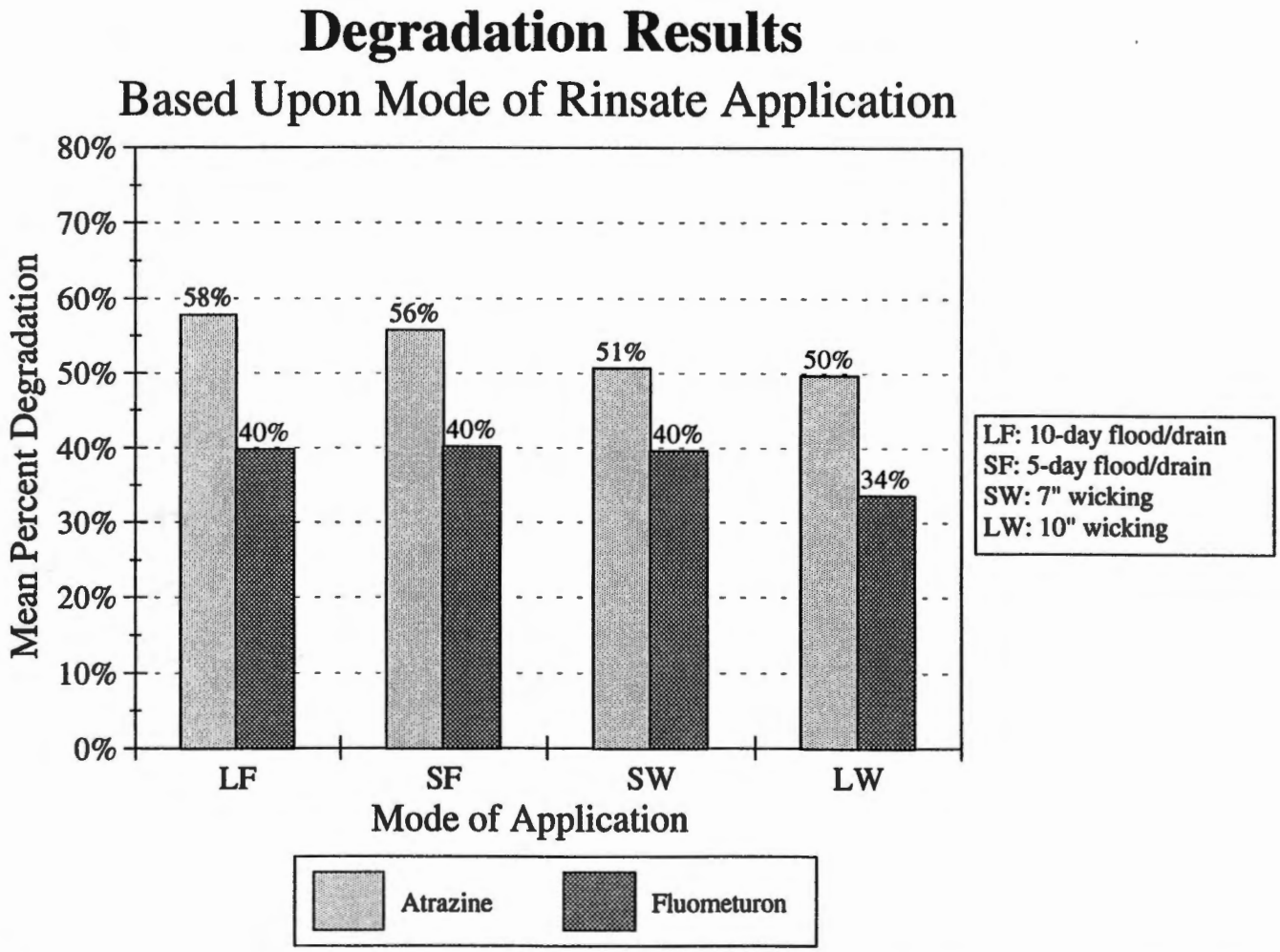


Figure 38. Rinsate application method effect on percent degradation of both herbicides. Values averaged over all similar column types, and represent percent degradation of the total amount applied.

Table 23. Mean percent herbicide degradation observed in columns with four levels of rinsate application methods.

Mode of Application	Percent degradation of that applied			
	Fluometuron		Atrazine	
	LSMEAN	Standard error	LSMEAN	Standard error
LF	39.75[A*]	0.6474	57.79[A*]	0.4634
SF	40.14[A]	0.6474	55.73[B]	0.4634
SW	39.56[A]	0.6507	50.57[C]	0.4658
LW	33.59[B]	0.6474	49.67[C]	0.4634

*Means with like letters within the same herbicide are not significantly different at $\alpha = 0.05$

Airflow

Airflow, the remaining main effect, although to a lesser degree did appear as contributing significantly (at $\alpha = 0.05$) to the atrazine degradation model. Surprisingly, though, it was not a significant factor in fluometuron degradation. Observation of the means (Table 24) show that the different levels of air flow are significantly different from one another for atrazine degradation, but are not so for fluometuron degradation.

Table 24. Mean percent herbicide degradation observed in columns exposed to two levels of airflow.

Airflow	Percent degradation of that applied			
	Fluometuron		Atrazine	
	LSMEAN	Standard error	LSMEAN	Standard error
L	38.83[A*]	0.4590	54.35[A*]	0.3285
H	37.69[A]	0.4578	52.53[B]	0.3277

*Means with like letters within the same herbicide are not significantly different at $\alpha = 0.05$

These results indicate that the rate of solution movement through the soil (controlled by evaporation) and hence the associated rate of herbicide applied to the soil, is less significant to atrazine degradation than several other factors, and is not significant (at $\alpha = 0.05$) in fluometuron degradation. Thus, from a design standpoint, effort given to facilitating air movement across the soil surface of a disposal bed system will not strongly affect degradation.

Two-way interactions

There were numerous two-way interaction terms which significantly contributed (at 95% confidence level) to the degradation models. From the F-values (Table 14), two of the most important two-way interactions influencing the degradation of atrazine were temp*soil and applic*soil. These interactions indicate that, in general, temperature and mode of application both significantly impact herbicide degradation for a specific soil type.

Of these two, the temperature/soil interaction was only significant for atrazine degradation. From the mean values of this interaction term (Table 25) it is apparent that, within each soil type, exposure to elevated temperatures significantly increased the average amount of degradation. However, it is important to realize that the addition of temperature to this particular interaction does not overshadow the huge differences observed between soil types.

Table 25. Mean percent atrazine degradation observed in columns containing each soil type and exposed to two levels of temperature.

Temperature	Soil Type	ATRAZ degradation (% of that applied)	
		LSMEAN	Standard Error
H	Sand	34.35^{C*}	0.4634
H	Silt	76.69^{A}	0.4658
L	Sand	32.65^{D}	0.4634
L	Silt	70.06^{B}	04634

*Means with like letter are not significantly different at $\alpha = 0.05$

In contrast to temp*soil, the applic*soil interaction was significant in both herbicide models. Table 26 displays the means associated with the interaction between application modes and soil types in the degradation of both herbicides.

Table 26. Mean herbicide degradation associated with the interaction between four modes of application and two soil types.

Application mode	Soil type	Percent degradation of that applied			
		Fluometuron		Atrazine	
		LSMEAN	Standard error	LSMEAN	Standard error
LF	sandy	39.38^{B*}	0.9156	38.19^{D}	0.6554
LF	silty	40.11^{B}	0.9156	77.39^{A}	0.6554
LW	sandy	31.07^{D}	0.9156	28.01^{F}	0.6554
LW	silty	36.10^{C}	0.9156	71.32^{B}	0.6554
SF	sandy	39.04^{B}	0.9156	34.23^{E}	0.6554
SF	silty	41.25^{A}	0.9156	77.23^{A}	0.6554
SW	sandy	36.23^{C}	0.9156	33.57^{E}	0.6554
SW	silty	42.89^{A}	0.9156	67.58^{C}	0.6622

*Means with like letters within the same herbicide are not significantly different at $\alpha = 0.05$

The following are note-worthy observations from this applic*soil table (Table 26):

Fluometuron:

- with the exception of the 10-day cycle flood/dry columns, degradation within similar column types was always significantly higher in those containing silty soil as opposed to the ones with sandy soil;
- regardless of soil type, the 10" wicking columns exhibited the lowest mean degradation (as also seen earlier).

Atrazine:

- the extremely large amounts of degradation within silty soil columns far overshadowed any distinctions between soil types for similar columns;
- the silty flood/dry cycling columns, although not significantly different from one another at $\alpha = 0.05$ (i.e., 5-day cycle vs. 10-day cycle), do significantly out-perform both wicking-type columns;
- also for the silty soil columns, the degradation within the 10" wicking columns is significantly higher than that in the shorter wicking columns; this is in contrast to earlier observed trends.

Although airflow by itself did not appear to significantly influence the degradation of fluometuron, the combinations of airflow and temperature or airflow and application modes did. These two interactions represent the last ones significantly impacting fluometuron, in general. Whereas airflow in conjunction with temperature only significantly influenced fluometuron degradation, airflow*application mode had a significant impact on both herbicide degradation models.

A closer inspection of the influence of chamber type (i.e., airflow*temp) upon herbicide degradation (Table 27 and Figure 39) reveals that temperature, regardless of varying airflow, was dominant in the interaction. Also of note, columns within the South chamber exhibited either the lowest significantly different mean percent degradation (as was the case for atrazine), or were not significantly different from those within the chamber producing the lowest mean percent degradation (as seen for fluometuron).

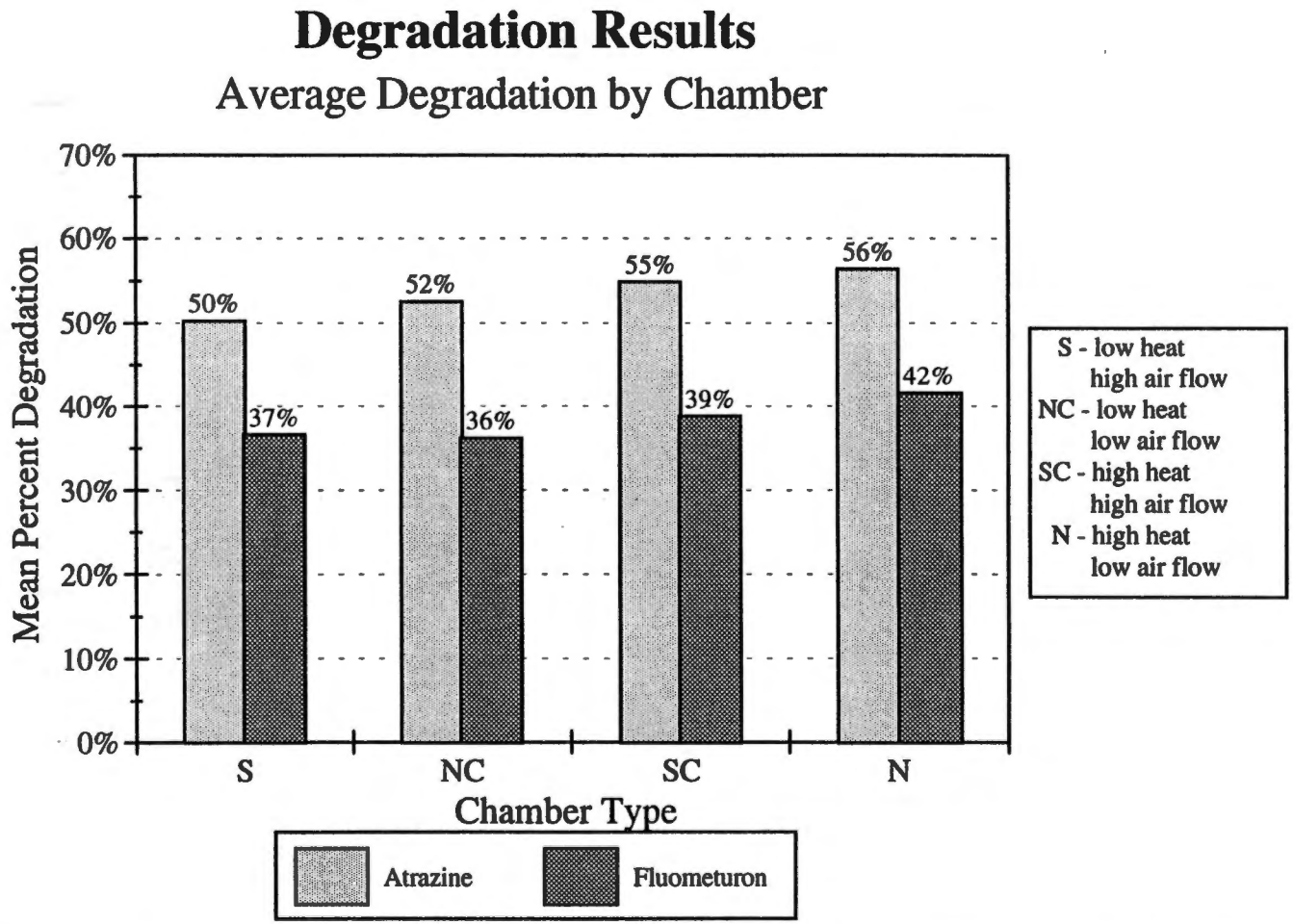


Figure 39. Effects of airflow plus temperature (as controlled by the chambers) on the degradation of both herbicides. Values are averaged over all columns within each chamber.

Table 27. Mean percent herbicide degradation observed from columns placed in the four chambers.

Air	Temp	Chamber	Percent degradation of that applied			
			Fluometuron		Atrazine	
			LSMEAN	Standard Error	LSMEAN	Standard Error
L	H	N	41.53[A*]	0.6508	56.21[A*]	0.4658
H	H	SC	38.79[B]	0.6474	54.84[B]	0.4634
L	L	NC	36.14[C]	0.6474	52.50[C]	0.4634
H	L	S	36.59[C]	0.6474	50.22[D]	0.4634

*Means with like letters within the same herbicide are not significantly different at $\alpha = 0.05$

The other significant two-way interaction term (airflow*application) indicates that airflow significantly influences the degradation of both herbicides within the various column types (i.e., columns with the same methods of rinsate application). Several points of interest may be made from observations of Table 28. In terms of airflow* application:

Fluometuron:

- degradation is statistically the same among all columns regardless of their type and/or the rate of solution movement through the soil profile, with the exception of the 10" wicking columns;
- the 10" wicking columns consistently produce lower degradation of fluometuron, regardless of airflow; however, lower rates of solution movement (i.e., lower airflow) through the LW columns significantly improved the degradation of fluometuron.

Atrazine:

- all flood/dry type columns, regardless of airflow, significantly out-performed the wicking-type columns;
- although both types of LF columns are statistically similar (@ $\alpha = 0.05$), the 10-day cycle flood/dry columns exposed to higher air flow rates had slightly higher mean atrazine degradation;
- of the wicking columns, regardless of which type, those exposed to lower airflows had significantly more degradation compared to those exposed to higher airflows; this indicates that the slower movement of solution through the columns (controlled by evaporation rates, in turn driven by airflow) allows for significantly increased degradation.

Table 28. Mean percent herbicide degradation observed from columns within each rinsate application method and with exposure to two levels of airflow.

Airflow	Mode of Applic.	Percent degradation of that applied			
		Fluometuron		Atrazine	
		LSMEAN	Standard Error	LSMEAN	Standard Error
H	LF	40.16^{A*}	0.9156	58.63^{A*}	0.6554
L	LF	39.33^{A}	0.9156	56.95^{A,B}	0.6554
L	SF	40.23^{A}	0.9156	55.84^{B}	0.6554
H	SF	40.05^{A}	0.9156	55.62^{B}	0.6554
L	SW	40.03^{A}	0.9251	52.53^{C}	0.6622
L	LW	35.72^{B}	0.9156	52.10^{C}	0.6554
H	SW	39.09^{A}	0.9156	48.62^{D}	0.6554
H	LW	31.45^{C}	0.9156	47.24^{D}	0.6622

*Means with like letters wihtin the same herbicide are not significantly different at $\alpha = 0.05$

The final two-way interaction shown to be significant is that of temperature*application mode, for atrazine degradation only. This term seems to indicate that among the four types of columns (i.e., as dictated by application methods), temperature has an impact upon atrazine degradation. Table 29 summarizes the mean values from this particular interaction.

Table 29. Mean percent atrazine degradation observed from columns within each rinsate application method and exposed to two levels of temperature.

Temperature	Application Mode	Atrazine degradation (% of that applied)	
		LSMEAN	Standard Error
H	LF	60.60[A*]	0.6554
H	SF	58.56[B]	0.6554
L	LF	54.98[C]	0.6554
L	SF	52.90[D]	0.6554
H	SW	51.79[D]	0.6622
H	LW	51.14[D,E]	0.6554
L	SW	49.35[E]	0.6554
L	LW	48.19[E]	0.6554

*Means with like letters are not significantly different at $\alpha = 0.05$

Observations from Table 29 reveal the following in terms of temp*application for the atrazine degradation model:

- regardless of temperature, all flood/dry-type columns experienced greater mean percent degradation of atrazine than the wicking-type columns;
- among the flood/dry columns, although all were significantly different from each other, those exposed to elevated temperatures experienced significantly higher amounts of atrazine degradation; likewise, for the wicking columns, those placed in higher temperatures achieved greater mean percent degradation of atrazine than those placed in ambient temperature environments;
- within each separate column type (i.e., application mode), those under higher temperature conditions experienced significantly more atrazine degradation, except for the LW columns which remained statistically the same under both temperature ranges.

Three-way interactions

From the full degradation model (Table 14), a couple of three-way interaction terms proved to be statistically significant (at $\alpha = 0.05$) in the degradation of atrazine only.

From their F-values, both of these interaction terms were low on the list of all significantly determined variables.

The first of these three-way interaction terms, airflow*temperature*application, suggests that columns with the same mode of application and level of temperature exposure are significantly influenced by their exposure to varying airflow conditions. A closer look at these interactions (Table 30) reveals:

- the 10-day cycle flood/dry columns with higher temperatures, regardless of airflow exposure, have significantly higher mean percent atrazine degradation from all others, except that of the 5-day flood/dry, high temperature, high airflow columns;
- of the 5-day cycle flood/dry columns placed in elevated temperatures, the ones exposed to higher airflow rates achieved significantly greater mean atrazine degradation percentages;
- for all wicking-type columns (both 7" and 10"), regardless of temperature (either high or low), significantly higher average atrazine degradation percentages were observed in those exposed to lower airflow rates.

In terms of the wicking column, this indicates that more degradation may be expected from the wicking columns at slower rates of solution movement through the soil profile, which is controlled by evaporation, in turn controlled by airflow. This allows the rinsate to remain within the soil longer, and thus to be exposed to the microbial populations for longer periods.

Table 30. Mean percent atrazine degradation observed from columns within each rinsate application method and exposed to two levels of temperature and airflow rates.

Airflow	Temp	Application Mode	Atrazine degradation (% of that applied)	
			LSMEANS	Standard Error
H	H	LF	61.34^{A*}	0.9268
L	H	LF	59.87^{A}	0.9268
H	H	SF	59.85^{A}	0.9268
L	H	SF	57.28^{B}	0.9268
H	L	LF	55.93^{B,C,D}	0.9268
L	L	SF	54.40^{C,D}	0.9268
L	H	LW	54.24^{C,D}	0.9268
L	L	LF	54.03^{C,D}	0.9268
L	H	SW	53.46^{D}	0.9459
L	L	SW	51.61^{D,E}	0.9268
H	L	SF	51.40^{D,E}	0.9268
H	H	SW	50.13^{E}	0.9268
L	L	LW	49.95^{E}	0.9268
H	H	LW	48.03^{E,F}	0.9268
H	L	SW	47.10^{F}	0.9268
H	L	LW	46.44^{F}	0.9268

*Means with like letters are not significantly different at $\alpha = 0.05$

The second three-way interaction term, temp*application*soil (Table 31), suggests that, in terms of atrazine degradation, columns containing the same type of soil and having the same rinsate application methods are significantly influenced by their exposure to different temperature conditions.

Table 31. Mean percent atrazine degradation observed from columns within each rinsate application method, containing two soil types and exposed to two levels of temperature.

Temp	Applic	Soil	Atrazine degradation (% of that applied)	
			LSMEAN	Standard Error
H	SF	silt	80.82[A*]	0.9268
H	LF	silt	80.29[A]	0.9268
H	LW	silt	75.35[B]	0.9268
L	LF	silt	74.49[B]	0.9268
L	SF	silt	73.65[B]	0.9268
H	SW	silt	70.32[C]	0.9459
L	LW	silt	67.28[D]	0.9268
L	SW	silt	64.83[D]	0.9268
H	LF	sand	40.91[E]	0.9268
H	SF	sand	36.31[F]	0.9268
L	LF	sand	35.46[F,G]	0.9268
L	SW	sand	33.87[F,G]	0.9268
H	SW	sand	33.27[G]	0.9268
L	SF	sand	32.15[G]	0.9268
L	LW	sand	29.10[H]	0.9268
H	LW	sand	26.92[H]	0.9268

*Means with like letters are not significantly different at $\alpha = 0.05$

A closer look at this particular interaction (Table 31) reveals:

- the extreme discrepancies between columns with different soil types completely overshadowed any interactions; all sandy soil columns had significantly less degradation than those containing silt;
- for the silty columns, in all cases, significantly higher amounts of atrazine degradation occurred in columns of like application methods to which heat was added;
- for the sandy columns:

- all like wicking columns performed the same statistically, regardless of temperature; however, the lower temperatures did average higher mean degradation than those at higher temperatures;
- the LW columns statistically showed the least amounts of atrazine degradation;
- the flood/dry-type columns still out-performed the wicking columns.

Summary of data analysis

From of all of these significant variables and interactions, several general trends and observations are noteworthy and listed here:

- all main effect variables appear as significant in all of the models, with the exception of airflow in fluometuron degradation; this seems to indicate that the main effects were appropriately chosen.

Evaporation:

- climatic conditions (temperature and airflow), as controlled by the chambers, were clearly the most dominant factors in terms of evaporation; both higher airflow rates and elevated temperatures resulted in significantly increased amounts of evaporation than did their counterparts;
- although statistically significant, the increased evaporation experienced in the sandy soils was slight, only about 10% higher than in silty soils;
- the LF columns (i.e., 10-day cycle duration flood/dry columns) consistently had the lowest amounts of evaporation, probably due to the extended drying cycle times they were exposed to; however, the SF (5-day cycle duration flood/dry columns) experienced the highest mean amounts of evaporation.

Degradation:

- signs of varying individual degradation performances tend to point out the role of different pesticides and their individual characteristics as playing a part in the overall performances of the system;
- there were consistenty lower soil concentrations and thus, higher percent degradation of atrazine than fluometuron;
- atrazine degradation is overwhelmingly soil influenced, with much greater degradation occurring in silty soils than in sandy soils;
- although not as influential upon herbicide degradation as upon evaporation,

elevated temperatures in general did cause higher mean percent degradation;

- in terms of airflow, the rate of solution movement through the soil (controlled by evaporation) and hence the associated rate of rinsate active ingredient application to the soil, is less significant to atrazine degradation than are several other factors, and is not significant at all (at α =0.05) in overall fluometuron degradation;
- investigation of the chambers revealed that temperature, regardless of varying airflows, was dominant in the interaction;
- the flood/dry-type columns consistently outperformed the wicking-type columns regardless of herbicide type; of these the 10-day cycle duration flood/dry columns generally produced the best degradation, while the 10"-wicking columns produced the least degradation. Of the wicking columns, those exposed to lower airflow rates had consistently better degradation than those exposed to higher airflow rates — again indicating that the slower rate of solution movement through the soil allows the rinsate to remain within the soil profile longer and, thus, be exposed to the microbial populations for longer periods.

CHAPTER VI:

SUMMARY AND CONCLUSIONS

A laboratory test apparatus was designed and constructed for the controlled evaluation of the evaporative and degradative performance of soil bed systems in the disposal of residual pesticide-laden wastewaters. Research efforts were directed towards determining the combination of factors (temperature, soil texture, airflow rate, rinsate application method, and time) yielding the optimal combination of volume reduction and chemical destruction of the waste material.

The laboratory set-up employed individual soil columns to simulate conditions in a soil bed. Four column types were constructed, based upon the methods of rinsate application, to provide various exposures to aerobic and anaerobic conditions. Packed with either a silty- or sandy-textured soil, the columns were placed in environmental control chambers and exposed to different combinations of temperature (ambient or ambient + 13°C [23.4°F]) and airflow rates (1.47 $^{m}/_{s}$ [56.72 cfm] or 3.80 $^{m}/_{s}$ [146.43 cfm]. A contaminant mixture made up of water and the herbicides atrazine and fluometuron at low concentrations (8-10 parts per million) was continuously supplied to the columns. Records were kept of the amount of contaminant solution supplied to each soil column to meet its evaporation requirements. At prescribed time intervals (30, 60, 120 and 180 days

after initiation), the soil in the columns was tested for pesticide concentration levels as an indication of the rate of microbial degradation. Atrazine and fluometuron concentrations were quantified with High Performance Liquid Chromatography (HPLC).

The experimental results obtained were promising. Both evaporation and average percent degradation (for each herbicide) significantly increased ($\alpha = 0.05$) the longer the columns were allowed to run. Although the herbicide concentrations in the soil went up, so too did the overall average percent herbicide degradation. Also, the rate at which the herbicide concentrations increased diminished over time. This indicates that, under conditions of continual loading, the columns' ability to degrade the herbicides increased substantially over time. These findings are comparable to the reports from the soil disposal pits used in Iowa and California. As the literature revealed, evaluations of both of these systems concluded that there was no appreciable chemical build-up within the soil over many years of operation.

Climatic conditions (temperature and airflow) were clearly the most dominant factors in controlling evaporation, but had less influence on herbicide degradation. Elevated temperatures did, in general, cause higher mean percent degradation. To a much lesser extent, airflow did influence degradation, but only at lower velocities. Although statistically significant ($\alpha = 0.05$), the evaporation increase in sandy soils was only slight compared to the dramatic increase in herbicide degradation in silty soils (especially for atrazine).

Columns alternated between saturated/unsaturated (i.e., anaerobic/ aerobic)

conditions consistently outperformed (i.e., had higher degradation) those having constant zones of both conditions. Although longer cycle durations (10-days) produced greater percent degradation, shorter cycle durations (5-days) yielded the best amounts of evaporation. Different degradation trends between atrazine and fluometuron point to individual pesticide characteristics as having a potential role in the performance of a soil bed system.

As indicated by these results, the laboratory set-up performed exceptionally well. It proved that relatively simple concepts can be employed to address a problematic waste material. The information gained through this research effort is readily transferrable and easily implemented into the design of a realistic disposal system. The methods employed are not overly complex, are easily managed, and are applicable to a wide variety of situations. Not only does this set-up provide excellent containment of the rinsate material, but it also exploits the characteristics of the waste solution for the ultimate disposal process. Additionally, the process yields no residual waste stream requiring further disposal.

The extensive use of pesticides in modern agriculture has resulted in several public and regulatory concerns, including the fate of pesticide residues in the environment. With a little refinement, the knowledge gained from this project can be utilized by farmers and other agricultural chemical applicators to intelligently and responsibly dispose of the waste they generate in a contentious manner. Doing so allows for continual use of these heavily relied upon chemicals with less potential of them polluting the environment.

CHAPTER VII:

RECOMMENDATIONS

Prior to conducting this research, little quantified data existed pertaining to the optimal conditions and/or techniques of a properly designed soil bed rinsate disposal system. Previous studies appeared to lack extensive background analysis, with the designs being fueled mainly by application needs. Little scientific consideration was given to their performance and applicability. Using the knowledge gained from this effort, a pesticide rinsate reduction/degradation unit based on the soil evaporation bed concept should prove to be an integral part of a complete pesticide waste management strategy. Incorporated into a complete pesticide handling facility (including rinse pad facility) and used in conjunction with an in-field rinse system (such as the TISMRS system developed by Davis, 1992), it should more than adequately address all residual rinsate materials.

It goes without saying that a soil digestion unit should be designed to meet or exceed all rinsate generation requirements. Although results indicate that a medium-textured loam soil is preferred, readily available agricultural soils should prove sufficient. The laboratory study proved that simple application methods can be successfully employed. In a realistic system, this can be implemented via elevated storage tanks to gravity supply the rinsate solution to the disposal unit, thus minimizing complicated

pumping and valving requirements. Additionly, design efforts should be geared towards heating the system instead of facilitating air movement across the bed's surface, thus negating expensive fan or blower systems. Simple passive solar technology (such as a greenhouse-type cover) could be employed to adequately elevate the temperatures. Another possibility would be to temper cool air conditions by passage through below-ground tubes.

Further studies should be conducted on two fronts. In-field prototype units based upon these results should be constructed and evaluated. Strictly controlled and monitored, these prototype units could successfully address any design, management, and operational concerns. Additionally, limitless research potential exists utilizing the laboratory apparatus constructed for this study. To begin with, studies should be conducted to gain a better understanding of the degree to which the pesticides degrade once continual loading ceases. In a realistic situation, rinsate will only be produced during the growing season, and no wastewater will be applied to the unit for a substantial portion of the year. Will, degradation continue, and if so how much and at what rate?

Future studies should also look at a wider variety of pesticides, including herbicides and insecticides, as well as other classes of agricultural chemicals. A realistic system will potentially be exposed to a variety of compounds and mixtures. From this initial study it is very apparent that different herbicides behave somewhat differently. Finally, a multitude of studies could be conducted to investigate such areas as soil additives or enhancements (e.g., food sources, organic material, lime, etc.), air quality issues (in terms of pesticide

volatilization), and specific degradation pathways (e.g., from a microbiology standpoint). These same types of studies could also be implemented on the future prototype unit once it has been successfully installed.

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APPENDICES

APPENDIX A:

STANDARD OPERATING PROCEDURES

The University of Tennessee
Agricultural Engineering Department
Pesticide-Contaminated Wastewater Research

Standard Operating Procedure

S.O.P. Number: BKC-1 Date: 1/10/96

Written by: Brian K. Corwin Revision Number: 4

Supersedes: 12/20/95

- CAUTION -

1. All federal, state, and local safety procedures are to be observed.
2. Good laboratory practices should also be observed.
3. Clean the laboratory both before and after the procedure.
4. Place plastic sheets on the laboratory floor to minimize the mess due to soil handling.
5. Observe all safety precautions, including the use of protective clothing and eyeware when necessary.
6. Do not allow the laboratory to become cluttered.

Soil Column Packing Procedure

I. Introduction:

1.1 This protocol covers the procedures and required steps involved in packing the individual soil columns. This procedure will take place in the Agricultural Engineering Laboratory under the direction of Brian Corwin, and can be broken down into two distinct stages: 1) preparing the soil, and 2) packing the columns with the soil. The steps outlined in this S.O.P. should be closely followed throughout the column packing process so as to assure uniform soil bulk densities among all 512 soil columns. Because of the mess caused from handling the soil, the laboratory floor needs to be covered with plastic sheets. Additionally, a dust mask-type respirator may be needed to keep from breathing in the soil dust.

II. Soil Preparation:

2.1 Obtain the necessary amounts of each soil type (enough soil to fill a total of 512 soil columns).

2.2 While the soil is moist, screen it twice:
- first, through a piece of 1/4" hardware cloth
- second, through a piece of 1/8" hardware cloth
- discard any material which does not pass through both screens

2.3 Spread the screened soil out to air dry.
- spread the soil out on the plastic sheets
- turn the soil with a rake as necessary to facilitate the drying process

2.4 Pass the dry soil back through the 1/8" hardware cloth to break up any clumps which might have formed during the drying process.

2.5 Store the screened and dried soil in clean (preferably new) plastic trash cans until needed for actual column packing.

III. Column Packing:

3.1 Number and label each soil column from 1 to 512.
- write the column number onto lab tape placed directly on each column

3.2 Utilizing a Sartorius IP65 kilogram scale, weigh the empty column and record.
- with the empty column remaining on the scale, tare the scale so that it is re-zeroed

3.3 Utilizing a funnel, pour soil into the column, one scoop at a time.
- while pouring the soil, continuously tap (or shake/vibrate) the column and rotate the funnel around the inside of the column; in this manner uniform packing and bulk density will be achieved
- fill the column until the soil is slightly rounded above the top rim of the column

3.4 Weigh and record the full column.
- if the full column weight does not fall within the bulk density range of ±2%, empty and repack the column
- in order to achieve a ±2% D_b range for the 10 inch columns, the full column soil weight should be between 2.766 Kg and 2.877 Kg
- in order to achieve a ±2% D_b range for the 7 inch columns, the full column soil weight should be between 1.957 Kg and 2.037 Kg

3.7 Set each soil column aside to be placed in the correct position within the air chambers at a later time.

3.8 With the column removed, tare the scale so that it again reads zero.

3.9 Return to step 3.2 and repeat the process until all 512 columns are

packed with soil.

3.10 Place each full column in the correct position within the air chambers.

The University of Tennessee
Agricultural Engineering Department
Pesticide-Contaminated Wastewater Research

Standard Operating Procedure

S.O.P. Number: BKC-2 Date: 1/10/96

Written by: Brian K. Corwin Revision Number: 4

Supersedes: 12/19/95

- CAUTION -

1. All federal, state, and local safety procedures are to be observed.
2. Good laboratory practices should also be observed.
3. Clean the laboratory both before and after the procedure.
4. Place plastic sheets on the laboratory floor to minimize the mess due to soil handling.
5. Observe all safety precautions, including the use of protective clothing and eyeware when necessary.
6. Do not allow the laboratory to become cluttered.

Pesticide Solution Mixing Procedure

I. Introduction:

1.1 This protocol covers the procedures and required steps involved in mixing the pesticide rinsate solution and the cleaning of the mixing equipment. Since this procedure will take place in two of the Agricultural Engineering (AE) Laboratories, extra care should be taken when transporting chemicals and/or equipment between the two. The steps outlined in this S.O.P. should be closely followed every time a batch of solution is mixed so as to ensure achieving proper solution concentrations and to minimize the possibility of contaminating the solution. This S.O.P. should also be referred to every time the mixing equipment is to be cleaned so as to assure that proper cleaning is achieved and nothing is contaminated. Additionally, due to the fact that hazardous chemicals are involved, extra safety considerations need to be observed. Protective clothing, including lab coat, goggles, gloves and dust/mist respirator, should be worn at all times.

II. Determination of Solution and Chemical Amounts Needed:

2.1 Estimate the amount of solution which needs to be mixed.
- base this estimate on the volume required to fill or re-fill the individual solution bottles
- can be accomplished via a visual estimation of all the bottles or via the use of a gauge and measuring each individual bottle and adding together
- estimate enough solution for one weeks worth of filling

2.2 Calculate the amount of each herbicide required for the tank mix based on the estimated solution volume needed.
- the solution is to be mixed at a concentration of 10 ppm for each herbicide
- calculation is as follows:

$$\left(10\frac{mg}{L}\right) * \left(\frac{3.785L}{1gal}\right) * (Xgal) * \left(\frac{1g}{1000mg}\right) = \text{\_\_\_\_\_}g \text{ of herbicide} \quad (24)$$

- solve using X gal as the estimated value of solution estimated in step 2.1
- the value obtained represents the quantity of each herbicide required to achieve a 10 ppm concentration when mixed with X gal of water

III. Chemical Weighing:

3.1 This portion of the procedure will take place in the AE Water Quality lab.

3.2 Remove both canisters of technical herbicide from the refrigerator, place them on the lab bench adjacent to the balances.

3.3 Turn on the balance (Sartorius, model B-120-S) and let it warm up.

3.4 Label two plastic trays with a lab marker.
- one indicating Atrazine
- one indicating Fluometuron

3.5 Proceed with the following steps with only one chemical at a time; when completely finished with one, repeat the steps with the others.

3.6 Open the door to the scale, place the plastic tray onto the balance plate, and then re-close the door.

3.7 Once the weight indicated on the balance has stabilized, tare the scale, thus re-zeroing it.

3.8 Open the door and remove the tray; place the tray on the lab bench.
3.9 Thoroughly clean the spatula with MeOH and a KIMWIPE before each use so as not to contaminate the herbicide supply (in canister).
3.10 Carefully open the canister of herbicide; place the lid on the bench top so as not to contaminate the foil seal.
3.11 Using the clean spatula, place a quantity of the herbicide from the canister into the tray.
3.12 Place the tray (with quantity of herbicide) onto the balance plate and close the door.
3.13 Observe the weight.
3.14 Add or remove herbicide to or from the tray with the spatula until the balance indicates the desired weight.
3.15 Remove the tray (with quantity of herbicide) from the balance plate and set it aside on the lab bench.
3.16 Carefully replace the lid onto the canister of herbicide; make sure the lid is tightly secured.
3.17 Clean the spatula with MeOH and a KIMWIPE.
3.18 Open the other canister of herbicide and weigh out a quantity of it in the same manner as described above.
3.19 After quantities of both herbicides have been weighed, turn off the balance and return the canisters to the refrigerator.
3.20 Carefully carry the trays of herbicides from the Water Quality lab to the table next to the mixing tank stand in the Power Machinery lab.

IV. Tank Filling and Agitation:

4.1 Check to make sure the centrifugal pump is turned off.
4.2 Close the ball valves on both the suction and pressure hoses on the tank mixing system.
4.3 Remove the tank lid.
- it may be necessary to first disconnect the re-circulation lines from the tank lid

4.4 Attach the garden hose to the sink faucet.
4.5 Attach a ball-valve to the other end of the garden hose.
4.6 Begin adding hot tap water to the tank until the water level in the tank is about 1/2 of the needed amount (or, on the initial tank mix, until the water level is the same as the level of the agitation nozzle).
4.7 For initial tank mix only (using 300 gal. tank), turn on the centrifugal re-circulating pump and let it run for several minutes.
- first make sure all hoses are properly attached
- this will ensure that everything is operating properly and the agitation nozzles are sloshing the water thoroughly

4.8 Add the chemical to the tank.
- one tray at a time, dump the herbicide into the tank
- holding the tray inside of the tank, wash all residue from it with the garden hose

4.9 Discard the empty weighing trays into the waste basket.

4.10 Replace the lid on the tank and attach all re-circulation hoses.

4.11 Open the ball-valves and turn on the centrifugal pump (recirculation pump).
- let the system agitate at this solution level for several hours

4.12 After several hours, turn off the ball-valves, then turn off the pump.

4.13 Remove the tank lid and wash down the inside walls of the tank with hot water from the garden hose.
- keep adding hot water and washing down the tank walls until the solution level in the tank reaches 2/3 of the desired amount
- spraying the inside walls of the tank will wash off any chemical particles sticking to the sides of the tank

4.14 When solution level reaches 2/3 of the desired amount, turn off the garden hose, replace the lid, and attach the recirculating lines.

4.15 Open the ball valves and turn on the pump.
- let the system agitate for 48 hours

4.16 After 48 hours of agitating:
- close ball valves and turn pump off
- remove re-circulation hoses from the lid
- remove the lid from the tank

4.17 Add the remaining amount of hot water to the tank, washing down the sides in the process.

4.18 Replace tank lid and recirculation hoses.

4.19 Insert the 200 mesh filter into the pressure line and the 100 mesh filter into the suction line.
- place the plastic dish pan underneath the in-line strainer bowl
- unscrew the strainer bowl, letting any and all excess solution overflow and drain into the dish pan
- insert the filter
- replace the strainer bowl; tighten snugly
- pour any solution caught in the dish pan into the 55 gal. waste barrel

4.20 Open ball valves and turn pump on.
- let the system agitate for 1-2 hours

4.21 After 1-2 hours, close valves, turn pump off, and remove recirculation hoses and tank lid.

4.22 With the fish net, skim any visible particles from the tank solution (chemical particles or trash).

4.23 Remove the filters in the same manner described in step 4.19.

4.24 Thoroughly rinse the filters to wash any particles off of them.
4.25 Replace the filters in the same manner as described in step 4.19.
4.26 Replace the tank lid and re-circulation lines; open the ball valves and turn on the pump.
4.27 The solution is now ready to be metered to the individual solution bottles.
- the pump is to remain on at all times when solution is in the tank so as to continuously mix and agitate the rinsate

V. Tank Samples:

5.1 Solution samples of the tank mix will be needed at times during the mixing process.
- during the initial tank mixing procedure, numerous samples will need to be taken because the time frame for the chemical to go into solution is unknown
- at any other time during other tank mixes when there are questions regarding the solution

5.2 Turn the centrifugal pump off.
5.3 Flush the sample line.
- open the ball valve on the sample line and let about 500 ml pass through the hose
- collect this flush solution in a nalgene waste bottle
- close ball valve
- dump this flushed solution into the 55 gal. waste barrel

5.4 Fill a 20 ml vial from the sample line.
- control the flow through the sample hose with the ball valve
- close ball valve after filling sample vial

5.5 Place lid tightly on sample vial.
5.6 Turn centrifugal pump back on and continue the agitation process.
5.7 Transport the sample(s) to the Weed Science Lab in the PSS Building for HPLC analysis.
- refer to S.O.P. #BKC-8 for the procedures involved in preparing these samples for actual analysis

VI. Tank and Equipment Cleaning: (Mixing and Distribution System Cleaning)

6.1 The mixing equipment should be internally cleansed between each new batch of solution mix.
- this includes the tank, pumps, lines, and strainers, etc.
- the triple rinse process is to be employed for this internal cleaning process
- for the triple rinse process, use clean water and rinse with 10% of the tank volume

- for the 300 gal tank, use 30 gal of water
- for the 80 gal tank, use about 10 gal of water
- all rinse water is to be pumped into the 55 gal waste barrels

6.2 Remove any remaining material left in the bottom of the tank after filling all necessary solution bottles.

- there will almost always be some unused mix solution
- pump this excess tank mix into the 55 gal waste barrel
  - close the ball valve at the bottom of the tank
  - close both ball valves at the centrifugal recirculation pump
  - disconnect the pressure line from the agitation port on the tank lid
  - connect extra hoses to this pressure line; usually requires two hoses in order to reach the 55 gal waste barrels
  - insert the free end of the hose into the opening of the 55 gal waste barrel
  - re-open all three ball valves
  - turn centrifugal pump on, thus removing the solution from the tank and placing it in the waste barrel
  - when all solution is removed from the tank, turn the pump off
  - re-close all three ball valves
  - remove the end of the pressure line from the waste barrel
  - disconnect the two extra hoses from the original pressure line

6.3 Fill the tank with the appropriate amount of rinse water.

- disconnect the metering pump recirculation line from the return port on the tank lid
- clamp off the end of this recirculation tube using pinchcock clamps
- the lid can now be unscrewed and removed from the top of the tank
- attach one end of the garden hose to the sink faucet and place the small ball valve on the other end
- turn sink on, open garden hose ball valve and add tap water to the tank until it reaches the desired level; use ball valve to turn off the garden hose (∴ can leave the sink faucet on)

6.4 Reconnect the tank recirculation system.

- screw lid back on to the tank
- connect the main pressure line to the rinse nozzle port on the tank lid

- reconnect the metering pump recirculation line
- reopen all three ball valves (one at bottom of tank and one on each side of the centrifugal pump)

6.5 Turn the centrifugal recirculation pump on and let it run for 10-15 minutes.

- thus, rinsing the inside of the tank and flushing the pump and hoses

6.6 Flush the metering system (i.e., metering pump, tubing, solenoid valve, etc.) while the tank and main lines are being cleaned and flushed.

- open ball valve in the metering pump suction hose
- turn metering pump on and let it run for 5-10 minutes
  - let the rinse water recirculate back to the tank
  - this flushes the metering pump and associated tubing
- thoroughly flush the solenoid valve
  - activate the solenoid valve with the foot switch
  - catch the solution in a small waste bottle (one liter Nalgene bottle)
  - dump this waste bottle into the 55 gal waste barrel
  - flush the solenoid valve several times (i.e., fill the small waste bottle several times)
- turn the metering pump off
- close the ball valve in the metering pump suction line

6.7 Turn pump off.

- first, close the ball valve at the bottom of the tank and the ball valve on the outlet side of the pump
- then turn pump off
- this empties all fluid from the lines

6.8 Pump the rinse water out of the tank into the 55 gal waste barrel.

- repeat the processes outlined in step 6.2 above

6.9 Now ready to refill the tank with more clean water and repeat the rinsing process two more times.

- thus, repeat steps 6.3 - 6.6 two times
- a total of three tank rinses (i.e., triple rinse)
- triple rinse the total system including the metering system
- the mixing equipment is now considered to be cleaned and ready for the next batch of solution to be mixed

The University of Tennessee
Agricultural Engineering Department
Pesticide-Contaminated Wastewater Research

Standard Operating Procedure

S.O.P. Number: BKC-3 Date: 1/10/96

Written by: Brian K. Corwin Revision Number: 2

Supersedes: 12/20/95

- CAUTION -

1. All federal, state, and local safety procedures are to be observed.
2. Good laboratory practices should also be observed.
3. Read all MSDS sheets which apply to the chemicals being used.
4. Clean the laboratory bench top being used both before and after the procedures.
5. Observe all safety precautions, including the use of protective clothing and eyeware when necessary.
6. Do not allow the laboratory to become cluttered.

Individual Solution Bottle Filling Procedure

I. Introduction:

1.1 This protocol covers the procedures and required steps involved in filling the individual solution bottles associated with each soil column. Under the direction of Brian Corwin, this procedure will take place in the Agricultural Engineering Laboratory where the one-liter nalgene solution bottles are located in the air chambers. The steps outlined in this S.O.P. should be closely followed every time pesticide solution is to be metered from the large mixing tank to the individual nalgene bottles so as 1) to ensure that each soil column maintains an adequate supply of pesticide solution with minimal disturbance to the continual running of the soil column, and 2) to maintain quality control in the manner in which solution samples are pulled for HPLC concentration analysis. Due to the fact that hazardous chemicals are involved, extra safety considerations need to be observed. Protective clothing, including lab coat, goggles, gloves and dust/mist respirator should be worn at all times.

II. **System Check**:

2.1 The pesticide solution is continuously agitated; therefore, the centrifugal pump should already be on, re-circulating solution through the system. If this is not the case and the solution is not being agitated for some reason, be sure to open the ball valve located at the bottom of the tank.

2.2 Turn on the electricity to the metering pumps and to the solenoid valve.

2.3 Open the ball valve on the suction line of the metering pump.

2.4 Turn the metering pump on.
- let it run for a few minutes so that solution gets distributed throughout all metering tubes

2.5 Check for leaks throughout the system.
- at the metering pump
- at the solenoid valve
- at all tubing connections

2.6 Check the solenoid valve to make sure that it will operate properly.

III. **Metering Pump Calibration**:

3.1 Calibrate the metering pump at the beginning of filling bottles associated with each air chamber.

3.2 Re-zero the elapsed time indicator.

3.3 Use a 250 ml graduated cylinder to measure the volume of dispersed solution.

3.4 Hold the end of the metering tube into the graduated cylinder.

3.5 Depress and hold the control switch with your foot, thus activating both the solenoid valve and timer simultaneously and allowing solution to flow into the graduated cylinder.

3.6 Release the control switch when the graduated cylinder is full.

3.7 Record the volume of solution in the graduated cylinder and the time shown on the elapsed time indicator.

3.8 Dividing the amount of solution by the time yields a flow rate (ml/sec).
- it is assumed that the metering pump will operate at this flow rate until the next calibration cycle

IV. **Solution Sample Pulling**:

4.1 Three solution samples are to be pulled per chamber (i.e., per filling of the solution bottles associated for each air chamber).
- one sample prior to filling the first bottle
- one sample after filling half of the bottles
- one sample after filling the last bottle

4.2 The following steps are to be followed for each solution sample that is

pulled.

4.3 Properly label the 20 ml scintillation vials with lab tape and sample number.
- use a three-part numbering scheme
- first number represents the sample number sequence pulled from a particular chamber (i.e., set of bottles associated with a particular air chamber)
- second set of letter(s) indicates the chamber from which the sample was taken
- third set of numbers indicates the date on which the sample was taken
- example: sample #1NC041695 indicated that this was the first sample pulled from bottles associated with the north central air chamber on April 16, 1995

4.4 Fill a small (25 ml) graduated cylinder in the same manner as described above in steps 3.4 - 3.6.

4.5 Empty this solution into the waste barrel (55 gal).

4.6 Repeat steps 4.4 and 4.5 three times.

4.7 On the fourth time, however, empty the solution into the labeled 20 ml scintillation vial.

4.8 Tightly secure the cap on the scintillation vial.

4.9 Set the full vial aside to be collected with all other samples at the end of the day.

4.10 Triple rinse the 25 ml graduated cylinder with distilled water.
- dump this rinse water into the 55 gal waste barrels
- let the graduated cylinder air dry

4.11 Now ready to collect the next sample in the same manner.

4.12 Upon completion of filling bottles and pulling samples, collect all sample vials and place in the refrigerator until time for concentration analysis using HPLC.

4.13 Refer to S.O.P. #BKC-8 for steps in preparing sample and actual analysis.

V. Bottle Filling:

5.1 There are three occasions to fill bottles:
- initially filling all empty bottles
- re-filling bottles while the soil columns remain running
- final filling for determination of the volume of solution remaining in the bottle at the end of the study (refer to S.O.P. #BKC-6 for this procedure)

A. Initial Bottle Filling:

5A.1 For the initial filling, all bottles are empty and all solution bottle

tubes are unclamped.

5A.2 Insert the end of the metering tube (from the solenoid valve) into one of the access tubes in the top of the solution bottle.

5A.3 Re-zero the elapsed time indicator.

5A.4 Depress and hold the control switch with your foot, thus activating both the solenoid valve and timer simultaneously and allowing solution to flow into the nalgene bottle.

5A.5 When the fluid level inside the bottle approaches the top, release the control switch with your foot, thus stopping both the flow and the timer simultaneously.

5A.6 Remove the metering tube from the solution bottle's access tube.

5A.7 Mark the fluid level on the outside of the bottle with a permanent marker.

5A.8 Record the time shown on the elapsed time indicator along with the corresponding solution bottle number.

- record all times on paper and at a later date transfer this data onto the computer
- save all hand-recorded data sheets

5A.9 Re-zero the elapsed time indicator.

5A.10 Move on to the next bottle and repeat steps 5A.2 - 5A.10.

5A.11 Upon filling the last bottle and pulling the last sample, turn off the metering pumps and solenoid valve, and close the ball valve in the suction line of the metering pump.

Notes:
- during the initial bottle filling-process, fill the bottles in numerical order per chamber, starting with the north air chamber (i.e., North #1-128, North Central #1-128, South Central #1-128, and South #1-128)
- pull a solution sample every 16th bottle (for a total of 33 samples); this is done because the exact concentrations of the solution are uncertain and to account for any unpredictable variations over time

B. Bottle Re-Filling:

Notes:
- re-filling occurs after the soil columns have been started, are established, and are up and running
- the bottles will need to be re-filled periodically as solution is evaporated from the soil, thus lowering the fluid level in the bottles
- the fluid level should drop no lower than one to two inches above the bottom of the bottle, thus ensuring that the end of the glass rod remains submerged in solution; if the end of the glass rod becomes exposed (i.e., fluid level drops below the end of glass rod) the vacuum is broken, essentially

stopping the continual uptake of solution by the soil columns

To re-fill a bottle:

5B.1 Using pinchcock clamps, clamp off both tubes connecting the solution bottle to the soil columns (i.e., the siphon tube and the vacuum tube).

5B.2 Unclamp the two access tubes located in the top of the solution bottle.
- unclamp paper binder clips from tubes
- with your fingers, squeeze the tubes at the bend points to ensure that they are fully open and not kinked

5B.3 Insert the metering tube (from the solenoid valve) into one of the two solution bottle access tubes.

5B.4 Re-zero the elapsed time indicator.

5B.5 Repeat steps 5A.4 - 5A.5 as described above, thus re-filling the solution bottle.
- fill the bottle with solution until the fluid level rises to the black mark on the outside of the bottle

5B.6 Remove the solenoid valve metering tube from the solution bottle access tube.

5B.7 Record the bottle number and time as described above in step 5A.8.

5B.8 Re-clamp the solution bottle access tubes.
- re-clamp paper binder clips to tubes

5B.9 Observe the solution bottle, the soil columns and all tubes for a few seconds.
- make sure everything appears to be in place and working properly
- make sure the column re-establishes itself

5B.10 Re-zero the elapsed time indicator.

5B.11 Move on to the next solution bottle and repeat steps 5B.1 - 5B.11 as described above.

The University of Tennessee
Agricultural Engineering Department
Pesticide-Contaminated Wastewater Research

Standard Operating Procedure

S.O.P. Number: BKC-4 Date: 1/10/96

Written by: Brian K. Corwin Revision Number: 2

Supersedes: 12/20/95

- CAUTION -

1. All federal, state, and local safety procedures are to be observed.
2. Good laboratory practices should also be observed.
3. Read all MSDS sheets which apply to the chemicals being used.
4. Clean the laboratory bench top being used both before and after the procedures.
5. Observe all safety precautions, including the use of protective clothing and eyeware when necessary.
6. Do not allow the laboratory to become cluttered.

Individual Soil Column Start-Up Procedure

I. Introduction:

1.1 This protocol covers the procedure and required steps involved in starting pesticide solution flow to the individual soil columns. Under the direction of Brian Corwin, this procedure will take place in the Agricultural Engineering Laboratory where the air chamber/soil column apparatus is located. The steps outlined in this procedure will need to be observed in three situations. To begin with, the steps outlined in this procedure are to be followed at day zero when all 512 columns are initially started. Second, these same guidelines can be used to re-start any column which has stopped running for any reason. Additionally, these steps can be followed to re-start the soil columns after they have been pulled at the specified time periods and replaced in the air chambers to be run with wastewater. By closely adhering to the steps outlined in this S.O.P., it can be ensured that all soil columns are started in the same manner and with minimal complications. Due to the fact that hazardous chemicals are involved, extra safety considerations

need to be observed. Protective clothing, including lab coat, goggles, gloves, and dust/mist respirator should be worn at all times.

II. Pressurizing Solution Bottle:

2.1 Attach the air hose to the air supply manifold system.

2.2 Turn on the air pressure with the main valve on the manifold system.

2.3 Adjust the pressure relief valve on the manifold system until the pressure gauge indicates an air pressure of about one psi or less.
- test the air pressure by blowing air onto your hand and feeling it
- the air pressure should feel very light and almost unnoticeable (about the same as blowing air out of your mouth in a normal manner)

2.4 Using pinchcock clamps, clamp off the vacuum tube connecting the solution bottle to the top fitting on the soil column.
- make sure that the clamp is secure and the tube is completely closed off

2.5 Unclamp one of the access tubes located on the top of the solution bottle.
- may unclamp either access tube, it does not matter
- unclamp by removing the paper binder clip
- ensure that the access tube is fully open by squeezing or pinching it with your fingers at the bend point of the tube

2.6 Insert the tip of the trigger valve (on the end of the air hose) into the open end of the unclamped access tube.

2.7 Activate the trigger valve, thus forcing air into the solution bottle.
- in effect, this pressurizes the bottle
- the air will force solution out of the bottle, down the supply tube and into the bottom fitting of the soil column

2.8 Immediately release the air trigger valve when the fluid reaches the bottom fitting of the soil columns.
- watch the solution flow down the tube and at the precise moment it enters the column, release the air trigger valve
- releasing the trigger valve stops the air flow into the bottle, thus stopping the fluid from being <u>forced</u> into the soil column
- the matric potential of the dry soil will now pull the solution out of the bottle, down the tube, and into the column

2.9 While the trigger valve remains inserted into the access tube:
- re-bend the access tube, thus pinching it shut
- while holding the access tube bent, remove the trigger valve
- replace the clamp (paper binder clip) on the access tube
- double check the binder clip to make sure that the access tube is securely clamped off

2.10 Remove the tip of the trigger valve (on the end of the air hose) from the access tube.

2.11 Remove the pinchcock clamp from the vacuum tube connecting the solution bottle to the top fitting of the soil column.
- pinch the tube with your fingers to ensure it is completely open
- the column should now be running again, on its own

2.12 Observe the column for several minutes.
- make sure that the fluid is flowing into the column properly
- solution will wick up through the soil and exit the top fitting, entering the vacuum tube
- the solution will rise up this vacuum tube until it is even with the fluid level in the solution bottle
- when this occurs, the column is fully established and running well
- also, observe the top of the soil columns to make sure that fluid is not overflowing the top of the column rim
- if the column is overflowing, refer to S.O.P. #BKC-6 for guidelines in solving this problem

2.13 Move to the next column and repeat steps 2.4 - 2.11 to start or re-start the next soil column.

2.14 After pressurizing all necessary bottles, turn off the air supply and roll up the air hose.
- turn off the main valve on the air pressure manifold system

The University of Tennessee
Agricultural Engineering Department
Pesticide-Contaminated Wastewater Research

Standard Operating Procedure

S.O.P. Number: BKC-5 Date: 1/10/96

Written by: Brian K. Corwin Revision Number: 4

Supersedes: 12/20/95

- CAUTION -

1. All federal, state, and local safety procedures are to be observed.
2. Good laboratory practices should also be observed.
3. Clean the laboratory both before and after the procedure.
4. Read all MSDS sheets which apply to the chemicals being used.
5. Observe all safety precautions, including the use of protective clothing and eyeware when necessary.
6. Do not allow the laboratory to become cluttered.

Initial System Start-Up Procedure

I. Introduction:

1.1 This protocol covers the procedures and required steps involved in the initial start-up of the system. Under the direction of Brian Corwin, this procedure will take place in the Agricultural Engineering Laboratory once all soil columns/solution bottles are placed within the air chambers and the pesticide solution mixture has been formulated. Due to the magnitude of work involved in starting all 512 columns in a timely and consistent manner, at least three people will be needed to assist. One person will pressurize the solution bottles, a second person will clamp and unclamp solution bottles, and a third person will re-fill solution bottles. The steps outlined in this S.O.P. should be closely followed during the initial start-up of the system so as to ensure that all columns are started in the same manner and at relatively the same time (i.e., time zero), thus minimizing any variations. Due to the fact that hazardous chemicals are involved, extra safety considerations need to be observed. Protective clothing, including lab coat, goggles, gloves, and dust/mist respirator should be worn at all times.

II. Initial Column Wetting:

2.1 Have the pesticide solution mixed and stored in the holding tank.
- refer to S.O.P. # BKC-2, for the pesticide mixing protocol

2.2 Fill all 512 solution bottles with rinsate solution.
- refer to S.O.P. # BKC-3, for the protocol describing the filling of each individual solution bottle with rinsate
- mark the initial solution level on each bottle with a permanent marker
- fill the bottles in numerical order, one air chamber at a time (begin with the North chamber, then North Central, South Central, and South chamber)

2.4 Start the soil columns.
- refer to S.O.P. # BKC-4, for the protocol on individual column start-up
- only start small groups of columns at a time
- it is best to start only one side of a chamber at a time (i.e., 64 columns at a time)

2.5 Let the columns get "wet" with the initial rinsate solution.
- let the columns absorb most of the solution from their respective bottles (be sure that they do not take up too much solution and break the vacuum in the bottle; let the solution level drop until the bottle is about 1/4 full)

2.6 Evaluate the columns as they take up solution.
- look for leaks in the column fittings, and around the column bottoms
- watch for column overflows (i.e., solution flowing up and over the rim of the column)
- refer to S.O.P. # BKC-6, for the procedures necessary to correct these types of problems

2.7 Stop the columns.
- clamp off the supply line and the vacuum line on the columns before the vacuum is broken; this automatically stops the column from taking up any more solution

III. Final Column Starting:

3.1 Refill the solution bottles with rinsate solution.
- re-fill to the initial fill mark on the bottles
- again, refer to S.O.P. # BKC-3

3.2 Restart the columns.
- take the clamps off of the supply and vacuum lines, and the columns will automatically begin running again

3.3 Evaluate the columns until they are fully established and successfully running.

3.4 Begin the start-up process for the next group of columns.
- repeat steps 2.2 - 3.3 as outlined above
- the second group of columns should be the columns on the opposite side of the same chamber
- work in these groups until all 512 soil columns are fully established and successfully running
- it may take several days to complete this process and have all 512 columns fully established

IV. Air Chamber Start-Up:

4.1 Place pieces of duct tape over all open tubing access holes.
- these are the holes in the chamber shelves which allow tubing to connect the soil columns to the solution bottles
- only half of the holes will have tubing running through them at any given time
- air loss from the chambers can be minimized by temporarily covering these holes with tape

4.2 Place all doors on the air chambers
- tightly secure the wing nuts on the doors, thus ensuring that they are properly sealed shut

4.3 Turn on electricity supplying all of the chamber system.
- all electricity is supplied from the main buss bar in the laboratory
- using a long pole, switch on the two buss bar boxes which have cables connected to the chamber breaker boxes (i.e.- the two boxes located at the end of the buss bar nearest to the garage door)

4.4 Turn on both ceiling exhaust fans.
- controlled by light switches located on the wall
- one switch (for the South exhaust fan) is located beside the garage door, next to the garage door controls
- the other switch (for the North exhaust fan) is located on the opposite side of the garage door, next to the exit door leaving the lab
- red lights on the switches should illuminate, indicating that the ceiling exhaust fans are on

4.5 Turn on the blowers.
- electricity to the 3/4 Hp blower is controlled by a breaker in the breaker box (labeled: "North blower")
- electricity to the 5 Hp blower is controlled by the 240 Volt safety switch (labeled "South blower")

4.6 Turn on the heat boxes.

- electricity to both heat boxes is controlled by breakers in the breaker box (one labeled "North heat" and the other labeled "South heat")

4.7 Day zero occurs when, after all columns are established, the blowers and heat boxes are turned on.

- allow several days for the temperature and air flow to stabilize inside the chambers

The University of Tennessee
Agricultural Engineering Department
Pesticide-Contaminated Wastewater Research

Standard Operating Procedure

S.O.P. Number: BKC-6 Date: 1/10/96

Written by: Brian K. Corwin Revision Number: 2

Supersedes: 1/5/96

- CAUTION -

1. All federal, state, and local safety procedures are to be observed.
2. Good laboratory practices should also be observed.
3. Clean the laboratory both before and after the procedure.
4. Read all MSDS sheets which apply to the chemicals being used.
5. Observe all safety precautions, including the use of protective clothing and eyeware when necessary.
6. Do not allow the laboratory to become cluttered.

Soil Column/Solution Bottle Operational Procedures

I. Introduction:

1.1 This protocol covers miscellaneous procedures and required steps for various tasks involved in the operation of the soil column/solution bottle system. Under the direction of Brian Corwin, these procedures will take place in the Agricultural Engineering Laboratory where the chamber apparatus is located. The miscellaneous operations outlined in this protocol include fixing problem columns, flooding and draining columns, collecting final solution bottle samples, and applying wastewater to columns after their analysis. This protocol does not cover such daily procedures as filling solution bottles and collecting regular solution samples. Standard Operating Procedure #BKC-3 should be referred to for these daily tasks. Due to the fact that hazardous chemicals are involved, extra safety considerations need to be observed. Protective clothing, including lab coat, goggles, gloves, and dust/mist respirator should be worn at all times.

II. Correcting/Repairing Faulty Columns and Bottles:

2.1 This section outlines the corrective measures undertaken to correct or repair

problems associated with either the actual soil columns or solution bottles. Such problems include column leaks, column overflows, clogged tubing, blown stoppers on the bottles, and stopped column/bottle systems.

A. Column Leaks:

2A.1 Leaks in the column may occur in either of two places or in both:
- around the elbow fittings in the side of the column
- around the bottom of the column (i.e., around the edge of the PVC bottom plate, where it was glued to the PVC pipe)

2A.2 Once a leak is detected, stop the column by clamping off both tubes connecting the column to its solution bottle.
- use pinchcock clamps
- clamp both the siphon tube and the vacuum tube

2A.3 After the column has been stopped for a few minutes, wipe away all visible fluid from around the point of leakage.
- use a paper towel and dispose of it after use

2A.4 Glob and smear silicon all over the leaky portion of the column.
- apply a lot of silicon; cannot apply too much
- use your finger to smear the silicon all around the leaky area

2A.5 Leave the column clamped off overnight.
- this allows the silicon sufficient time to cure and seal the leak

2A.6 The next morning, remove the pinchcock clamps, thus re-starting the column.
- observe the column for several minutes; make sure that fluid begins to re-enter the column; also observe the repaired area for any more leaks
- if the column does not re-start on it's own, the solution bottle may have to be re-pressurized to initiate fluid flow into the column (refer to S.O.P. #BKC-4)
- if the leak persists, clamp off the column again and repeat the above repair process
- if the leak appears to be fixed, continue to observe the column periodically throughout the day to make sure the column becomes re-established and running properly

2A.7 If the leak was repaired successfully, the column is then assumed to be O.K.
- all leaks can be repaired in the above described process

B. Column Overflows:

2B.1 The only way for solution to overflow a column is if the vacuum on the bottle is broken. If this vacuum is broken, solution basically free-flows out of the bottles, into the column and over the column rim. There are only a couple of ways in which this vacuum can be broken. First, the paper binder clamps on the bottle access tubes may not be pinching the tube closed tightly enough. Also, sometimes this clamp may pop completely off. Second, the stopper may not be properly sealed in the top

of the bottle. In some cases, this may not be obvious and in others the stopper may be popped completely off the bottle. In instances where everything appears normal but the column is overflowing, the seal between the stopper and the bottle is leaking somewhere (the silicon around the stopper/bottle interface may be cracked, for instance). When either of these things happen, the seal keeping the bottle pressurized is broken and air seeps into the bottle.

2B.2 Upon notice of a column overflow, immediately stop the column.
- use pinchcock clamps to clamp off both the siphon tube and the vacuum tube connecting the column to the bottle

2B.3 Clean up the spill.
- be sure to wear gloves
- use paper towels to absorb all spilled solution
- properly dispose of these used paper towels

2B.4 If the problem is determined to be clamp-related, double check the clamp and replace if necessary. For the most part, these clamps do an excellent job of pinching the tubing closed.
- in most cases, the clamps were not replaced on the tubes after re-filling the bottle (simple oversight)
- or, the clamps popped off the tubing due to careless replacement after bottle re-filling (hastily replaced and not double checked)

2B.5 If the problem is determined to be stopper-related (i.e., the stopper popped off or leaks around the stopper), silicon should be applied in the same manner as used to fix column leaks.
- refer to step 2A.4 above
- remove the old silicon seal from around the stopper and bottle
- make sure the stopper is firmly inserted into the top of the bottle
- glob and smear silicon all over and around the stopper/bottle interface
- also, smear silicon all over the top surface of the stopper and around the glass rods protruding through the stopper

2B.6 Observe steps 2A.5 - 2A.7 as outlined above to ensure sufficient silicon curing and sealing.
- all stoppers can be repaired in this manner

C. Clogged Tubes:

2C.1 Clogged tubes are caused by soil particles bubbling out of the column and into the tubing. These particles eventually settle down in the tubing finally resting in the elbow fitting. Thus, the fitting becomes clogged and in some instances soil gets clogged in the tubing also. When this clogging occurs, in essence the system becomes clamped off and stops.

2C.2 Once a clogged tube is detected, clamp off both the siphon and vacuum tubes connecting the columns to the solution bottle.
- use pinchcock clamps

2C.3 Disconnect the clogged tube(s) from the column fitting.
- twist the tubing to break the seal formed between the tubing and fitting

- now, it should be easier to pull the tubing off the fitting
- the fittings are barely inserted into the column and thus, great care should be taken when pulling the tubing off the fitting; hold and support the fitting with one hand and disconnect the tubing with the other

2C.4 Clean the soil out of the clogged fitting and/or tube.
- use a toothpick to dig all soil out of the fitting or tube

2C.5 Re-connect the tubing to the fitting.

2C.6 Unclamp the tubes and re-start the column.
- remove the pinchcock clamps from both the vacuum and siphon tubes
- if the column doesn't re-start automatically, one may have to re-pressurize the bottle (refer to S.O.P. #BKC-4)

2C.7 Observe the column for several minutes.
- in particular, watch the unclogged tube
- many times it will still have a lot of loose soil particles bubbling up in the tube and fitting
- in essence, the unclogged tube/fitting is flushing any remaining soil out of the way

2C.8 Repeat the unclogging procedure several times until all soil is flushed out of the clogged fitting/tubing.
- repeat steps 2C.2 - 2C.7 as described above

D. Blown Stoppers:

2D.1 The rubber stoppers are not very securely inserted into the top of the solution bottles. These stoppers are easily pulled or blown out of the bottles. Stoppers can come off due to several things: 1) accidentally pulled or knocked off during the bottle filling process, 2) accidentally pulled or knocked off while moving the solution bottles during the flood/drain process, or 3) blown off while pressurizing the solution bottle.

2D.2 Once a stopper is dislodged from a bottle, immediately stop the column by clamping off the tubes.
- with pinchcock clamps, clamp off both the siphon and vacuum tubes connecting the column to the bottle
- if the tubes are not immediately clamped off, the column will overflow

2D.3 Remove the blown stopper from the bottle.
- clean all old silicon from around the edge of the stopper and the edge of the bottle

2D.4 Re-insert the stopper into the bottle.
- press the stopper firmly into the bottle

2D.5 Glob and smear silicon all over and around the stopper/bottle interface.
- refer to steps 2A.4 and 2B.5 as described earlier

2D.6 Observe steps 2A.5 - 2A.7 as outlined to ensure sufficient silicon curing and sealing and proper re-starting.
- all stoppers can be repaired in this manner

III. Flood/Drain Procedure:

3.1 One half of all soil columns are of the flood/drain type. Additionally, these can be divided into two groups: the five-day cycle columns and the ten-day cycle columns. Thus, there are 256 total flood/drain columns, 128 five-day cycle columns and 128 ten-day cycle columns. Breaking these categories down even further, there are 32 of each cycle type columns per air chamber. The flood/drain concept was designed to supply these soil columns with pesticide solution for a specified period of time, thus, flooding the entire soil matrix and creating an anaerobic condition. Then, completely stop this supply of pesticide solution to the column for the same amount of time. During this time, the soil will dry out via evaporation, thus creating an aerobic condition. These columns are to be alternated between these aerobic/anaerobic conditions in either five-day or ten-day cycles. The following guidelines should be followed every time the columns need to be cycled between the flood and drain conditions.

3.2 First, determine which bottles need to be moved (i.e., either flooded or drained).
- refer to the flood/drain schedule for this information
- label the five-day and ten-day solution bottles associated with the respective soil columns
- place lab type on the solution bottles for easy visual identification
  - use yellow lab tape for all five-day columns
  - use blue lab tape for all ten-day columns
  - with a lab marker write either "5" or "10" on the tape placed on the appropriate solution bottles

3.3 Move bottles in groups associated with individual air chamber doors.
- move all necessary bottles associated with one air chamber door before moving on to the next door
- it is best to proceed from upper level door to lower level door and then move down the length of the chamber until all bottles associated with one side of the air chamber are moved
- it is best to complete one side of a chamber at a time (i.e., move all bottles associated with one side of an air chamber and then move all bottles associated with the other side of the same chamber, then go to the next air chamber), then go to the next air chamber and continue in this manner until all 256 bottles are moved

3.4 Begin by removing an individual air chamber door.
- unscrew all five wing nuts securing the door in place
- remove the door from the chamber and set it aside
  - care should be taken in handling the door so as not to rip or tear the foam seal around the edge of the door

3.5 This section can be divided into two parts:

A. Draining Procedure:

3A.1 The following draining procedures should be applied to every flood-type

column which needs to be cycled from anaerobic status to aerobic status.

3A.2 Remove the two tubes from the holes in the chamber upper shelf.
- the shelf directly above the soil column
- these tubes are the siphon and vacuum tubes connecting the solution bottle to the soil column
- it is best to squeeze and roll the tubes out of the holes (slots) in the shelf

3A.3 Move the solution bottle from the shelf above the associated soil column to the shelf below the column.
- place the bottle directly below the column

3A.4 Remove the tape covering the holes in the lower shelf associated with this column/bottle pair.
- place this tape over the holes in the upper shelf
- in some cases, you may have to use new tape to cover the upper shelf holes

3A.5 Place the two tubes into the holes in the lower shelf on which the column sits.
- place the vacuum tube in first and push it into the back hole
- next, place the siphon tube into the front hole
- it is best to squeeze and roll the tubes into the holes

3A.6 Clamp off the siphon tube.
- the siphon tube is the tube connected to the bottom elbow fitting in the column
- pinch the tube in half
- place a paper binder clip over the pinched tube

3A.7 Replace the door onto the chamber and securely tighten all wing nuts.
- make sure all tubing is inside the air chamber and will not be closed in the door

3A.8 Move to the next air chamber door and repeat steps 3A.2 - 3A.7.
- continue in this manner until all columns which needed to be drained have been
- it will take approximately four hours to complete this process on all 256 flood/drain type columns

B. <u>Flooding Procedure</u>:

3B.1 The following flooding procedure should be applied to every flood-type column which has been draining for the specified time period and needs to be re-supplied with pesticide solution (i.e., cycled from aerobic status to anaerobic status).

3B.2 Remove the two tubes from the holes in the chamber lower shelf.
- these tubes are the siphon and vacuum tubes connecting the solution bottle to the soil column
- it is best to squeeze and roll the tubes out of the slots (holes) in the shelf

3B.3 Unclamp the siphon tube.

- remove the paper binder clip which is pinching closed the tube connected to the bottom column fitting
- with your fingers, squeeze the tube at the bend point to ensure that the tube is fully open

3B.4 Move the solution bottle from the shelf below the associated soil column to the shelf above the column.
- place the bottle directly above the column

3B.5 Remove the tape covering the holes in the upper shelf associated with this column/bottle pair.
- place this tape over the holes in the lower shelf
- in some cases, you may have to use new tape to cover the lower shelf holes

3B.6 Place the two tubes into the holes in the upper shelf above the soil column.
- place the vacuum tube in first and push it into the back hole
- next, place the siphon tube into the front hole
- it is best to squeeze and roll the tubes into the holes

3B.7 Check the column to make sure it re-started.
- the column should have re-started by itself upon unclamping the tube and moving the bottle to the upper shelf
- if the column did not re-start automatically, it will have to be re-started by re-pressurizing the solution bottle (refer to S.O.P. #BKC-4).

3B.8 Replace the door onto the chamber and securely tighten all wing nuts.

3B.9 Once the column is running again, closely observe the solution bottle because it will need to be refilled fairly soon.
- refer to S.O.P. #BKC-3 for bottle filling

3B.10 Move to the next air chamber door and repeat steps 3B.2 - 3B.9.
- continue in this manner until all columns which needed to be flooded have been
- it will take approximately four hours to complete the process on all 256 flood/drain type columns

IV. <u>Final Solution Bottle Samples</u>:

4.1 At the end of each specified time period, after the soil columns have been pulled out of the air chambers, it is necessary to determine the amount and concentration of the solution remaining in the solution bottle. This remaining volume represents solution that was added to the system but not used by the column. It is important to have both the volume of fluid remaining and the mass of each herbicide associated with this volume of fluid so that it can be accounted for in the final mass balance calculation. The following procedure outlines the steps required in collecting a sample of this solution for concentration analysis on the HPLC.

4.2 These procedures take place after the columns have been removed from the air chamber and the bottles and tubing remain (refer to S.O.P. #BKC-8, steps 2.2 - 2.3).

4.3 Determine which bottles need to be sampled.
- the bottles to be sampled will have a piece of green lab tape on the outside of the bottle with writing indicating which time period the bottle is associated with

4.4 Properly label 128 20mL scintillation vials with lab tape and sample number.
- refer to the column pulling schedule for determination of appropriate sample numbers
- place a piece of lab tape onto the outside of the 20mL scintillation vial
- with a permanent lab marker, write the sample number on the lab tape
- use the column location number for the sample number (e.g., SC128)

4.5 Collect samples from bottles in groups associated with individual air chamber doors.
- collect all necessary samples from bottles associated with one air chamber door before moving on to the next door
- it is best to proceed from upper level door to lower level door and then move down the length of the chamber until all necessary bottles associated with one side of the air chamber are sampled
- it is best to complete one side of a chamber at a time, then complete the other side before proceeding to the next air chamber
- continue in this manner until all 128 necessary solution bottles have been sampled

4.6 Remove the individual air chamber door.
- unscrew all five wing nuts holding the door in place
  - set the wing nuts aside on one of the chamber shelves
- remove the door from the chamber and set it aside
  - care should be taken in handling the door so as not to rip or tear the foam seal from around the edge of the door

4.7 Flush 130mL through the siphon tube.
- unclamp the vacuum tube (i.e., the tube which normally would be connected to the top fitting of the column; usually the shorter of the two tubes)
- completely remove the pinchcock clamp
- place the end of the siphon tube into a 250mL graduated cylinder
  - (i.e., the tube normally connected to the bottom fitting of the column; normally the longer of the two tubes).
- open the siphon tube clamp
  - barely squeeze the pinchcock clamp open
  - do not remove it from the tube
  - use it to control the fluid flow
- fluid should flow out of the tube and into the graduated cylinder automatically
  - if not, you may have to re-pressurize the bottle to initiate fluid flow (refer to S.O.P. BKC-4)
- close the siphon tube clamp once the level of fluid in the graduated cylinder reaches the 130mL mark, thus stopping the flow
- only flush 130mL from bottles containing a sufficient amount of solution

- make a note of the bottles which do not contain a sufficient amount of fluid or which had some other amount flushed through the siphon tube
- in some cases, the bottle may be empty and no sample will be collected; make a special note of all such bottles
- dispose of the 130mL of solution into the 55 gal waste barrel

4.8 Collect a 20mL sample (thus a total of 150mL of solution removed from the bottle).
- unscrew the cap to the 20mL scintillation vial labeled with the sample number corresponding to the solution bottle number
- place the end of the siphon tube into the open scintillation vial
- fill the vial in the same manner as described in step 4.7 for flushing the tube
- replace cap on scintillation vial after filling

4.9 Re-clamp the vacuum tube.
- replace the pinchcock clamp
- also, double check the clamp on the siphon tube making sure it is clamped off properly

4.10 Replace the individual air chamber door and securely tighten all wing nuts.
- make sure all tubing is inside the air chamber and will not be closed in the door

4.11 Move to the next air chamber door and repeat steps 4.6 - 4.10.
- continue in this manner until all necessary solution bottles have had samples collected from them

V. Final Solution Bottle Volumes:

5.1 The volume of fluid remaining in the individual solution bottles at the end of the experiment represents solution that was added to the system but not used by the soil column. This volume of fluid must be accounted for in the final mass balance calculations. The following steps outline the procedure for determining the volume.

5.2 These procedures should be followed after the soil columns have been removed from the air chambers at the end of each specified time period.
- additionally, solution samples should be collected from the corresponding bottles (as described in section IV) before determination of the final solution bottle volumes

5.3 Determine which bottles need to be refilled.
- the bottles to be refilled will have a piece of green lab tape on the outside of the bottle with writing indicating which time period the bottle is associated with

5.4 These bottles will be refilled with waste solution from the 55 gal waste barrels.
- they will be refilled in the same manner as all previous bottle filling procedures except that the fluid will be waste solution
  - follow the filling procedures outlined in S.O.P. #BKC-3 (refer to sections II, III, and VB)

- swap the tubing at the solenoid valve
  - disconnect the two lines labeled as "pesticide solution"
  - connect the two lines labeled as "waste solution"
- be sure to use the waste solution metering pump
  - it is already connected to the 55 gal waste barrel
- fill the bottles with waste solution until the fluid level rises exactly to the black mark on the outside of the solution bottle
  - this black mark represents the original filling volume

5.5 Replace the green lab tape on the solution bottles with a piece of red lab tape.
- label this red tape with the letters "H_2O"
- this indicates that the bottle contains waste solution instead of the pesticide solution normally used

5.6. Move on to the next air chamber door and repeat steps 5.4 - 5.5.
- continue in this manner until all 128 necessary solution bottles have been refilled with waste solution

5.7 Calculation of final solution bottle volume.
- to the original filling volume, add the volume associated with the collection of the solution bottle sample (i.e., 150 total mL in most cases)
- from this total, subtract the final refill volume determined in step 5.4 above
- this total represents the amount of solution which did not actually enter the soil column but was added to the solution bottle
  - this amount can now be accounted for in the final mass balance calculations

VI. Return of Soil Columns to Air Chambers:

6.1 At the end of each of the four specified time periods, the soil columns associated with each time period were removed from the air chambers for soil concentration analysis. In order to keep the conditions within the air chamber system as close to the same as possible throughout the experiment, it is important to return these columns to the air chamber as quickly as possible. Additionally, these returned columns need to be operating exactly as normal. Thus, it was decided to re-pack these columns with soil and run wastewater through them. The following procedure describes the necessary steps required to get these columns back into the air chamber and running again.

6.2 At this point, the soil columns are at the stage where they have been removed from the air chamber and all the soil has been removed.
- refer to S.O.P. #BKC-8, steps 2.1 - 2.8

6.3 Re-pack these empty columns with soil.
- use the extra soil saved from the initial column packing procedure
- all additional soil needed will come from the leftover soil sub-sampling procedure (refer to step 3.8 in S.O.P. #BKC-8)
- make sure that the columns are re-packed with the same soil type which they initially contained

- re-pack the column as outlined in step 3.3 of S.O.P. #BKC-1
  - no need to worry about re-packing the column to within a certain bulk density range
  - just re-pack the column until it is full of soil

6.4 Place each full soil column back into its correct location within the air chambers.
- remove the necessary air chamber doors
- attach both the siphon and vacuum tubes connected to the solution bottle
  - the siphon tube (the longest of the two tubes) should be connected to the bottom fitting in the column
  - the vacuum tube (the shortest of the two tubes) should be connected to the top fitting in the column
- replace the air chamber door

6.5 Replace all soil columns into the air chamber before re-starting any of them.

6.6 Re-start the soil column.
- the solution bottles should already have been refilled with waste solution
  - due to the refilling for determination of the final solution bottle volumes (section V above)
- remove both pinchcock clamps
  - one of the siphon tube and one on the vacuum tube
- the column should re-start automatically
- is it does not re-start automatically, the solution bottle will have to be re-pressurized
  - refer to S.O.P. #BKC-4

6.7 These columns will behave exactly like the ones that were started during the initial system start-up.
- therefore, refer to S.O.P. #BKC-5, sections II and III describing the initial column wetting and the immediate re-filling of the solution bottle
  - in section II of S.O.P. #BKC-5, follow steps 2.4 - 2.7
  - in section III of S.O.P. #BKC-5, be sure to refill these columns with <u>waste solution</u> instead of the actual pesticide solution

The University of Tennessee
Agricultural Engineering Department
Pesticide-Contaminated Wastewater Research

Standard Operating Procedure

S.O.P. Number: BKC-7 Date: 2/23/96

Written by: Brian K. Corwin Revision Number: 4

Supersedes: 1/10/96

- CAUTION -

1. All federal, state, and local safety procedures are to be observed.
2. Good laboratory practices should also be observed.
3. Read all MSDS sheets which apply to the chemicals being used.
4. Clean the laboratory bench top being used both before and after the procedures.
5. Observe all safety precautions, including the use of protective clothing and eyeware when necessary.
6. Do not allow the laboratory to become cluttered.

Preparation of Chemical Standards For the High Performance Liquid Chromatography (HPLC) System

I. Introduction:

1.1 This protocol covers the procedures and required steps necessary for the preparation of the chemical standards needed by the HPLC machine. In order to quantitate the output generated by the HPLC for a soil sample analysis, the actual chemical at a desired concentration must first be analyzed. These results can then be used as a background from which to make comparisons with an actual soil sample analysis. Thus, stock solution of each chemical to be tested for, at various concentration levels, is run through the HPLC. Additionally, standards are made to detect any of the pesticide metabolites which may have formed and for mixtures of the various pesticides. For this particular research project, standards were generated for the herbicides atrazine and fluometuron, for the initial fluometuron metabolite DMFM, and for a mixture the of three. The procedure for creating the HPLC standards is the same for all these pesticides.

II. Preparation of Stock Solution:

2.1 Remove the cap from the bottle of technical grade chemical.

2.2 Weigh the bottle plus chemical.
- weigh the material to four decimal points
- record the weight as "beginning weight"

2.3 Remove the bottle from the scale and place a tiny amount of the chemical into a clean, dry 250mL Erlenmeyer flask.
- use a small, clean spatula to transfer the chemical from the bottle to the flask
- make sure that the spatula has been thoroughly cleaned both before and after use

2.4 Weigh the bottle plus chemical again.
- again, weigh it to four decimal places
- record this weight as "ending weight"

2.5 Take the difference of the two weights.
- record this difference as "weight of chemical"

2.6 Replace the cap on the chemical bottle and return it to its proper place of storage.

2.7 Add 200.0 mL of Methanol (MeOH) to the Erlenmeyer flask.

2.8 Place aluminum foil over the top of the flask, then screw the top onto the flask.

2.9 Gently swirl the flask in order to get the chemical to go into solution.
- may have to place the flask on a stir plate for a little while; if so, will need to place a stir bar in the flask
- the chemical is in solution when no material is visible in the flask (i.e.- the solution appears clear)

2.10 Calculate the concentration of the stock solution as follows:
- divide the "weight of chemical" by the amount of MeOH added (i.e., weight of chemical in g. ÷ 200mL)
- multiply the answer from above (g/mL) by $1x10^6$ to get the concentration of the chemical in the solution in ppm

2.11 Label the flask accordingly and store in the freezer (@ -10°C) until needed, to prevent degradation.

III. Prepare Samples of Varying Concentrations:

3.1 Calculate the amount of stock solution (prepared above) needed to add to 20 mL of MeOH to obtain a concentration of 1000ppb.
- set up a simple ratio to accomplish this
- (1000ppb)*(20mL) = (known Xppb of stock soln.)*(XmL of stock soln. needed)
- solve for XmL

3.2 Fill a 20mL scintillation vial with MeOH.

3.3 With a calibrated pipette, remove XmL of MeOH from the 20mL scintillation vial.
- use the Wheaton 5mL Adjustable Micropipette
- discard this XmL of MeOH
- discard the plastic pipette tip and replace with a new one

3.4 With the calibrated pipette, place XmL of the stock solution into the 20mL scintillation vial of MeOH.

3.5 Place cap on the scintillation vial and shake.

3.6 This scintillation vial now contains the desired concentration of chemical.

3.7 Label the 20mL scintillation vial accordingly.

3.8 Repeat steps 3.1 - 3.7 for concentrations of 50, 100, 250, 500, 1000, 2000, 6000, and 12000 ppb.

3.9 Using a pipette, fill 4mL auto-sampler vials with each of the different concentration solutions.
- use the Wheaton 5mL Adjustable Micropipette
- dispose of the pipette tips after each use and replace with a new tip

3.10 Label each 4mL vial accordingly and place in the freezer (@ -10°C) until analysis to prevent herbicide degradation.

The University of Tennessee
Agricultural Engineering Department
Pesticide-Contaminated Wastewater Research

Standard Operating Procedure

S.O.P. Number: BKC-8 Date: 2/24/96

Written by: Brian K. Corwin Revision Number: 4

Supersedes: 1/10/96

- CAUTION -

1. All federal, state, and local safety procedures are to be observed.
2. Good laboratory practices should also be observed.
3. Read all MSDS sheets which apply to the chemicals being used.
4. Clean the laboratory bench top being used both before and after the procedures.
5. Observe all safety precautions, including the use of protective clothing and eyeware when necessary.
6. Do not allow the laboratories or growth chamber to become cluttered.

Chemical Analysis Procedure For Soil and Solution Samples

I. Introduction:

1.1 This protocol covers the procedures and required steps for the chemical analysis of both solution and soil samples for herbicide concentrations. This chemical analysis will be performed using a HPLC (High Performance Liquid Chromatography) apparatus in the Plant & Soil Science Laboratory under the direction of Dr. Tom Mueller and Todd Willian. The steps outlined in this S.O.P. should be closely followed each time samples (either soil or solution) are to be analyzed so as 1) to maintain quality control throughout the sampling and analysis procedures for both types of samples, 2) to ensure that a representative sample of soil is collected from each soil column, and 3) to maintain accurate record keeping of all results, including data management and computations. Sections II, III, and IV pertain to soil sample preparation, while section V outlines solution sample preparations. The actual HPLC analysis and data management procedures as outlined in sections VI and VII should be applied to both types of samples. Since

these steps will take place in several different locations (i.e., Agricultural Engineering Laboratory, Plant and Soil Science Growth Chamber Laboratory, and Plant and Soil Science Laboratory), great care should be taken in the handling and transportation of these samples between the various locations. Additionally, due to the fact that hazardous chemicals are involved, extra safety considerations need to be observed. Protective clothing, including lab coat, goggles, gloves and dust/mist respirator should be worn at all times.

II. Soil Preparation:

2.1 Label the 128 appropriate solution bottles with lab tape to indicate which soil columns are to be pulled for analysis.
- use green lab tape
- label only the bottles associated with the respective set of columns which pertain to the analysis time period (i.e., 30-, 60-, 120-, or 180-day time period)

2.2 Remove the doors from the air chambers.
- remove only one door at a time, pulling the necessary soil columns from behind it before moving on to the next door
- detach the door by unscrewing the five wing nuts securing it to the air chamber frame
- set the wing nuts aside for the time being

2.3 Stop the column by clamping off the siphon and vacuum tubes.
- use pinchcock clamps to clamp off both tubes connecting the solution bottle to the soil column

2.4 Remove all tubes from the soil column.
- detach the ends of the tubes from the column fittings
- immediately place your finger over the bottom fitting to prevent any excess solution from running out of the fitting
- leave the tubes clamped off and attached to the solution bottle, letting them hang down inside the air chamber

2.5 Remove the soil column from the air chamber.
- carefully transport it to the lab bench where the scale is set up

2.6 Weigh and record the soil column weight.
- utilize the Sartorius IP65 kilogram scale
- first, with a permanent marker label an empty aluminum pan (half size cooking pan, 10.5" x 13" x 3") with the appropriate column number
- then, place the empty aluminum pan on the scale and tare its weight
- leave the aluminum pan on the scale
- next, place the soil column in the aluminum pan and record the weight of the "wet" soil column

2.7 Remove the soil column (still in the aluminum pan) from the scale.
- place the column on the floor of the lab, out of the way

2.8 Replace the door on the air chamber.
- tighten all five wing nuts securing the door in place

2.9 Repeat steps 2.2 - 2.8 for all soil columns to be analyzed per time period (i.e., for 128 columns each time period).
- all 128 columns (for a time period), in their respective aluminum pans, should be lined up on the floor of the lab
- it will take almost a full day to pull all 128 columns out of the air chambers and weigh them, thus they may remain in this condition overnight

2.10 Remove ALL of the soil from the column, placing it in the aluminum pan.
- perform this task on the lab bench; thus, the columns and aluminum pans will have to be picked up from the floor and carried over to the lab bench
- utilize a plastic knife to help dig the soil out of the column
- use a different knife for each soil column so as not to cross-contaminate the soil samples; the knife can remain in each aluminum pan after being used to remove the soil from the column
- extra care should be taken so as not to spill any of the soil

2.11 Triple rinse the inside of the column with water.
- use the sink located next to the lab bench
- pour the water and any soil residue into the aluminum pan with the rest of the soil

2.12 Cut the soil clumps into pieces.
- using the plastic knife, chop and mix the soil until there are no large clumps

2.13 Place the aluminum pan (full of soil) back onto the lab floor.

2.14 Place the empty column on the lab floor, out of the way.

2.15 Repeat steps 2.7 - 2.11 for all soil columns.
- it will take about one full day to empty all 128 soil columns

2.16 Air dry the soil:
- using fans, blow air across the soil (in the aluminum pans) to facilitate drying
- may have to dry the soil for 3-4 days (soil should be completely air dry)
- may have to periodically stir and chop the soil with the plastic knives

2.17 While the soil is drying, re-pack the empty columns with more soil and return them to their proper locations within the air chambers.
- refer to S.O.P. # BKC-1 for procedures associated with the soil packing process

- also, the final solution bottle samples can be taken from the solution bottles while the soil is drying; refer to S.O.P. # BKC-6, section IV, for these procedures

2.18 Once the soil is completely air dry, screen it by passing ALL of the soil through a 2mm sieve.

- the screening process is to take place on the lab bench, thus requiring the movement of the aluminum soil pan from the floor to the lab bench
- screen only one soil sample at a time; once completely finished with it, move on to the next sample
- using a paraffin-lined paper cup, scoop about 1/3 of the soil from the aluminum pan and pour it into a plastic bag
  - great care should be taken to prevent cross-contamination of the soil sample, thus use a different paper cup for each sample
  - use the smaller sized plastic bags (10" x 16")
- fold the end of the bag over several times and lay the bag flat on the lab bench
  - remove as much air from the bag as possible
  - place a brick or other heavy object on the folded end of the bag
- using a rolling pin, crush the soil (in the bag) into fine particles
- pour the crushed soil out of the plastic bag into the sieve
  - use a No. 10 USA Standard Testing Sieve with 2mm openings
  - place a catch pan underneath the sieve
- any soil not passing through the sieve must be crushed further until all of it will pass through the sieve
- place the sieved soil into another plastic bag
  - use the larger sized plastic bags (12" x 18")
  - with a permanent marker, carefully label the bag with the soil sample number (written on the aluminum pan)
  - all of the soil sample from the aluminum pan will be contained in this larger plastic bag
- repeat the crushing/sieving process until all soil is removed from the aluminum pan and passed through the 2mm sieve
  - may have to use the plastic knife to scrape some of the soil residue out of the aluminum pan
- use a rubber band to close the plastic bag
- set the plastic bag aside on the lab floor
- dispose of the paper cup and plastic knife
- thoroughly clean the sieve and catch pan
  - wash them with warm water in the sink, using your hands to rub away any remaining soil residue
  - using an air hose, completely dry them

2.19 Repeat the process outlined in step 2.18 for each of the remaining soil samples.
- be sure to use separate paper cups, plastic knives, and plastic bags for each soil sample
- be sure to carefully label the plastic bags with the appropriate soil sample number
- it may take 4-5 days to sieve all 128 soil samples

2.20 Thoroughly mix the soil sample after it has been sieved.
- shake the bag containing the soil sample for several minutes
- this ensures that the soil is thoroughly mixed and a representative sub-sample can be pulled
- shake all of the bags in this manner

III. Soil Sub-Samples and Soil Moistures:

3.1 This section describes the procedures and required steps in pulling sub-samples of soil from the columns and determining the exact moisture content of the air dried soil. Sub-samples and soil moistures can only be obtained after the soil has been air dried, screened, and thoroughly mixed.

3.2 The process of pulling sub-samples and soil moisture samples is to take place on the lab bench, thus requiring the movement of the plastic bags containing the soil from the lab floor to the bench. Only work with one bag of soil at a time, completing the sub-sampling process before starting on the next bag.

3.3 Remove the rubber band securing the plastic bag.
- save the rubber bands for reuse

3.4 With a permanent marker, label a 6 oz. whirl-pack bag with the appropriate soil sample number.
- the sample number should be located on the large plastic bag containing the entire soil sample

3.5 Using a paraffin-lined paper cup, scoop soil out of the large plastic bag and pour it into the whirl-pack bag.
- completely fill the whirl-pack bag
- after filling, close the whirl-pack bag
- set the full whirl-pack bag aside for the time being

3.6 Collect the soil moisture sample:
- utilize the Mettler PM4000 scale, and record all weights to three decimal places
- label an aluminum weighing boat with the appropriate sample number by etching the sample number into the bottom of the pan with a ball point pen
- place the empty aluminum weighing boat on the scale, record its

weight, and then tare the scale
- using the same paper cup mentioned above, scoop a small amount of soil out of the plastic bag and pour it into the aluminum weighing boat
- record the weight of the soil as "wet soil weight"
- remove the full aluminum weighing boat from the scale and place it on an oven rack

3.7 Dispose of the paper cup.

3.8 Dump out all remaining soil in the large plastic bag into one of the rubber trash cans.
- there are two rubber trash cans, one containing the sandy soil and the other containing the silty soil
- all soil is to be saved in the cans for future use

3.9 Dispose of the plastic bag.

3.10 Repeat steps 3.2 - 3.9 for each and every soil sample.
- it will take 5-6 hours to complete all 128 soil samples

3.11 All whirl-pack bags containing the soil sub-samples can be placed in the freezer until needed for the extraction process at a later date.
- place them in the freezers located in the PSS Growth Chamber lab
- they will have to be transported to the Growth Chamber lab

3.12 All soil moisture samples are to be oven dried.
- utilize the ovens located in the Ag. Engineering Soils lab
- great care should be taken in transporting the samples so as not to spill any soil out of the pans
- the oven should be set at a temperature of 105°C (± 5°C)
- the samples should remain in the oven for 24 hours

3.13 Remove the samples from the oven after 24 hours.
- the samples will be hot, therefore use heat gloves

3.14 Re-weigh the oven dried samples.
- utilize the Mettler PM4000 scale and record all weights to three decimal places
- record these weights as "total oven dry weight"
- dispose of the soil and aluminum weighing boats

3.15 At a later date, this moisture data can be entered in a spreadsheet on the computer and the actual moisture content of the samples can be calculated.
- first, subtract the weight of the empty aluminum weighing boat from the "total oven dry weight" to obtain the "oven dry weight" of the soil itself
- then, compute the percent moisture content of the soil sample:

$$\% \ moisture = \left(\frac{wet-dry}{dry}\right)*100 \qquad (25)$$

IV. Soil Extraction:

4.1 Since analysis of the soil samples on the HPLC is to be performed on a block basis (i.e., samples analyzed in groups broken down on the basis of rep. # per time period), only the samples corresponding to one particular rep. from one specified time period are to be extracted at a time.
- for example, extract all 30-day, rep.#1 soil samples
- thus, each set of extractions will contain 32 soil samples
- the full extraction process takes 24 hours to complete, thus only one set of samples are to be extracted per day

4.2 Thaw the frozen soil sub-samples.
- remove the whirl-pack bags from the freezer
- remove only the samples corresponding to the particular set to be extracted
- transport them from the PSS Growth Chamber lab to the Ag. Engineering lab
- spread the whirl-pack bags across the lab bench
- allow them to thaw for 3-4 hours

4.3 Remove a smaller sub-sample of soil from the whirl-pack bag.
- these sub-samples are to be placed into 250mL Nalgene plastic bottles
- remove the cap from the Nalgene bottle
- place a strip of lab tape across the outside of the Nalgene bottle
- with a lab marker, label the bottle with the appropriate sample number
    - mark on the tape, not the bottle itself
- place the empty bottle on the Mettler PM4000 scale and tare its weight
- open the whirl-pack bag
- using a small metal spatula, carefully remove soil from the whirl-pack bag and place it into the Nalgene bottle
- for the 30- and 60-day samples:
    - place 40g (±0.05g) of soil into the bottle
- for the 120- and 180-day samples:
    - place 20g (±0.05g) of soil into the bottle
- check the amount of soil by weighing it (in the bottle) on the scale
- after obtaining the correct amount of soil, tightly replace the cap on the Nalgene bottle and set it aside

- close the whirl-pack bag and set it aside

4.4 Repeat step 4.3 for all samples to be extracted.
- between each use (i.e., between each different soil sample) wash the spatula with water and dry it with a paper towel in order to minimize the possibility of cross-contaminating the soil samples

4.5 Archive all of the whirl-pack bags containing the remaining soil sub-samples.
- place them in the freezers located in the PSS Growth Chamber lab
- they will have to be transported to the Growth Chamber lab
- these archived samples will be available for re-analysis purposes

4.6 Transport all of the sample bottles (containing the soil extraction sample) to the Weed Science lab in the PSS Building.
- the remaining extraction process and subsequent HPLC analysis will be performed in the Weed Science lab

4.7 Calibrate two Repipet dispensers, one for use with water and one for use with methanol
- weigh an empty beaker on the scale in the lab
- with the empty beaker remaining on the scale, tare the scale so that it is re-zeroed
- for the dispenser used with water, set the Repipete at 16mL
- dispense water from the Repipete into the empty beaker
- re-weigh the beaker
- divide the weight shown on the scale by the specific gravity of water (i.e., 1)
- this calculated value should be equal to the setting on the Repipete
- repeat this process for the methanol and its associated dispenser
- for the dispenser used with methanol, set the Repipete at 64mL
- the specific gravity of methanol is 0.792

4.8 Into the sample bottle containing the 40g (or 20g) sub-sample, add 80mL of methanol solution (i.e.- 80% MeOH, 20% H_2O).
- remove the caps from the sample bottles
- utilizing Repipet dispensers attached directly to the bottles of solvent
  - dispense 64mL of MeOH into the sample bottle
  - dispense 16mL of H_2O into the sample bottle
- tightly replace the caps on the sample bottles
- add these amounts of solvent to every sample bottle

4.9 Shake the sample bottles overnight.
- place all of the sample bottles on the reciprocating shaker in the lab
- use lab tape to secure the bottles in the shaker
- turn shaker on high (280 oscillations per minute) for a few minutes
- then, reduce the speed to low (180 oscillations per minute) and leave on overnight

- the samples must shake for a minimum of 16 hours

4.10 After running overnight, turn off shaker and remove bottles.

4.11 Place the sample bottles along the lab bench.
- allow the samples to settle for about 30 minutes

4.12 While the samples are settling, set up the filter procedure:
- set up the funnel stand
- place four plastic funnels in the stand
- label the 4mL auto-sampler vials accordingly
  - write the sample number directly on the vial with a permanent marker
- place one 4mL vial under each funnel
- wash hands with soap and water before handling the filter papers
- clean the filter paper tweezers with methanol
- place two #1 Whatman brand filter papers into each funnel (stagger the filters in the funnel)

4.13 Once the samples have settled, pour the solution out of the sample bottles, through the filter lined funnels, and into the 4mL vials.
- double check all labeling; make sure the sample number on the Nalgene bottle matches that on the 4mL auto-sampler vial
- only capable of filtering four samples at a time
- fill the funnel about 3/4 full, thus the vial will be filled to the rim
- after the vials are filled, immediately remove the filter papers with the tweezers so that the vials will not overflow; discard the filter papers in the waste basket
- place the caps tightly on the 4mL vials, and place them in the vial tray
- rinse the inside of each funnel with methanol between each sample, and dry with a Chem-wipe

4.14 After filtering all samples, place the sample vials (in the tray) in the freezer until needed for the actual HPLC analysis.
- refer to section VI of this S.O.P. for actual procedures in the HPLC analysis

4.15 Clean lab work area.
- store all materials and equipment back in their proper place
- some equipment will need to be thoroughly cleaned by the lab staff

V. Solution Sample Preparation:

5.1 Three types of solution samples will need to be prepared for analysis on the HPLC.
- solution samples collected from the tank mixes at various times (refer to S.O.P. #BKC-2, section V, for the actual procedure involved in collecting the samples)

- solution samples collected during the bottle filling process (refer to S.O.P. #BKC-3, section IV, for the actual procedure involved in collecting the samples)
- solution samples collected from the individual solution bottles at the end of each of the four run times (refer to S.O.P. #BKC-6, section IV, for the actual procedure involved in collecting the samples)

5.2 At this point, all solution samples will be contained in labeled 20mL scintillation vials.
- the following steps are to be followed for every sample

5.3 With a permanent marker, label a 4mL auto-sampler vial with the appropriate sample number.
- write the sample number directly on the 4mL auto-sampler vial

5.4 Remove the cap from the 4mL auto-sampler vial and place it on the lab bench.
- care should be taken so as not to contaminate the seal underneath the cap

5.5 Briefly shake the 20mL scintillation vial.

5.6 Remove the cap from the 20mL scintillation vial and place it on the lab bench.
- care should be taken so as not to contaminate the seal underneath the cap
- set the open 20mL scintillation vial on the lab bench

5.7 Using a pipette, dispense solution from the 20mL scintillation vial to the 4mL auto-sampler vial.
- utilize the Wheaton 5mL Adjustable Micropipette
- set the pipette to dispense 4mL
- place a new tip on the pipette for each separate solution sample
- discard the plastic pipette tip after each use

5.8 Tightly replace the caps on both the 20mL scintillation vial and the 4mL auto-sampler vial.

5.9 Return both vials to their respective trays.

5.10 Repeat steps 5.3 - 5.9 for each separate solution sample.

5.11 Store all sample vials in the refrigerator.
- the 20mL scintillation vial samples will remain archived for future reference if needed
- the 4mL auto-sampler vial samples will remain in the refrigerator until time for actual analysis on the HPLC

VI. <u>HPLC Check List</u>:

The following steps should be observed and followed each time the HPLC machine is to be used for sample analysis. If errors occur or the machine does not function properly, <u>do not</u> try to correct the problem yourself; get Todd

Willian or Dr. Tom Mueller to check out the situation and correct any problems.

6.1 Check the solvent bottle levels (water & acetonitrile); if the levels are low (< 1/3 bottle), add more solvent

6.2 Check for air bubbles in the lines; if any are found, report them to Todd and let him purge the lines

6.3 Check the amount of paper in the integrator (printer); if low, report it to Todd and let him add more paper

6.4 Check the fluid levels in the waste bottles; if they are high, replace them with empty waste bottles

6.5 Turn on all of the machines (except the integrator, it stays on all of the time)

6.6 Check the fluid level of the 30% aqueous Methanol (70% MeOH / 30% H_2O) solution bottle; if low, mix more and replace.

6.7 Integrator:

- Press the LIST button twice; it will print out the conditions it is using
- Type ID_CORWIN <return>; this tells it to label each page accordingly; will not have to enter an ID or the date/time unless the power fails; if the power fails, the integrator will notify you
- The run time for water samples is 15 min.
  - therefore, the integrator needs to be stopped at 12 min. so as to be ready for the next sample
  - to set this: press the TIME button, then type "12," and then press the STOP button
- The run time for soil samples is 30 min.
  - therefore, the integrator needs to be stopped at 27 min
  - set the integrator time for soil analysis in the same manner as described above.

6.8 Detector:

- The UV detector should always be set at 220 nm, which will be displayed on the screen; if it is not, report it to Todd and he can re-set it

6.9 Controller:

- For every sample, the controller runs at:
  A: 60% acetonitrile
  B: 40% water
- To change the flowrate:
  - press the ISOCRATIC button twice
  - press OPERATE GRADIENT button
  - select gradient #1 **(for water samples)**; press ENTER twice
  - select gradient #3 **(for soil samples)**; press ENTER twice

- Wait a few minutes for the controller to come up to operating pressure (around 1900 psi)

6.10 Autosampler:

- To purge the system (once flow has been initiated):
  - press PURGE PAGE
  - press START PURGE
  - after purging, press MAIN PAGE
  - purge the system while the controller comes up to pressure and also load the tray at this time
  - the standards should be loaded in the same tray position every time (place the standards in tray location #'s 1, 2, 7, 13, 19, 25, 31, 37, and 41)
  - place the actual sample vials in the remaining tray locations
- Open the door, insert the loaded tray, and then close the door
- The system is now ready to analyze the samples
  - press AUTO PAGE
    - enter the vials to be run; (the ENTER button allows you to move the curser across the screen)
    - #INJ will always be set at 1
    - INJ VOL will be set at 20µL
    - RUN TIME will be set at 15 (for **water** samples)
    - RUN TIME will be set at 30 (for **soil** samples)
    - press AUTO START to start the system running

6.11 After the system has finished running all of the samples:

- Remove the tray from the autosampler, and label the printouts
- In order to form feed the paper, press and hold both the SHIFT & ENTER buttons at the same time
- Try to tear the paper along the perforated page breaks
- Starting from the back of the paper stack, label the print-outs with the corresponding sample number (write the sample number next to the peaks; note that the data corresponding to each set of peaks is located below the peaks)

6.12 Special note:

If the machine has been shut off, run vial #1 first by itself, and then run all of the samples. Under this circumstance, the first sample always seems to be "jittery" and look incorrect. Therefore, by running one sample by itself, the problem is corrected before the remaining samples are run.

VII. Interpretation and Management of HPLC Results:

7.1 Remove the printed chromatographs from the integrator after the HPLC has analyzed all loaded samples.

- simultaneously press and hold the "SHIFT" and "ENTER" keys to form feed the paper through the integrator
- tear off the printed results and fold the paper

7.2 Immediately label the chromatographs.

- on the top sheet, indicate the group of samples corresponding to the chromatographs
- also on the top sheet, indicate 1) the date of analysis, 2) the date the chromatographs were labeled, 3) the date the chromatographs were recorded into the logbook and 4) the date the chromatograph data were entered on a spreadsheet in the computer
- next to each individual chromatograph, label the corresponding vial number (i.e., the sample number)
  - begin at the end of the output and work toward the front
  - ensure that each sample vial has a respective chromatograph associated with it

7.3 Observe the individual peaks associated with each individual chromatograph to make sure that they all look normal and nothing appears unusual.

7.4 Interpret each individual chromatograph and record the pertinent information into the logbook.

- seven pieces of information need to be recorded from each individual chromatograph:
  - the sample number
  - the retention times (RT) associated with the DMFM peak, the FLMT peak, and the ATRAZ peak
  - the areas (recorded on a times 1000 basis) associated with the DMFM peak, the FLMT peak, and the ATRAZ peak (i.e., AREA*1000)
- the RT's associated with each pertinent chemical can be found from the chromatograph associated with its respective standard (e.g., find the RT for DMFM by looking at the peak on the chromatograph for the DMFM standard vial)

7.5 Transfer the data recorded in the logbook to a spreadsheet on the computer.

- use a separate spreadsheet for each chemical
- in one section of the spreadsheet, enter the concentrations (ppb) of all the standards into one column and their respective chromatograph areas in an adjacent column
- utilize the spreadsheet software to perform regression analysis on these standards
  - set the independent variable equal the column of concentration values

- set the dependent variable equal to the column of respective areas
- set the y-intercept equal to zero

- in another section of the spreadsheet, enter the remaining sample numbers in one column and their respective chromatograph areas in an adjacent column
  - for soil samples, the respective soil moisture information (previously collected as outlined in section III of this S.O.P.) needs to be entered in adjacent columns

7.6 Utilize the following equations to calculate the actual concentrations of the samples:

- for solution samples, simply multiply the area (associated with the sample's peak) by the X-coefficient value generated from the regression analysis
  - this calculation yields the concentration of that particular chemical in the sample in terms of ng/mL (ppb)
- for soil samples, the process goes one step further
  - first, multiply the area by the X-coefficient value to yield a concentration in terms of ng/mL (ppb), exactly like the solution samples
  - however, because these are soil samples instead of solution samples, this concentration result must be amended to account for the extraction process, the soil moisture content, and the simple fact of dealing with soil samples instead of water samples; therefore, the following correction equation should be used:

$$\left[\frac{ng}{mL} * \left(80 + \left(40 * \left(\frac{\%moisture}{100}\right)\right)\right)\right] \div \left[40 * \left(1 - \left(\frac{\%moisture}{100}\right)\right)\right] \qquad (17)$$

where:

80 = the amount (mL) of MeOH used in the extraction process

40 = the amount (g) of soil sub-sample extracted

100 = used to transform the moisture content to a fractional basis

- note: in some cases, only 20g of soil sub-sample was extracted; in these cases be sure to make the proper correction in the above equation (simply change the 40 to a 20)
- the answer yielded from this equation represents the concentration of the chemical in the soil sample in terms of ng/g soil (ppb)

APPENDIX B

CONSTRUCTION DETAILS

Soil Column System

Column Assembly

The actual construction of the soil columns was done in stages because of the large number (512) to be built. This involved cutting the PVC pipe to the desired lengths (384 @ 25 cm [10 in.] and 128 @ 18 cm [7 in.]), and cutting and attaching the PVC bottom plates to the columns. The bottom plates were cut from the PVC sheets with a 11.43 cm [4½"] circular hole saw. Prior to being glued together (using PVC primer-cleaner and then PVC cement) the edges of both the pipe and the plates were deburred on a grinder to smooth the points of contact. After all of the columns had been assembled, and the cement given sufficient time to cure, each column was tested for leaks. An additional 7.62 cm [3"] PVC pipe base was added to the bottom of all the short 17.78 cm [7"] wicking columns. This was done in order to raise the top surface of the columns even with all of the tall 25.4 cm [10"] ones.

Fitting Installation

The fittings were installed in holes drilled (1.786 cm [$^{45}/_{64}$"] and tapped (1.27 cm [½"]-14 NPT threads) in the side of each column. The holes were tapped so that the fittings could easily be screwed into the columns and to get a better seal After the screen and fittings were installed, silicone was applied around the edge of each fitting to help seal the fittings to the pipe. Finally, after all fittings were installed and sealed, each column was tested with water for leaks. Column construction was completed by labeling each column for easy reference and tracking. A piece of lab tape was placed on each column and they were numbered from #1 - #512. Figure B-1 may be seen for a schematic of the columns.

Solution Bottle Components and Assembly

Preparation of the glass tubing involved not only cutting to the desired lengths, but also polishing both ends to smooth the jagged sharp edges. The exact quantity and lengths needed were as follows:

- 512 @ 24 cm [9½ in.] long; for all siphon tubes;
- 1536 @ 9 cm [3½ in.] long; for all vacuum, vent, and funnel tubes.

In order to assemble the solution containers, four 0.635 cm [¼"] holes were drilled in the rubber stoppers to accommodate the glass tubes. The glass tubes were then cut and inserted into the stoppers. The stopper assembly was placed on the bottles just prior to beginning the experiment, and secured/sealed in place with a bead of silicon sealant.

This completed the construction of the soil columns except for connecting the vinyl tubing from the solution containers to the soil columns. Since each solution bottle needed to be placed above its respective soil column, the exact length of tubing was dependent upon the air chambers relative to the height associated in setting the bottles above the columns. Also, consideration had to be given to the varying sizes of the columns (for the short 18 cm [7 in.] and the tall 25 cm [10 in.] columns) and the location of the fittings within each type of column. Thus, by setting the bottles at an elevated height of approximately 33 cm [13 in.] above the bottom of the columns, the following lengths and quantities of tubing were needed for the 512 soil column systems: 384 pieces of tubing @ 70 cm [27½ in.] long, 128 pieces @ 66 cm [26 in.], 512 pieces @ 58 cm [23 in.], and 1024

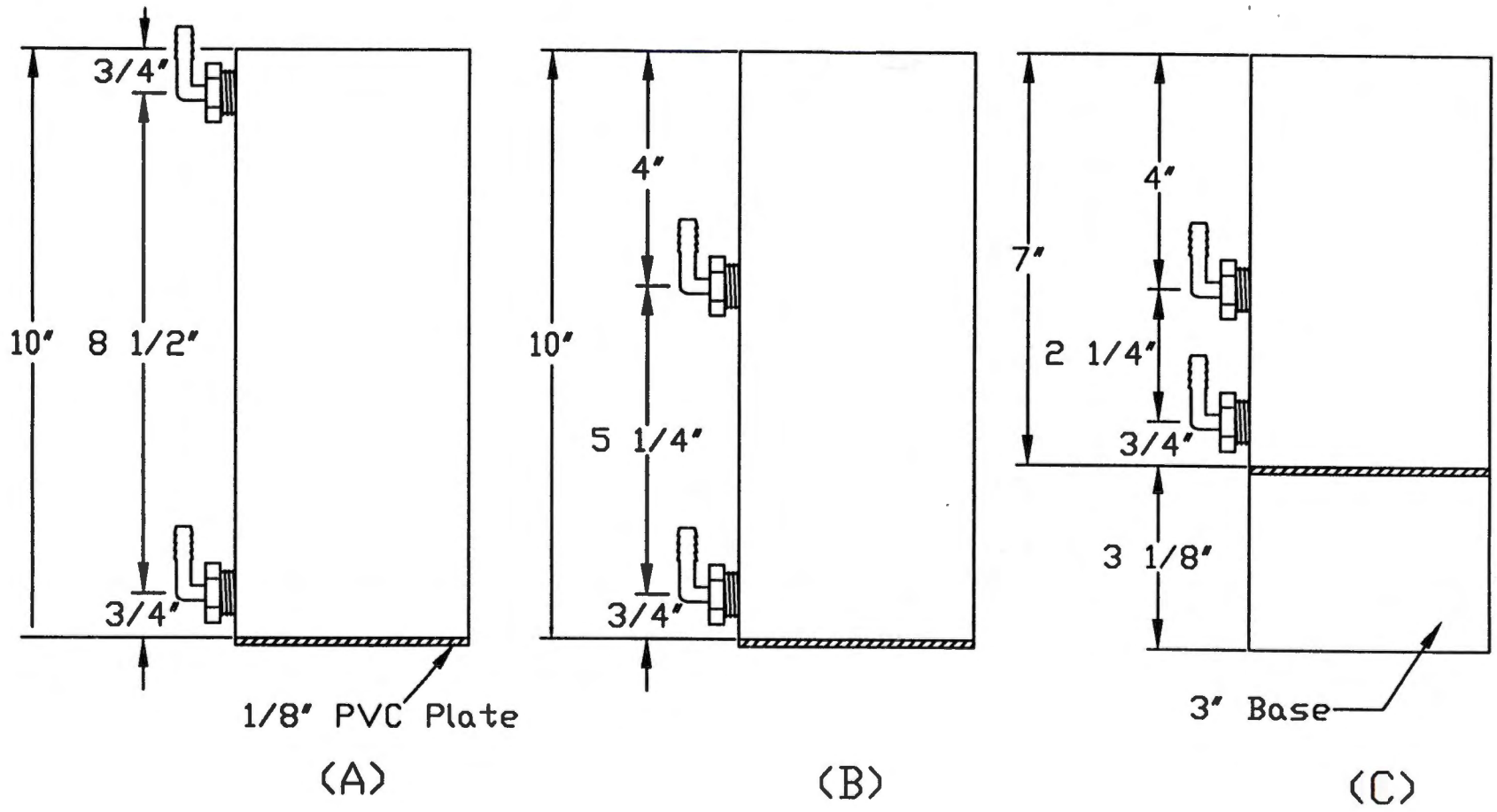


Figure B-1. Detail drawing showing column dimensions and fitting locations. Column (A) is a flood/dry column; column (B) is a 10"-wicking column; and column (C) is a 7"-wicking column.

pieces @ 18 cm [7¼in.]. They were connected as follows:

- 70 cm [27½ in.] siphon tube for the 256 flooded columns and for the 128 25 cm [10 in.] wicking columns;
- 66 cm [26 in.] siphon tube for the 128 18 cm [7 in.] wicking columns;
- 58 cm [23 in.] vacuum tube for all 512 columns;
- two 18 cm [7¼ in.] access tubes for all 512 columns.

For installation, one end of the vinyl tubing was placed over the exposed end of the appropriate glass rod. Likewise, the other end of the tubing was easily inserted over the exposed end of the appropriate hose barb fitting in the side of the columns.

Chamber Construction

Structural Frame

Construction of the structural frame involved simple lumber materials. Each chamber was built in four complete, identical sections. These sections, measuring 1.2 m [4 ft.] in length, were bolted together to give a total chamber length of 4.88 m [16 ft.]. Such sectional building allowed for much easier construction. Each section measured approximately 40.64 cm [16"] wide x 246.38 cm [97" high] and was built out of 5.08 cm x 10.16 cm [2" x 4"] boards and 1.27 cm [½"] plywood. The 5.08 cm x 10.16 cm [2" x 4"] studs were ripped lengthwise and used for all structural framing members. All required pieces (i.e., every support member for all 16 chamber sections) were cut at the same time. This allowed for easy assembly with #10 x 3.81 cm [1½"] wood screws. All shelves and gusset plates were cut from 1.27 cm [½"] CDX plywood. Number 6 galvanized nails were used to attach all shelves to the frames. Gusset plates were screwed into place at every corner joint, providing structural reinforcement. After assembly of all 16 individual sections, four sections were placed end-to-end and bolted together with 0.635 cm x 11.43 cm [¼" x 4½"] long carriage bolts, thus creating one 4.88 m [16 ft.] long chamber. During this bolting together procedure, a bead of silicon was placed between the butted sections for enhanced sealing. All four complete chambers were assembled in this fashion. Additionally, cover plates were placed on the ends of the shelves to enclose the soil columns. These end plates were also constructed from 1.27 cm [½"] CDX plywood. To these end plates were attached the inlet and outlet airflow manifolds. Thus, 13.97 cm [5½"] diameter holes were cut out in the centers of the end plates. For the upper and lower shelves providing the enclosure for the columns, silicon was applied along every joint and crack for an airtight seal.

Doors

Due to the special requirements associated with the vinyl tubing connecting the bottles to the columns, the chamber doors received a lot of special consideration. The major concern dealt with being able to adequately control the loss of air around the vinyl tubing (since it had to penetrate through the shelf enclosure to connect the bottles to the columns). Also of concern was the need to easily raise or lower the solution bottles (from above to below the column, or vice versa), yet still provide for minimal air/heat loss. This goal was accomplished by modifying the upper and lower enclosure shelves to

accommodate the tubing.

Two 3.97 cm [1 $^{9}/_{16}$"] wide strips of 1.27 cm [½"] plywood were added along each shelf edge to extend it out flush with the framing studs. Then, two 0.992 cm [$^{25}/_{64}$"] diameter holes were drilled back-to-back along the outside edge of the shelf extension. These holes were placed such that they accommodated both vinyl tubes from one column/bottle set-up. Since each chamber section would contain eight columns per side per level, two shelf extensions were needed per sectional shelf (each extension could accommodate the tubing of four columns). Note also that these extensions were needed along both shelves above and below the columns.

Finally, 1.27 cm [½"] CDX plywood doors were bolted in place, fitting snugly against the framing studs and the shelf edges. A single door covered the length of one section, on one side and level. This required a total of 64 doors, each measuring 35.56 cm x 121.285 cm [14" x 47¾"]. The doors were hung via five 0.635 cm [¼"] - 20 x 7.62 cm [3"] long hanger bolts installed into the chamber frames. Holes were drilled into the doors such that they would slide over the bolts and be secured by 0.635 cm [¼"] wing nuts (in much the same way that the lid to the air cleaner of an automobile engine is attached to the carburetor). Additionally, 1.27 cm [½"] thick and 1.905 cm [¾"] wide foam weatherstripping was placed all around the inside edges of the door where they contacted either the shelf edges or framing structure. When the wing nuts were tightened, this foam sufficiently sealed the doors to the chambers and around the vinyl tubing.

Utilizing this design facilitated easy movement of the solution bottles from above the soil columns to below them for the flooding/drying (saturation) cycles. After removal of the wing nuts, the doors could be simply pulled off. Once exposed, the tubing could be "unlocked" from the shelves and the bottles moved (either raised above or lowered below the columns). After "re-locking" the tubing into the new shelf position, the doors could then be easily replaced. Thus, the chambers were only "open" for a very short amount of time. As an additional note, since only half of the soil columns were of the flood/dry-type, only 256 required cycling of the bottles. Thus, shelf tubing holes not in use were simply covered with a piece of duct tape to prevent air flow leakage. This design provided excellent control of air loss both from around the vinyl tubing and from the bottle cycling procedures.

Additional Chamber Notes

Since both the solution bottles and the soil columns were to be placed back-to-back on the chamber shelves, it was desired to separate them so as to help alleviate any concern of them touching or bumping into one another and possibly turning over. Dividers were placed along the center of each shelf, running the length of the chambers. For these dividers, 2.54 cm x 2.54 cm x 1.22 m [1" x 1" x 4'] long strips of wood were screwed along the center of each shelf. The columns and bottles from both sides of the chamber could then be butted up against the dividers without fear of touching and interfering with other columns/bottles. Additionally, a strand of wire cable (small diameter) was placed along the front of the solution bottles, again running the length of the entire chamber. Because the bottles were fairly light in weight when not full of solution, this cable

prevented them from tipping over and falling out of the chambers.

Chamber numbering scheme

The second numbering scheme involved the 128 column locations within each chamber. Recall that each chamber contained columns on two levels and on both sides. Thus, each side, per level, contained a total of 32 soil columns. Beginning at the air inlet end of the chamber along the northern side of the chamber, and at the upper level, the column locations were numbered in consecutive order from #1 - 32 down the length of the entire chamber. Wrapping around the end of the chamber, the number scheme continued along the upper level of the other side, consecutively from #33 - 64. This completed the number of all upper level locations (i.e., #1 - 64). Now, the numbering sequence resumed along the lower level of the chamber in the same fashion; beginning with #65 and ending with #128.

Individual locations within all four separate chambers were numbered in this fashion. However, to distinguish between-chamber locations, the separate chamber labels were added as a prefix to the location numbers (e.g., all column locations in the NORTH chamber begin with N). As an example, location #1 of the North chamber was actually identified as #N1; of the North-Central chamber as #NC1; of the South-Central chamber as #SC1; and of the South chamber as #S1. Thus, all 128 locations of each chamber were similarly numbered. This numbering scheme was relied upon heavily throughout the data collection phase of this study.

Airflow System Assembly

Blowers

After considerable preliminary calculations, testing and evaluation of several blowers, two particular blowers were purchased and installed. To generate the higher air flow rate, a high pressure direct drive blower was purchased. This blower was operated by a 3.73 KW [5 Hp], 200-230/460 3-phase motor and rated at 60.6 m^3/sec [2140 cfm @ 1" S.P. For generation of the lower air flows, a high volume direct drive blower was acquired. At 1725 rpm, , this 0.56 KW [¾ Hp], 115/230 volt, 60 Hz motor was rated at 28.32 m^3/sec [1000 cfm] @ 1¼" S.P. Although the large blower was equipped with radial, paddle-wheel-type blades, the smaller blower differed in that a squirrel cage-type wheel generated air movement.

Since each blower was required to operate two chambers, common sense dictated that each fan control side-by-side chambers. Thus, it was arbitrarily decided that the South and South-central chambers be declared high air flow chambers and controlled by the 3.73 KW [5 Hp] blower. Subsequently, this left the North and North-central chambers as the lower air flow rates chambers and controllable by the 0.56 KW [¾ Hp] blower. Fan mounting platforms were constructed out of lumber and placed on top of the chambers. The five Hp blower was mounted to a platform spanning the tops of the S and SC chambers. Likewise, the 0.56 KW [¾ Hp] blower was mounted above the N and NC chamber onto a platform spanning the two. Thus, the blowers actually set above and directly between their respective chambers.

Chamber Intake Manifold

Flanged collars were attached to the inlets of each chamber (i.e., enclosure end cover plates), one for the upper chamber level and one at the lower chamber level. These flanges came equipped with a foam gasket, enabling an air-tight seal. From these two collared flanges, flexible duct was extended horizontally a short distance; protruding from the upper and lower chamber levels these ducts were parallel to each other. After this short horizontal extension, the duct was curved upward and attached to a common tee, thus connecting the piping of chamber levels. More flexible duct was attached to the third branch of the tee. This duct extended up, vertically parallel to the end of the chamber, and finally curved around the top of the chamber and either attached to a heat box or left as an open inlet.

Chamber Exhaust (Blower Intake) Manifold

Since each blower controlled two side-by-side chambers, the exhaust ducts from these two chambers had to be connected together and attached to the blower inlet port. To accomplish this, the upper pieces of vertical flexible duct from each of the two chambers (i.e., the ducts extending upward from the tee connecting the chamber levels) were curved inward toward one another, and connected to a common tee at the blower elevation level (thus, connecting the conduit of the two chambers). Finally, from this common tee, flexible duct was extended directly into the blower intake port. Both blower intake systems were assembled in this fashion. Reducers or expansions were used as needed to connect the flexible duct to the blower inlet ports. This was because the blower intake ports were of different diameters than the duct diameters. This was only a minor modification.

Blower Exhaust Conduit

In connecting the blower outlet ports to the existing ceiling exhaust fan duct required only one minor alteration to each blower. The geometry of the outlet ports for both fans was rectangular, while all other duct work was circular in shape. Thus, rectangular-to-circular transition pieces were required. A local sheet metal fabrication shop was contracted to construct these two pieces.

Manifold Modifications

The manifold diffusers added to the chamber's inlet duct were constructed from 24 ga. sheet metal arranged in a cross-type configuration with fins approximately 10.16 cm [4"] long. The edges of the fins were flared so as to be spot welded into place within the duct. They were placed toward the end of each duct extension, furthest from the actual chamber entrance. A conceptual view of the diffusers may be seen in Figure B-2.

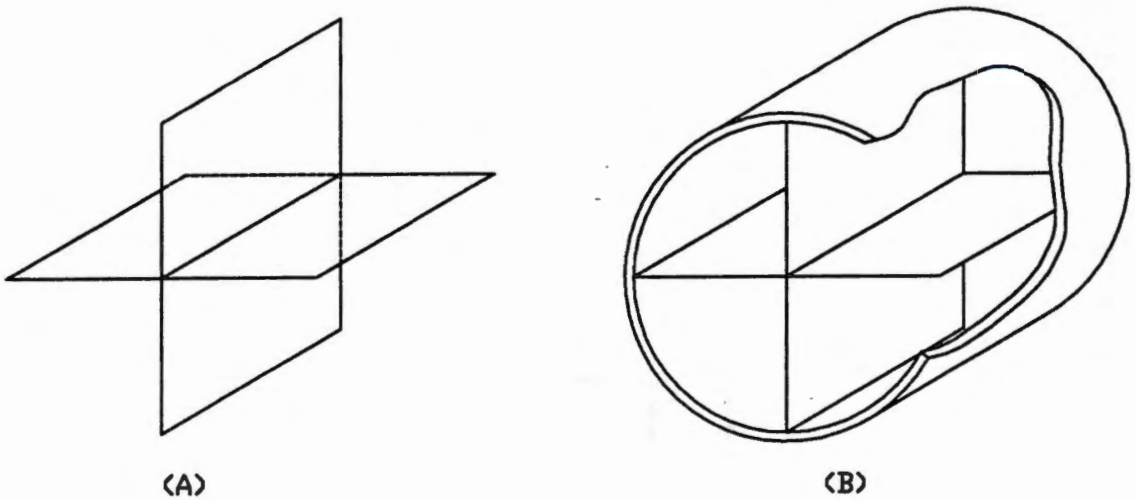


Figure B-2. (A): Conceptional drawing of diffuser fins. (B): Diffuser fin placed inside the inlet duct.

Heat Box

Construction and Installation

The heat boxes were constructed from 20 ga. sheet metal with a funnel-shaped geometry to facilitate better air flow from the inlet to the exit of the box. When assembled, the heat box measured 25.4 cm x 45. 09 cm [10" high x 17¾"] long, with the inlet end being 10.16 cm [16"] wide while the outlet end was reduced to 20.32 cm [8"] wide. In order to get the appropriate angle for the funnel shape, the sides of the heat box consisted of two appropriately bent pieces of sheet metal. The top and bottom pieces were flanged to fit snugly around the edge of the sides. The two sides and the top piece were all drilled and riveted together. The elements were centered within this metal box and placed side-by-side. When assembled, the elements were inverted and attached to the top of the heat boxes, thus hanging down. This was done so as to provide easy access to all wiring needed for the elements. A flanged collar and an expansion were riveted in place at the inlet and outlet ports, respectively.

Upon consultation with Wilkerson (1994), it was decided that some type of safety switch was needed to turn off the elements to prevent over heating in case the air flow stopped. To accomplish this, a thermal fuse was installed between the elements within each heat box. This safety switch was a Therm-O-Disc brand SPDT Fixed Temperature Snap-Disc Control rated at:

- CRCT #1 ⇒ close @ 49°C [120°F], open @ 60°C [140°F]
- CRCT #2 ⇒ close @ 60°C [140°F], open @ 49°C [120°F]

• 25 amps

It was wired such that the circuit would be open at the higher temperature (CRCT #1). Thus, if the temperature inside the box reaches 60°C [140°F], the control opens, breaking the circuit and shutting off electricity to the elements. Figure B-3 displays a simple electrical schematic of the operation of the safety switch.

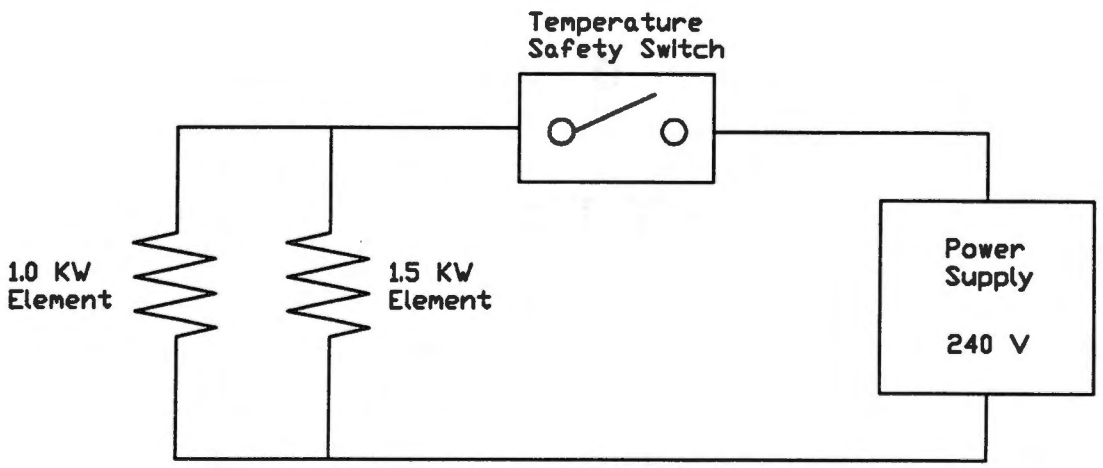


Figure B-3. Electrical schematic of heat box wiring.

The final assembly of the heat boxes involved mounting them on the appropriate chambers. The bottom plates of the heat boxes were attached directly to lumber mounting platforms secured on top of the necessary chambers. The heat box was then inverted and placed inside the bottom plate and secured via sheet metal screws. Thus, the element and safety switch leads were easily accessible on top of the heat box. Finally, the chamber inlet manifold duct was attached to the box's flanged exit collar with duct tape. Figure B-4 may be seen for a picture of a heat box.

Insulation

Another important consideration to the heat boxes and, in general, to the temperature integrity, centered around providing sufficient insulation to minimize heat loss. In the original conceptual design of the heat boxes, they were to be double walled with spray foam insulation applied between them. However, upon further thought, it was decided that the easiest insulation method would be to wrap material around the outside of the boxes. This greatly reduced the complexity and amount of work required in the

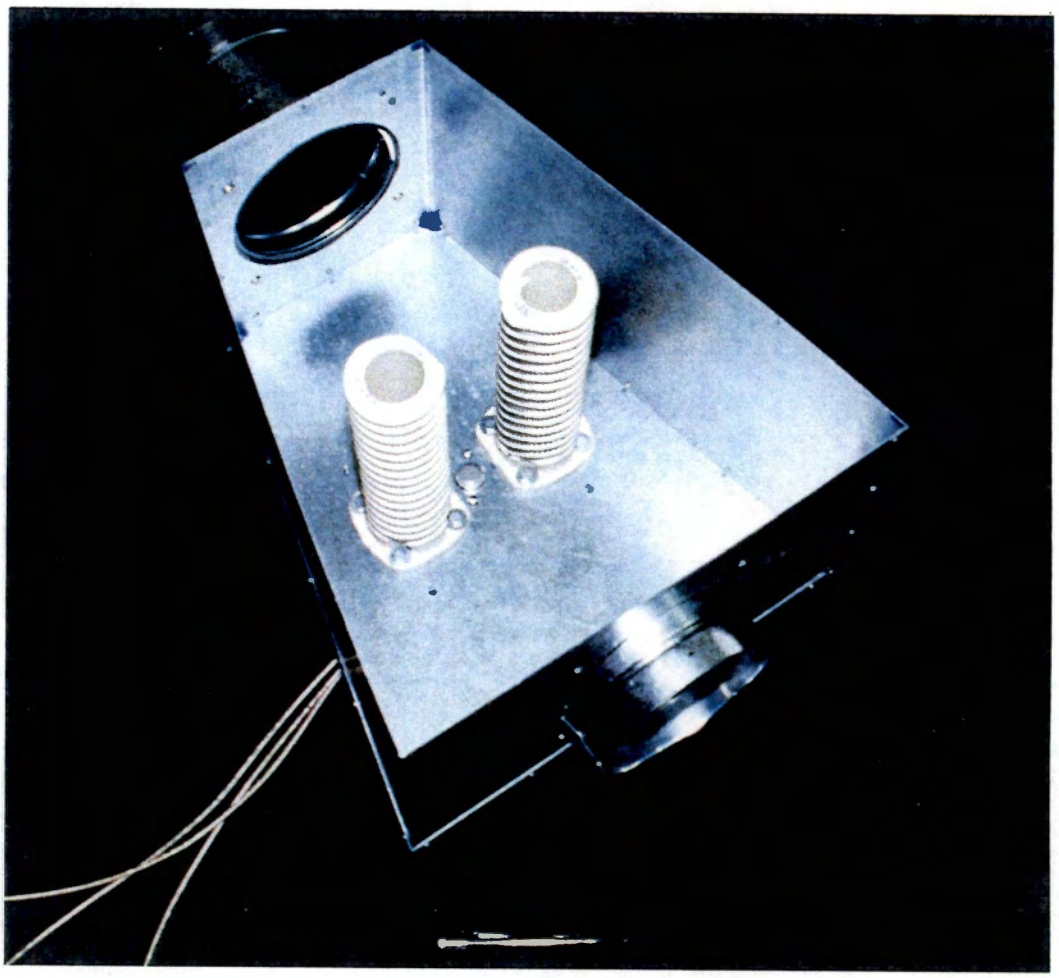


Figure B-4. Photograph of a heat box illustrating the placement of the heating elements and the thermal fuse (located between the elements).

construction of the boxes. In choosing an insulation material, several qualities were desired: 1) it had to provide sufficient heat retention at the expected operating temperature range of 49-54°C [120-130°F], 2) it had to be easily applied to the outside of the boxes, 3) for safety purposes, it should insulate enough so the outside is not hot to the touch, and 4) it had to be economical.

The actual insulation sheathing material used was 1.27 cm [½"] thick semi-rigid polyisocyanurate foam board insulation with an aluminum foil face on both sides. The ASHRAE Handbook (1981) rates polyisocyanurate with an R-value equal to 7.04 per inch of thickness. As described by MWPS (1987), the resistance of a material to heat flow is indicated by its R-value; with good insulators having high R-values. Although not specifically listed in the ASHRAE Handbook (1981), it was assumed that polyisocyanurate had a similar "accepted maximum temperature for use" rating as other similar rigid board insulators, which would be very acceptable for our use.

Since this insulation sheathing was only 1.27 cm [½"] thick, two layers were applied around the outside of the heat boxes. Individual panels of insulation board were cut to fit the dimensions of the heat boxes. All joints were sealed together using 7.62 cm [3"] wide foil tape and the panel edges were offset to achieve maximum heat retention.

Another insulation consideration involved potential heat loss from the airflow manifold ducts. To minimize this, insulation was wrapped around the ducts leading from the heat boxes to the actual entrance into the chambers. Standard flexible duct insulation, 3.81 cm thick x 60.96 cm wide [1½" thick x 24" wide] with reinforced foil liner on one side, was cut to the desired length and secured around the manifold conduit with duct tape. Neither the material composition, or the R-value was known for this particular insulation, but, the MWPS (1987) indicates that most batt or blanket insulation of this type consists of either fiberglass, mineral wool, or cellulose fiber material with a general R-value equal to 3.0-3.8 per inch of thickness.

Chamber Electrical Considerations

Only four aspects of the air chamber apparatus required the use of electricity: the two blower motors and the two heat boxes. For safety reasons and to allow for easy access and control, all electrical components were wired into a common breaker box. The breaker box itself controlled the heating elements of both heat boxes and the smaller blower (i.e., 0.56 KW[¾ Hp] motor controlling the N and NC chambers). Thus, the breaker box had to support both 110 and 220 volts. Provisions were also made so that the breaker box could support several extra outlets. An individual switch box was mounted next to the breaker box to accommodate the special needs of the 3-phase 3.73 KW [5 Hp] blower motor (controlling both the S and SC chambers).

To supply the switch box and the breaker box, electrical cable was run from the overhead power distribution system located in the laboratory building. Each electrical box was thus supplied by a separate power source to accommodate their respective special needs. Leaving the breaker box, 12 gage wire was run along the top of the chamber frames to the respective appliance. For the small blower, an electrical plug-type outlet box

was used so that the fan could be easily plugged in and unplugged. An electrical junction box placed next to each heat box housed the wiring connections between the Romex supply cable and the heating element wire leads. For the larger blower, six gage electrical cable was wired directly into the motor from the control switch box.

Pesticide Mixing System

Tank Stand

The basic framework of the tank stand consisted of 2.54 cm x 1.27 cm [1" x ½"] square steel tubing welded vertically onto a 7.62 cm x 1.27 cm [3" x ½"] steel channel base. This tripod stand was equipped with a support cradle assembled from a 0.635 cm [¼"] thick steel base plate and 3.81 cm x 0.3175 cm [1½" x ⅛"] flat steel. The saddle straps were fashioned in such a manner so as to allow sturdy vertical upright positioning of the conical tank.

Plumbing components

The pump and tank were plumbed separately. While the pump inlet port was fitted with a quick disconnect fitting and an in-line strainer, the outlet pump port was plumbed with a pressure regulator valve, glycerine filled pressure gage, manual ball valve, and quick disconnect fitting. At the tank drain outlet a manual ball valve and another quick disconnect fitting were installed. A second in-line strainer was placed in the pressure hose to help trap and disintegrate any undissolved chemical particles. Into this stainer housing was inserted a 200 mesh filter, while a 100 mesh filter was placed in the strainer on the suction side of the pump inlet. The quick disconnect couples attached to the hoses, tank and fluid delivery system simplified fluid circuit changes. A photograph of the mixing system can be seen in Figure B-5.

Miscellaneous set-up notes

Air Pressure Manifold

The air supply manifold system consisted of a pressure regulating valve (with pressure gage), an air/water separator, three hose quick-disconnects and enough tees, elbows, and nipples to connect these pieces. All plumbing components were 0.635 cm [¼"] in size and either steel or brass. The manifold was assembled in such a manner as to be directly hooked to a wall air line outlet. This manifold system thus provided the capability to "throttle-back" the air pressure as desired, and to supply up to three air lines.

The air hoses used with this manifold system required minor modifications. A trigger valve was attached via quick-disconnect unions to the outlet end of the air hose. A 0.635 cm [¼"] hose barb fitting was then installed into the end of the trigger valve. This allowed for the fitting to be placed in one of the bottle access tubes for easy pressurization.

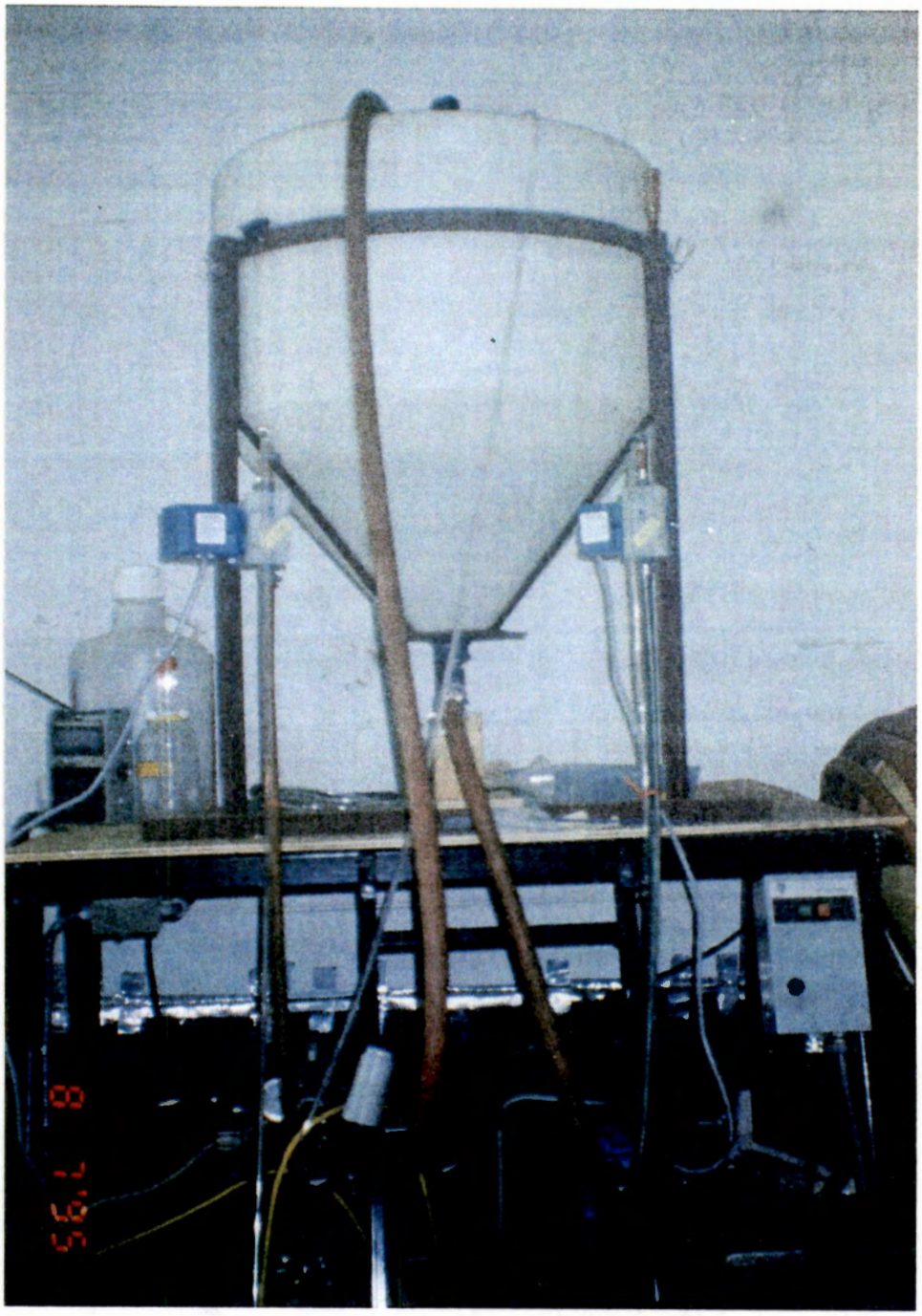


Figure B-5. Photograph of the herbicide mixing system illustrating the 80 gal. conical tank, the tank stand, and the plumbing hardware connecting to the centrifugal pump (underneath the tank). Note the two metering pumps (blue) mounted on the tank stand.

APPENDIX C:

COMPUTER PROGRAMS

Program #1: Interpolation of input solution concentration from bottle filling volumes.

```
#include    <stdio.h>
#include    <fcntl.h>   /* for O_RDONLY, etc */
#include    <string.h>  /* for strcpy()... */
#include    <ctype.h>   /* for iscntl(), isupper(), etc */
#include    <math.h>

void        ReadJunk(numLines, fpIn)
int         numLines;
FILE        *fpIn;
{
            int         jnkLines;
            char        jnk[250];
            for (jnkLines = 0; jnkLines < numLines; jnkLines++) {
                        fGetLine(fpIn, jnk, 250);
            }
}
void        WriteJunk(numLines, fpOut)
int         numLines;
FILE        *fpOut;
{
            int         jnkLines;
            for (jnkLines = 0; jnkLines < numLines; jnkLines++) {
                        fprintf(fpOut, "\n");
            }
}
int         fGetLine(fp, string, length_limit)
FILE        *fp;
char        string[];
int         length_limit;
{
            int
                        fields = 0,
                        in_field = 0,
                        c,
                        i = 0;

            while (--length_limit > 0 && (c = fgetc(fp)) != EOF && c != '\n') {
                        if (c == ' ' || c == '\t' || c == ',') {
                                    in_field = 0;
                        } else {
                                    if (in_field == 0) {
                                                fields++;
                                                in_field = 1;
                                    }
                        }
                        string[i++] = c;
            }

            if (length_limit == 0 || c == EOF)
                        return(-1);
            else
                        return(fields);

}
main()
{
            int         i;
            int         iNet = 0;
            int         colFillOrder[512];
            int         calFillOrder[50];
            int         numCalValues;
            int         numLoops = 4;
            int         loops;
            FILE        *fpIn, *fpOut;
```

```
	float	colVol[512];
	float	colFlmtConc[512];
	float	colAtrConc[512];
	float	calFlmtConc[50];
	float	calAtrConc[50];

	for (i = 0; i < 512; i++) {
		colFillOrder[i] = 0;
		colFlmtConc[i] = colAtrConc[i] = 0.0;
	}
	for (i = 0; i < 50; i++) {
		calFillOrder[i] = 0;
		calFlmtConc[i] = calAtrConc[i] = 0.0;
	}
	if ((fpIn = fopen("in.txt", "r")) == NULL) {
		printf("ERROR:  can't read in.txt");
		exit();
	}
	if ((fpOut = fopen("out.txt", "w")) == NULL) {
		printf("ERROR:  can't open out.txt");
		exit();
	}
	for (loops = 0; loops < numLoops; loops++) {
		int	jnkLines;
		if (loops == 0) jnkLines = 3;
		else jnkLines = 5;
		ReadJunk(jnkLines, fpIn); /* header lines */
		for (i = 0; i < 128; i++) {
			char	inLine[250];
			char	jnk[10];
			int	iDum1, iDum2;
			int	fields;
			float	fDum1, fDum2;
			fields = fGetLine(fpIn, inLine, 250);
			if (fields == 5) {
				sscanf(inLine, "%s\t%d\t%d\t%d\t%f", jnk, &colFillOrder[iNet], &iDum1, &iDum2,
&colVol[iNet]);
			} else {
				sscanf(inLine, "%s\t%d\t%d\t%d\t%f\t%f", jnk, &colFillOrder[iNet], &iDum1, &iDum2,
&fDum1, &colVol[iNet]);
			}
			iNet++;
		}
	}
	ReadJunk(3, fpIn);
	i = 0;
	while ((fscanf(fpIn, " %d\t%f\t%f", &calFillOrder[i], &calFlmtConc[i],
			&calAtrConc[i])) != EOF) i++;
	numCalValues = i;
	for (i = 1; i < numCalValues; i++) {
		int	lowCalNum = calFillOrder[i - 1];
		int	highCalNum = calFillOrder[i];
		int	j;
		float	sumVol = 0.0;
		float	flmtSlope;
		float	atrSlope;
		for (j = 0; j < 512; j++) {
			int	k = colFillOrder[j];
			if ((k >= lowCalNum) && (k < highCalNum)) {
				sumVol += colVol[j];
			}
		}
		if (sumVol > 0.0001) {
			flmtSlope = (calFlmtConc[i - 1] - calFlmtConc[i]) /
					sumVol;
			atrSlope = (calAtrConc[i - 1] - calAtrConc[i]) / sumVol;
```

```
                } else {
                        flmtSlope = 0.0;
                        atrSlope = 0.0;
                }
                sumVol = 0.0;
                for (j = lowCalNum; j < highCalNum; j++) {
                        int     k = 0;
                        while ((colFillOrder[k] != j) &&
                                (k < 512)) k++;
                        if (k == 512) {
                                printf("problem: searching for column 512\n");
                                exit(1);
                        }
                        colAtrConc[k] = calAtrConc[i - 1] - (atrSlope *
                                        (sumVol + (colVol[k] / 2.0)));
                        colFlmtConc[k] = calFlmtConc[i - 1] - (flmtSlope *
                                        (sumVol + (colVol[k] / 2.0)));
                        sumVol += colVol[k];
                }
        }
        iNet = 0;
        WriteJunk(3, fpOut); /* header lines */
        for (i = 0; i < 128; i++) { /* NORTH CHAMBER */
                fprintf(fpOut, "%f %f\n", colFlmtConc[iNet], colAtrConc[iNet]);
                iNet++;
        }
        WriteJunk(5, fpOut);
        for (i = 0; i < 128; i++) { /* NORTH CENTRAL CHAMBER */
                fprintf(fpOut, "%f %f\n", colFlmtConc[iNet], colAtrConc[iNet]);
                iNet++;
        }
        WriteJunk(5, fpOut);
        for (i = 0; i < 128; i++) { /* SOUTH CENTRAL CHAMBER */
                fprintf(fpOut, "%f %f\n", colFlmtConc[iNet], colAtrConc[iNet]);
                iNet++;
        }
        WriteJunk(5, fpOut);
        for (i = 0; i < 128; i++) { /* SOUTH CHAMBER */
                fprintf(fpOut, "%f %f\n", colFlmtConc[iNet], colAtrConc[iNet]);
                iNet++;
        }
        fclose(fpIn);
        fclose(fpOut);
}
```

Program #2: SAS® program used to analyze data sets; check for normal distribution.

```
options  ls = 72   ps = 60;

data pesticid;
    infile 'a:\result6b.txt';
        input column $ chamber $ airflow $ temp $ applic $ soil $
            time rep evap flmt atraz;
        levap = log(evap);
proc glm data = pesticid;
        class airflow temp applic soil time;
        model levap flmt atraz = airflow | temp | applic | soil | time;
        output out = rrr  r = revap rflmt ratraz;
        means airflow*temp*applic*soil*time;
proc univariate data = rrr plot normal;
        var revap rflmt ratraz;
run;
```

Program #3: SAS® program to analyze data sets; analysis of variance procedure.

```
options ls=72 ps=60;

data pesticid;
    infile 'a:\result6b.txt';
        input column $ chamber $ airflow $ temp $ applic $ soil $
            time rep evap flmt atraz;
        levap = log(evap);
proc glm data = pesticid;
        class airflow temp applic soil time;
        model levap flmt atraz = airflow | temp| applic | soil | time;
        lsmeans airflow | temp | applic | soil | time / s;
run;
```

APPENDIX D:

RAW DATA SET

Table D-1.Final raw data set; lists total volume of water evaporated and the overall percent degradation of each herbicide (of the amount applied).

Column #	Chamber	Airflow	Temp.	Applic.	Soil	Time	Reps	Total Water Evaporated Volume (ml)	Total % FLMT Degraded	Total % ATRAZ Degraded
1	SC	High	High	SFlood	Sandy	30	1	3120.61	13.45%	27.79%
2	SC	High	High	SFlood	Sandy	30	2	4352.60	17.16%	28.34%
3	SC	High	High	SFlood	Sandy	30	3	3727.67	23.46%	24.36%
4	SC	High	High	SFlood	Sandy	30	4	3391.33	17.23%	25.11%
5	NC	Low	Low	SFlood	Sandy	30	1	1922.38	25.44%	37.28%
6	NC	Low	Low	SFlood	Sandy	30	2	1910.12	22.02%	28.59%
7	NC	Low	Low	SFlood	Sandy	30	3	1680.19	27.75%	33.54%
8	NC	Low	Low	SFlood	Sandy	30	4	1495.18	31.16%	36.21%
9	S	High	Low	SFlood	Sandy	30	1	2107.82	25.03%	37.69%
10	S	High	Low	SFlood	Sandy	30	2	2273.79	18.19%	23.92%
11	S	High	Low	SFlood	Sandy	30	3	2017.01	33.92%	34.57%
12	S	High	Low	SFlood	Sandy	30	4	2155.18	23.15%	27.22%
13	N	Low	High	SFlood	Sandy	30	1	2797.48	27.06%	38.89%
14	N	Low	High	SFlood	Sandy	30	2	2091.50	20.56%	24.56%
15	N	Low	High	SFlood	Sandy	30	3	1595.39	13.90%	20.89%
16	N	Low	High	SFlood	Sandy	30	4	2415.62	21.66%	24.35%
17	S	High	Low	SFlood	Sandy	60	1	3557.20	32.78%	26.08%
18	S	High	Low	SFlood	Sandy	60	2	4783.54	20.83%	24.19%
19	S	High	Low	SFlood	Sandy	60	3	5592.68	25.79%	11.40%
20	S	High	Low	SFlood	Sandy	60	4	4649.41	20.40%	25.70%
21	SC	High	High	SFlood	Sandy	60	1	7294.07	16.75%	22.05%
22	SC	High	High	SFlood	Sandy	60	2	7772.50	12.78%	24.19%
23	SC	High	High	SFlood	Sandy	60	3	7525.99	35.85%	27.63%
24	SC	High	High	SFlood	Sandy	60	4	10842.47	43.26%	36.79%
25	N	Low	High	SFlood	Sandy	60	1	4818.66	34.57%	28.69%
26	N	Low	High	SFlood	Sandy	60	2	4625.26	23.68%	28.07%
27	N	Low	High	SFlood	Sandy	60	3	3958.65	36.26%	42.96%
28	N	Low	High	SFlood	Sandy	60	4	4170.52	38.05%	38.24%
29	NC	Low	Low	SFlood	Sandy	60	1	2754.38	18.01%	25.00%
30	NC	Low	Low	SFlood	Sandy	60	2	3393.57	35.07%	37.03%
31	NC	Low	Low	SFlood	Sandy	60	3	2414.49	23.67%	34.66%
32	NC	Low	Low	SFlood	Sandy	60	4	2366.03	35.32%	24.09%
33	NC	Low	Low	SFlood	Sandy	120	1	5892.69	48.08%	38.09%
34	NC	Low	Low	SFlood	Sandy	120	2	5524.49	33.95%	25.51%
35	NC	Low	Low	SFlood	Sandy	120	3	5718.07	33.29%	19.75%
36	NC	Low	Low	SFlood	Sandy	120	4	4803.44	57.90%	42.57%
37	SC	High	High	SFlood	Sandy	120	1	14908.92	48.49%	38.95%
38	SC	High	High	SFlood	Sandy	120	2	18363.06	61.64%	49.45%

Column #	Chamber	Airflow	Temp.	Applic.	Soil	Time	Reps	Total Water Evaporated Volume (ml)	Total % FLMT Degraded	Total % ATRAZ Degraded
39	SC	High	High	SFlood	Sandy	120	3	15487.83	65.99%	53.69%
40	SC	High	High	SFlood	Sandy	120	4	15432.81	35.77%	39.31%
41	S	High	Low	SFlood	Sandy	120	1	9860.42	49.52%	31.90%
42	S	High	Low	SFlood	Sandy	120	2	9185.44	44.38%	28.06%
43	S	High	Low	SFlood	Sandy	120	3	10304.13	42.40%	26.67%
44	S	High	Low	SFlood	Sandy	120	4	9934.44	47.88%	23.15%
45	N	Low	High	SFlood	Sandy	120	1	10654.75	51.49%	33.19%
46	N	Low	High	SFlood	Sandy	120	2	8626.85	54.13%	38.02%
47	N	Low	High	SFlood	Sandy	120	3	7865.44	38.42%	24.02%
48	N	Low	High	SFlood	Sandy	120	4	10941.16	36.81%	28.97%
49	NC	Low	Low	SFlood	Sandy	180	1	8790.77	53.09%	38.20%
50	NC	Low	Low	SFlood	Sandy	180	2	10876.43	67.75%	53.00%
51	NC	Low	Low	SFlood	Sandy	180	3	8969.94	52.08%	40.50%
52	NC	Low	Low	SFlood	Sandy	180	4	8942.98	57.12%	40.35%
53	SC	High	High	SFlood	Sandy	180	1	24730.02	70.40%	57.12%
54	SC	High	High	SFlood	Sandy	180	2	22559.05	59.51%	42.92%
55	SC	High	High	SFlood	Sandy	180	3	21033.64	58.98%	45.46%
56	SC	High	High	SFlood	Sandy	180	4	28206.75	68.71%	64.55%
57	N	Low	High	SFlood	Sandy	180	1	15332.30	61.58%	45.00%
58	N	Low	High	SFlood	Sandy	180	2	17583.97	61.39%	48.63%
59	N	Low	High	SFlood	Sandy	180	3	19828.49	63.16%	54.11%
60	N	Low	High	SFlood	Sandy	180	4	21909.54	53.90%	35.54%
61	S	High	Low	SFlood	Sandy	180	1	18296.27	53.88%	42.21%
62	S	High	Low	SFlood	Sandy	180	2	12189.50	40.49%	28.16%
63	S	High	Low	SFlood	Sandy	180	3	12030.00	54.05%	45.80%
64	S	High	Low	SFlood	Sandy	180	4	13154.91	58.33%	37.74%
65	SC	High	High	LFlood	Sandy	30	1	3049.87	24.64%	35.06%
66	SC	High	High	LFlood	Sandy	30	2	4284.45	18.12%	25.98%
67	SC	High	High	LFlood	Sandy	30	3	3098.36	22.13%	28.61%
68	SC	High	High	LFlood	Sandy	30	4	4750.49	17.19%	27.11%
69	NC	Low	Low	LFlood	Sandy	30	1	1945.28	26.48%	39.30%
70	NC	Low	Low	LFlood	Sandy	30	2	1410.06	25.70%	28.18%
71	NC	Low	Low	LFlood	Sandy	30	3	1598.09	22.25%	27.05%
72	NC	Low	Low	LFlood	Sandy	30	4	1554.89	21.53%	27.56%
73	S	High	Low	LFlood	Sandy	30	1	1985.98	19.25%	37.21%
74	S	High	Low	LFlood	Sandy	30	2	1841.44	12.26%	22.84%
75	S	High	Low	LFlood	Sandy	30	3	2987.75	22.80%	29.08%
76	S	High	Low	LFlood	Sandy	30	4	2455.99	19.35%	25.71%
77	N	Low	High	LFlood	Sandy	30	1	1917.14	26.25%	35.88%
78	N	Low	High	LFlood	Sandy	30	2	2064.33	19.96%	25.76%
79	N	Low	High	LFlood	Sandy	30	3	2121.08	11.42%	20.59%

Column #	Chamber	Airflow	Temp.	Applic.	Soil	Time	Reps	Total Water Evaporated Volume (ml)	Total % FLMT Degraded	Total % ATRAZ Degraded
80	N	Low	High	LFlood	Sandy	30	4	2028.35	20.40%	28.11%
81	S	High	Low	LFlood	Sandy	60	1	4826.20	19.97%	28.03%
82	S	High	Low	LFlood	Sandy	60	2	3555.07	23.28%	32.34%
83	S	High	Low	LFlood	Sandy	60	3	3990.63	23.14%	34.18%
84	S	High	Low	LFlood	Sandy	60	4	3398.30	40.49%	29.60%
85	SC	High	High	LFlood	Sandy	60	1	6108.99	30.11%	36.06%
86	SC	High	High	LFlood	Sandy	60	2	6562.86	28.88%	35.23%
87	SC	High	High	LFlood	Sandy	60	3	6530.77	15.45%	31.83%
88	SC	High	High	LFlood	Sandy	60	4	7001.95	25.19%	33.25%
89	N	Low	High	LFlood	Sandy	60	1	4412.39	40.62%	41.24%
90	N	Low	High	LFlood	Sandy	60	2	3959.40	17.62%	30.10%
91	N	Low	High	LFlood	Sandy	60	3	4367.81	29.88%	17.51%
92	N	Low	High	LFlood	Sandy	60	4	5183.72	23.91%	36.61%
93	NC	Low	Low	LFlood	Sandy	60	1	3098.37	5.55%	20.99%
94	NC	Low	Low	LFlood	Sandy	60	2	2565.85	7.91%	27.60%
95	NC	Low	Low	LFlood	Sandy	60	3	2967.13	13.41%	30.71%
96	NC	Low	Low	LFlood	Sandy	60	4	2337.22	25.25%	30.56%
97	NC	Low	Low	LFlood	Sandy	120	1	5345.61	32.54%	26.72%
98	NC	Low	Low	LFlood	Sandy	120	2	6060.29	40.07%	27.76%
99	NC	Low	Low	LFlood	Sandy	120	3	4692.89	66.76%	56.82%
100	NC	Low	Low	LFlood	Sandy	120	4	9232.11	47.93%	42.44%
101	SC	High	High	LFlood	Sandy	120	1	11084.36	51.21%	43.92%
102	SC	High	High	LFlood	Sandy	120	2	12532.13	44.63%	40.75%
103	SC	High	High	LFlood	Sandy	120	3	15846.23	58.28%	45.71%
104	SC	High	High	LFlood	Sandy	120	4	16347.89	48.12%	47.24%
105	S	High	Low	LFlood	Sandy	120	1	7533.61	49.19%	37.25%
106	S	High	Low	LFlood	Sandy	120	2	8904.18	36.83%	34.91%
107	S	High	Low	LFlood	Sandy	120	3	8330.70	52.91%	39.32%
108	S	High	Low	LFlood	Sandy	120	4	9123.96	47.88%	42.25%
109	N	Low	High	LFlood	Sandy	120	1	8959.83	54.72%	41.58%
110	N	Low	High	LFlood	Sandy	120	2	7721.92	51.06%	36.42%
111	N	Low	High	LFlood	Sandy	120	3	9352.97	51.40%	44.45%
112	N	Low	High	LFlood	Sandy	120	4	9670.33	66.55%	53.94%
113	NC	Low	Low	LFlood	Sandy	180	1	8348.82	59.44%	48.20%
114	NC	Low	Low	LFlood	Sandy	180	2	8207.26	58.63%	43.34%
115	NC	Low	Low	LFlood	Sandy	180	3	6748.82	44.64%	37.68%
116	NC	Low	Low	LFlood	Sandy	180	4	8541.78	49.64%	35.95%
117	SC	High	High	LFlood	Sandy	180	1	21823.28	73.69%	73.41%
118	SC	High	High	LFlood	Sandy	180	2	18989.80	73.90%	56.84%
119	SC	High	High	LFlood	Sandy	180	3	21410.99	67.18%	57.39%
120	SC	High	High	LFlood	Sandy	180	4	22386.26	70.48%	63.52%

Table D-1. Continued.

Column #	Chamber	Airflow	Temp.	Applic.	Soil	Time	Reps	Total Water Evaporated Volume (ml)	Total % FLMT Degraded	Total % ATRAZ Degraded
121	N	Low	High	LFlood	Sandy	180	1	15065.17	72.13%	59.10%
122	N	Low	High	LFlood	Sandy	180	2	13490.53	74.41%	60.76%
123	N	Low	High	LFlood	Sandy	180	3	13339.55	63.19%	47.54%
124	N	Low	High	LFlood	Sandy	180	4	12952.98	59.14%	47.75%
125	S	High	Low	LFlood	Sandy	180	1	13032.02	65.56%	54.50%
126	S	High	Low	LFlood	Sandy	180	2	11505.96	66.16%	46.20%
127	S	High	Low	LFlood	Sandy	180	3	11332.04	67.73%	49.41%
128	S	High	Low	LFlood	Sandy	180	4	12906.96	54.00%	41.16%
129	SC	High	High	LWick	Sandy	30	1	5136.56	13.43%	29.94%
130	SC	High	High	LWick	Sandy	30	2	4446.17	12.48%	23.62%
131	SC	High	High	LWick	Sandy	30	3	4219.01	15.63%	22.41%
132	SC	High	High	LWick	Sandy	30	4	4713.36	10.74%	20.60%
133	NC	Low	Low	LWick	Sandy	30	1	1825.54	21.03%	35.88%
134	NC	Low	Low	LWick	Sandy	30	2	1310.14	22.80%	29.98%
135	NC	Low	Low	LWick	Sandy	30	3	1502.94	23.79%	31.86%
136	NC	Low	Low	LWick	Sandy	30	4	1415.84	17.46%	27.90%
137	S	High	Low	LWick	Sandy	30	1	2617.34	16.09%	30.07%
138	S	High	Low	LWick	Sandy	30	2	2080.58	16.92%	25.63%
139	S	High	Low	LWick	Sandy	30	3	2009.96	21.77%	27.81%
140	S	High	Low	LWick	Sandy	30	4	1833.10	14.74%	25.43%
141	N	Low	High	LWick	Sandy	30	1	1800.18	16.61%	32.83%
142	N	Low	High	LWick	Sandy	30	2	3227.81	15.11%	26.65%
143	N	Low	High	LWick	Sandy	30	3	2513.98	21.89%	29.56%
144	N	Low	High	LWick	Sandy	30	4	1909.47	17.32%	27.67%
145	S	High	Low	LWick	Sandy	60	1	4528.50	13.22%	18.84%
146	S	High	Low	LWick	Sandy	60	2	5223.94	22.22%	29.68%
147	S	High	Low	LWick	Sandy	60	3	3645.77	14.22%	29.96%
148	S	High	Low	LWick	Sandy	60	4	3391.83	22.59%	27.88%
149	SC	High	High	LWick	Sandy	60	1	7304.76	14.09%	21.36%
150	SC	High	High	LWick	Sandy	60	2	8365.44	11.71%	22.34%
151	SC	High	High	LWick	Sandy	60	3	7286.51	29.31%	20.86%
152	SC	High	High	LWick	Sandy	60	4	11355.72	19.32%	23.30%
153	N	Low	High	LWick	Sandy	60	1	8457.26	29.44%	20.95%
154	N	Low	High	LWick	Sandy	60	2	3919.30	24.72%	33.55%
155	N	Low	High	LWick	Sandy	60	3	3822.66	45.37%	34.34%
156	N	Low	High	LWick	Sandy	60	4	5081.90	22.69%	14.91%
157	NC	Low	Low	LWick	Sandy	60	1	2806.18	22.44%	32.47%
158	NC	Low	Low	LWick	Sandy	60	2	2410.60	25.36%	29.69%
159	NC	Low	Low	LWick	Sandy	60	3	2731.18	16.69%	32.13%
160	NC	Low	Low	LWick	Sandy	60	4	3006.29	36.71%	23.77%
161	NC	Low	Low	LWick	Sandy	120	1	4540.65	45.68%	37.32%

Table D-1. Continued.

Column #	Chamber	Airflow	Temp.	Applic.	Soil	Time	Reps	Total Water Evaporated Volume (ml)	Total % FLMT Degraded	Total % ATRAZ Degraded
162	NC	Low	Low	LWick	Sandy	120	2	6158.51	47.67%	43.98%
163	NC	Low	Low	LWick	Sandy	120	3	4902.90	31.67%	26.54%
164	NC	Low	Low	LWick	Sandy	120	4	5373.44	32.46%	26.05%
165	SC	High	High	LWick	Sandy	120	1	19483.78	24.85%	12.65%
166	SC	High	High	LWick	Sandy	120	2	16419.13	33.80%	20.76%
167	SC	High	High	LWick	Sandy	120	3	14131.75	28.58%	17.16%
168	SC	High	High	LWick	Sandy	120	4	15476.30	25.10%	11.49%
169	S	High	Low	LWick	Sandy	120	1	7827.29	35.50%	24.54%
170	S	High	Low	LWick	Sandy	120	2	7759.69	41.28%	25.67%
171	S	High	Low	LWick	Sandy	120	3	9821.85	28.94%	24.39%
172	S	High	Low	LWick	Sandy	120	4	7343.32	28.83%	20.29%
173	N	Low	High	LWick	Sandy	120	1	8479.15	43.92%	33.06%
174	N	Low	High	LWick	Sandy	120	2	9230.92	41.89%	38.71%
175	N	Low	High	LWick	Sandy	120	3	6955.17	30.57%	22.04%
176	N	Low	High	LWick	Sandy	120	4	6438.32	42.18%	31.02%
177	NC	Low	Low	LWick	Sandy	180	1	8590.95	32.93%	26.21%
178	NC	Low	Low	LWick	Sandy	180	2	8122.16	41.94%	30.36%
179	NC	Low	Low	LWick	Sandy	180	3	7110.31	43.72%	33.69%
180	NC	Low	Low	LWick	Sandy	180	4	12486.22	48.87%	30.67%
181	SC	High	High	LWick	Sandy	180	1	21544.26	45.17%	27.74%
182	SC	High	High	LWick	Sandy	180	2	19709.98	53.66%	34.63%
183	SC	High	High	LWick	Sandy	180	3	19090.15	42.48%	27.97%
184	SC	High	High	LWick	Sandy	180	4	19494.48	48.86%	36.07%
185	N	Low	High	LWick	Sandy	180	1	12454.35	50.93%	33.77%
186	N	Low	High	LWick	Sandy	180	2	15643.05	86.75%	37.31%
187	N	Low	High	LWick	Sandy	180	3	11037.85	51.97%	38.93%
188	N	Low	High	LWick	Sandy	180	4	10203.36	48.85%	33.38%
189	S	High	Low	LWick	Sandy	180	1	16352.64	51.59%	35.25%
190	S	High	Low	LWick	Sandy	180	2	11797.15	39.24%	22.67%
191	S	High	Low	LWick	Sandy	180	3	11772.86	47.78%	34.73%
192	S	High	Low	LWick	Sandy	180	4	10643.16	42.66%	29.97%
193	SC	High	High	SWick	Sandy	30	1	3057.92	16.69%	32.64%
194	SC	High	High	SWick	Sandy	30	2	4077.69	25.72%	32.93%
195	SC	High	High	SWick	Sandy	30	3	3629.31	21.17%	28.37%
196	SC	High	High	SWick	Sandy	30	4	3513.48	27.79%	34.18%
197	NC	Low	Low	SWick	Sandy	30	1	1598.67	39.66%	46.81%
198	NC	Low	Low	SWick	Sandy	30	2	1779.89	20.87%	29.78%
199	NC	Low	Low	SWick	Sandy	30	3	1849.36	25.65%	28.66%
200	NC	Low	Low	SWick	Sandy	30	4	1969.77	20.57%	31.93%
201	S	High	Low	SWick	Sandy	30	1	2319.67	21.63%	34.96%
202	S	High	Low	SWick	Sandy	30	2	2118.99	23.41%	31.61%

Column #	Chamber	Airflow	Temp.	Applic.	Soil	Time	Reps	Total Water Evaporated Volume (ml)	Total % FLMT Degraded	Total % ATRAZ Degraded
203	S	High	Low	SWick	Sandy	30	3	1901.69	20.85%	28.89%
204	S	High	Low	SWick	Sandy	30	4	2322.17	20.83%	29.97%
205	N	Low	High	SWick	Sandy	30	1	3327.17	21.98%	35.77%
206	N	Low	High	SWick	Sandy	30	2	2294.99	26.89%	33.82%
207	N	Low	High	SWick	Sandy	30	3	1530.66	29.23%	33.82%
208	N	Low	High	SWick	Sandy	30	4	2351.16	20.10%	28.29%
209	S	High	Low	SWick	Sandy	60	1	3677.58	7.11%	19.56%
210	S	High	Low	SWick	Sandy	60	2	3573.38	18.87%	28.83%
211	S	High	Low	SWick	Sandy	60	3	5021.05	18.12%	31.78%
212	S	High	Low	SWick	Sandy	60	4	4284.14	14.07%	22.73%
213	SC	High	High	SWick	Sandy	60	1	7196.22	16.10%	23.47%
214	SC	High	High	SWick	Sandy	60	2	13566.10	44.17%	50.41%
215	SC	High	High	SWick	Sandy	60	3	7705.20	21.52%	32.91%
216	SC	High	High	SWick	Sandy	60	4	11020.87	15.21%	19.92%
217	N	Low	High	SWick	Sandy	60	1	4899.71	33.87%	36.53%
218	N	Low	High	SWick	Sandy	60	2	4186.70	25.10%	32.28%
219	N	Low	High	SWick	Sandy	60	3	4542.27	41.02%	26.65%
220	N	Low	High	SWick	Sandy	60	4	3282.52	28.34%	30.92%
221	NC	Low	Low	SWick	Sandy	60	1	2356.48	23.59%	32.08%
222	NC	Low	Low	SWick	Sandy	60	2	2881.85	23.47%	34.29%
223	NC	Low	Low	SWick	Sandy	60	3	2579.33	17.48%	36.36%
224	NC	Low	Low	SWick	Sandy	60	4	3750.52	32.78%	38.82%
225	NC	Low	Low	SWick	Sandy	120	1	6313.25	48.29%	39.53%
226	NC	Low	Low	SWick	Sandy	120	2	6001.03	52.85%	42.01%
227	NC	Low	Low	SWick	Sandy	120	3	5603.07	41.67%	35.36%
228	NC	Low	Low	SWick	Sandy	120	4	4844.55	50.57%	41.03%
229	SC	High	High	SWick	Sandy	120	1	14805.26	39.08%	25.57%
230	SC	High	High	SWick	Sandy	120	2	15782.37	50.23%	39.47%
231	SC	High	High	SWick	Sandy	120	3	12653.03	50.70%	40.02%
232	SC	High	High	SWick	Sandy	120	4	16771.22	54.66%	36.19%
233	S	High	Low	SWick	Sandy	120	1	10703.51	56.64%	44.10%
234	S	High	Low	SWick	Sandy	120	2	13352.44	47.08%	35.07%
235	S	High	Low	SWick	Sandy	120	3	9746.41	38.71%	29.65%
236	S	High	Low	SWick	Sandy	120	4	8726.58	38.22%	21.08%
237	N	Low	High	SWick	Sandy	120	1	10089.88	44.92%	28.32%
238	N	Low	High	SWick	Sandy	120	2	13362.72	49.86%	30.43%
239	N	Low	High	SWick	Sandy	120	3	8139.55	51.59%	38.49%
240	N	Low	High	SWick	Sandy	120	4	7895.23	40.92%	32.72%
241	NC	Low	Low	SWick	Sandy	180	1	10050.52	42.60%	31.20%
242	NC	Low	Low	SWick	Sandy	180	2	8931.87	41.64%	31.98%
243	NC	Low	Low	SWick	Sandy	180	3	9311.97	48.60%	36.67%

Column #	Chamber	Airflow	Temp.	Applic.	Soil	Time	Reps	Total Water Evaporated Volume (ml)	Total % FLMT Degraded	Total % ATRAZ Degraded
244	NC	Low	Low	SWick	Sandy	180	4	9002.31	47.86%	31.19%
245	SC	High	High	SWick	Sandy	180	1	22863.51	46.52%	32.21%
246	SC	High	High	SWick	Sandy	180	2	21678.64	39.15%	19.01%
247	SC	High	High	SWick	Sandy	180	3	23598.91	53.55%	33.42%
248	SC	High	High	SWick	Sandy	180	4	25393.73	59.31%	38.62%
249	N	Low	High	SWick	Sandy	180	1	18247.84	58.66%	38.53%
250	N	Low	High	SWick	Sandy	180	2	11730.38	54.14%	44.29%
251	N	Low	High	SWick	Sandy	180	3	12794.22	51.81%	41.47%
252	N	Low	High	SWick	Sandy	180	4	12858.81	46.07%	32.97%
253	S	High	Low	SWick	Sandy	180	1	15185.04	51.71%	38.13%
254	S	High	Low	SWick	Sandy	180	2	10648.82	58.28%	49.40%
255	S	High	Low	SWick	Sandy	180	3	12352.03	49.79%	35.35%
256	S	High	Low	SWick	Sandy	180	4	11007.70	49.31%	35.06%
257	SC	High	High	SFlood	Silty	30	1	3502.12	33.80%	74.75%
258	SC	High	High	SFlood	Silty	30	2	4468.19	32.05%	74.12%
259	SC	High	High	SFlood	Silty	30	3	3219.85	27.81%	64.50%
260	SC	High	High	SFlood	Silty	30	4	3684.98	28.13%	65.73%
261	NC	Low	Low	SFlood	Silty	30	1	1311.42	28.80%	63.05%
262	NC	Low	Low	SFlood	Silty	30	2	1607.79	28.65%	62.09%
263	NC	Low	Low	SFlood	Silty	30	3	1480.72	29.14%	59.55%
264	NC	Low	Low	SFlood	Silty	30	4	1339.96	23.11%	58.28%
265	S	High	Low	SFlood	Silty	30	1	2670.52	22.20%	57.25%
266	S	High	Low	SFlood	Silty	30	2	2000.12	23.39%	57.28%
267	S	High	Low	SFlood	Silty	30	3	3342.90	21.44%	52.05%
268	S	High	Low	SFlood	Silty	30	4	1815.64	16.87%	51.83%
269	N	Low	High	SFlood	Silty	30	1	2046.57	29.42%	65.93%
270	N	Low	High	SFlood	Silty	30	2	1517.42	26.75%	60.59%
271	N	Low	High	SFlood	Silty	30	3	2371.54	27.67%	64.00%
272	N	Low	High	SFlood	Silty	30	4	2033.86	28.96%	65.69%
273	S	High	Low	SFlood	Silty	60	1	3538.14	27.21%	69.02%
274	S	High	Low	SFlood	Silty	60	2	3687.50	31.40%	67.20%
275	S	High	Low	SFlood	Silty	60	3	4416.00	21.82%	68.79%
276	S	High	Low	SFlood	Silty	60	4	4420.97	27.11%	69.03%
277	SC	High	High	SFlood	Silty	60	1	8100.68	40.21%	82.96%
278	SC	High	High	SFlood	Silty	60	2	7566.82	28.34%	79.98%
279	SC	High	High	SFlood	Silty	60	3	6861.03	28.58%	82.84%
280	SC	High	High	SFlood	Silty	60	4	6579.12	27.97%	78.94%
281	N	Low	High	SFlood	Silty	60	1	3414.11	29.48%	75.07%
282	N	Low	High	SFlood	Silty	60	2	4684.12	34.06%	79.93%
283	N	Low	High	SFlood	Silty	60	3	3429.31	25.71%	74.74%
284	N	Low	High	SFlood	Silty	60	4	3748.93	22.87%	75.20%

Column #	Chamber	Airflow	Temp.	Applic.	Soil	Time	Reps	Total Water Evaporated Volume (ml)	Total % FLMT Degraded	Total % ATRAZ Degraded
285	NC	Low	Low	SFlood	Silty	60	1	3179.25	29.91%	70.17%
286	NC	Low	Low	SFlood	Silty	60	2	2619.99	28.57%	67.29%
287	NC	Low	Low	SFlood	Silty	60	3	2228.19	23.55%	72.14%
288	NC	Low	Low	SFlood	Silty	60	4	2717.69	21.65%	64.27%
289	NC	Low	Low	SFlood	Silty	120	1	5840.40	56.40%	85.04%
290	NC	Low	Low	SFlood	Silty	120	2	5346.43	48.20%	78.00%
291	NC	Low	Low	SFlood	Silty	120	3	5021.23	43.60%	74.00%
292	NC	Low	Low	SFlood	Silty	120	4	5442.73	41.38%	82.95%
293	SC	High	High	SFlood	Silty	120	1	13468.90	54.32%	86.79%
294	SC	High	High	SFlood	Silty	120	2	12644.82	58.97%	89.54%
295	SC	High	High	SFlood	Silty	120	3	16652.52	40.17%	83.12%
296	SC	High	High	SFlood	Silty	120	4	16219.11	45.98%	89.85%
297	S	High	Low	SFlood	Silty	120	1	7175.50	55.91%	87.00%
298	S	High	Low	SFlood	Silty	120	2	8471.17	31.35%	74.47%
299	S	High	Low	SFlood	Silty	120	3	8652.27	41.59%	77.65%
300	S	High	Low	SFlood	Silty	120	4	9005.74	55.66%	86.41%
301	N	Low	High	SFlood	Silty	120	1	7033.92	55.62%	88.02%
302	N	Low	High	SFlood	Silty	120	2	7426.72	47.55%	87.33%
303	N	Low	High	SFlood	Silty	120	3	9658.53	56.94%	87.24%
304	N	Low	High	SFlood	Silty	120	4	6706.76	34.76%	85.94%
305	NC	Low	Low	SFlood	Silty	180	1	8621.66	60.75%	89.46%
306	NC	Low	Low	SFlood	Silty	180	2	8716.51	59.64%	87.36%
307	NC	Low	Low	SFlood	Silty	180	3	7259.37	56.18%	87.27%
308	NC	Low	Low	SFlood	Silty	180	4	8628.26	38.90%	85.51%
309	SC	High	High	SFlood	Silty	180	1	20857.96	64.77%	89.02%
310	SC	High	High	SFlood	Silty	180	2	19351.46	56.88%	89.39%
311	SC	High	High	SFlood	Silty	180	3	19538.41	62.64%	91.37%
312	SC	High	High	SFlood	Silty	180	4	20986.72	46.97%	84.48%
313	N	Low	High	SFlood	Silty	180	1	12714.87	73.95%	91.46%
314	N	Low	High	SFlood	Silty	180	2	11355.44	62.53%	92.68%
315	N	Low	High	SFlood	Silty	180	3	16403.41	70.60%	92.91%
316	N	Low	High	SFlood	Silty	180	4	16962.22	71.61%	92.04%
317	S	High	Low	SFlood	Silty	180	1	10892.76	87.85%	88.24%
318	S	High	Low	SFlood	Silty	180	2	12646.30	70.73%	89.33%
319	S	High	Low	SFlood	Silty	180	3	17843.50	59.42%	88.22%
320	S	High	Low	SFlood	Silty	180	4	12824.48	51.23%	86.61%
321	SC	High	High	LFlood	Silty	30	1	3575.83	26.09%	69.90%
322	SC	High	High	LFlood	Silty	30	2	3212.08	26.58%	63.96%
323	SC	High	High	LFlood	Silty	30	3	2841.59	35.38%	61.56%
324	SC	High	High	LFlood	Silty	30	4	4719.71	26.53%	62.59%
325	NC	Low	Low	LFlood	Silty	30	1	1357.44	23.28%	59.94%

Column #	Chamber	Airflow	Temp.	Applic.	Soil	Time	Reps	Total Water Evaporated Volume (ml)	Total % FLMT Degraded	Total % ATRAZ Degraded
326	NC	Low	Low	LFlood	Silty	30	2	1148.00	19.89%	53.84%
327	NC	Low	Low	LFlood	Silty	30	3	940.42	13.35%	54.44%
328	NC	Low	Low	LFlood	Silty	30	4	1463.09	15.14%	57.55%
329	S	High	Low	LFlood	Silty	30	1	2370.81	25.25%	60.09%
330	S	High	Low	LFlood	Silty	30	2	1718.86	26.67%	57.67%
331	S	High	Low	LFlood	Silty	30	3	2205.67	13.07%	47.85%
332	S	High	Low	LFlood	Silty	30	4	2302.74	23.17%	56.79%
333	N	Low	High	LFlood	Silty	30	1	1861.67	18.41%	57.78%
334	N	Low	High	LFlood	Silty	30	2	1541.32	23.33%	59.00%
335	N	Low	High	LFlood	Silty	30	3	1423.25	22.46%	57.40%
336	N	Low	High	LFlood	Silty	30	4	1860.56	24.57%	61.56%
337	S	High	Low	LFlood	Silty	60	1	3678.52	25.19%	72.73%
338	S	High	Low	LFlood	Silty	60	2	3516.69	25.83%	72.77%
339	S	High	Low	LFlood	Silty	60	3	3225.93	23.48%	70.50%
340	S	High	Low	LFlood	Silty	60	4	3432.52	25.50%	71.85%
341	SC	High	High	LFlood	Silty	60	1	5680.04	23.42%	79.13%
342	SC	High	High	LFlood	Silty	60	2	5721.98	28.42%	80.74%
343	SC	High	High	LFlood	Silty	60	3	6186.35	16.78%	74.17%
344	SC	High	High	LFlood	Silty	60	4	5582.17	29.06%	83.47%
345	N	Low	High	LFlood	Silty	60	1	4196.13	41.27%	87.79%
346	N	Low	High	LFlood	Silty	60	2	4895.75	36.58%	82.79%
347	N	Low	High	LFlood	Silty	60	3	3299.92	24.81%	81.02%
348	N	Low	High	LFlood	Silty	60	4	3524.30	34.00%	82.73%
349	NC	Low	Low	LFlood	Silty	60	1	2061.89	22.70%	66.50%
350	NC	Low	Low	LFlood	Silty	60	2	2360.95	12.76%	62.04%
351	NC	Low	Low	LFlood	Silty	60	3	2923.70	16.85%	67.99%
352	NC	Low	Low	LFlood	Silty	60	4	2471.38	24.63%	67.07%
353	NC	Low	Low	LFlood	Silty	120	1	5344.95	55.55%	82.21%
354	NC	Low	Low	LFlood	Silty	120	2	6185.92	49.43%	87.08%
355	NC	Low	Low	LFlood	Silty	120	3	5212.28	37.69%	84.71%
356	NC	Low	Low	LFlood	Silty	120	4	5529.61	31.97%	82.07%
357	SC	High	High	LFlood	Silty	120	1	11214.73	51.66%	83.13%
358	SC	High	High	LFlood	Silty	120	2	10843.85	58.03%	89.72%
359	SC	High	High	LFlood	Silty	120	3	12216.75	58.64%	89.78%
360	SC	High	High	LFlood	Silty	120	4	11521.00	47.61%	86.44%
361	S	High	Low	LFlood	Silty	120	1	7186.65	57.10%	85.76%
362	S	High	Low	LFlood	Silty	120	2	7774.83	41.64%	84.90%
363	S	High	Low	LFlood	Silty	120	3	8380.47	49.55%	82.89%
364	S	High	Low	LFlood	Silty	120	4	7084.38	60.00%	87.39%
365	N	Low	High	LFlood	Silty	120	1	5653.71	62.55%	90.28%
366	N	Low	High	LFlood	Silty	120	2	8854.82	49.63%	87.62%

Table D-1. Continued.

Column #	Chamber	Airflow	Temp.	Applic.	Soil	Time	Reps	Total Water Evaporated Volume (ml)	Total % FLMT Degraded	Total % ATRAZ Degraded
367	N	Low	High	LFlood	Silty	120	3	8845.45	52.81%	84.48%
368	N	Low	High	LFlood	Silty	120	4	6304.09	42.74%	88.54%
369	NC	Low	Low	LFlood	Silty	180	1	7268.11	60.70%	87.30%
370	NC	Low	Low	LFlood	Silty	180	2	7726.50	63.80%	87.94%
371	NC	Low	Low	LFlood	Silty	180	3	8630.14	65.25%	90.20%
372	NC	Low	Low	LFlood	Silty	180	4	7190.91	49.91%	87.09%
373	SC	High	High	LFlood	Silty	180	1	17783.75	63.59%	89.78%
374	SC	High	High	LFlood	Silty	180	2	18453.13	60.50%	89.60%
375	SC	High	High	LFlood	Silty	180	3	16220.71	52.01%	85.62%
376	SC	High	High	LFlood	Silty	180	4	15466.45	59.97%	91.23%
377	N	Low	High	LFlood	Silty	180	1	10478.20	82.42%	90.85%
378	N	Low	High	LFlood	Silty	180	2	9989.92	84.24%	90.52%
379	N	Low	High	LFlood	Silty	180	3	10771.19	65.41%	92.04%
380	N	Low	High	LFlood	Silty	180	4	11458.65	58.84%	94.05%
381	S	High	Low	LFlood	Silty	180	1	10950.38	56.55%	91.35%
382	S	High	Low	LFlood	Silty	180	2	10849.66	51.12%	88.24%
383	S	High	Low	LFlood	Silty	180	3	11397.93	54.73%	86.29%
384	S	High	Low	LFlood	Silty	180	4	11792.31	57.21%	88.61%
385	SC	High	High	LWick	Silty	30	1	4450.30	19.54%	61.37%
386	SC	High	High	LWick	Silty	30	2	5520.36	35.42%	69.78%
387	SC	High	High	LWick	Silty	30	3	4979.38	22.17%	59.29%
388	SC	High	High	LWick	Silty	30	4	3321.82	20.71%	61.54%
389	NC	Low	Low	LWick	Silty	30	1	1857.12	35.43%	65.34%
390	NC	Low	Low	LWick	Silty	30	2	930.30	17.46%	55.75%
391	NC	Low	Low	LWick	Silty	30	3	1913.05	23.89%	57.83%
392	NC	Low	Low	LWick	Silty	30	4	1413.33	22.48%	58.27%
393	S	High	Low	LWick	Silty	30	1	2954.46	20.69%	59.52%
394	S	High	Low	LWick	Silty	30	2	2435.55	19.62%	51.29%
395	S	High	Low	LWick	Silty	30	3	2162.09	22.03%	51.13%
396	S	High	Low	LWick	Silty	30	4	2286.73	18.91%	53.46%
397	N	Low	High	LWick	Silty	30	1	2700.73	27.94%	68.46%
398	N	Low	High	LWick	Silty	30	2	2263.02	31.25%	64.13%
399	N	Low	High	LWick	Silty	30	3	1698.19	22.18%	55.13%
400	N	Low	High	LWick	Silty	30	4	3299.26	23.89%	63.19%
401	S	High	Low	LWick	Silty	60	1	3340.38	15.83%	56.37%
402	S	High	Low	LWick	Silty	60	2	3572.81	24.80%	60.53%
403	S	High	Low	LWick	Silty	60	3	3753.55	16.59%	58.54%
404	S	High	Low	LWick	Silty	60	4	3303.06	14.08%	55.40%
405	SC	High	High	LWick	Silty	60	1	7389.07	22.87%	63.59%
406	SC	High	High	LWick	Silty	60	2	7859.35	41.13%	64.82%
407	SC	High	High	LWick	Silty	60	3	7947.25	36.25%	72.84%

Table D-1. Continued.

Column #	Chamber	Airflow	Temp.	Applic.	Soil	Time	Reps	Total Water Evaporated Volume (ml)	Total % FLMT Degraded	Total % ATRAZ Degraded
408	SC	High	High	LWick	Silty	60	4	6639.66	20.00%	63.98%
409	N	Low	High	LWick	Silty	60	1	4271.08	24.74%	69.16%
410	N	Low	High	LWick	Silty	60	2	4645.65	24.48%	68.37%
411	N	Low	High	LWick	Silty	60	3	3920.82	25.22%	71.95%
412	N	Low	High	LWick	Silty	60	4	6029.58	34.76%	81.25%
413	NC	Low	Low	LWick	Silty	60	1	2657.59	21.87%	64.32%
414	NC	Low	Low	LWick	Silty	60	2	3134.00	21.79%	62.06%
415	NC	Low	Low	LWick	Silty	60	3	2742.07	27.32%	67.56%
416	NC	Low	Low	LWick	Silty	60	4	2785.88	24.28%	62.75%
417	NC	Low	Low	LWick	Silty	120	1	5780.97	44.89%	67.95%
418	NC	Low	Low	LWick	Silty	120	2	6419.79	33.33%	62.15%
419	NC	Low	Low	LWick	Silty	120	3	4959.04	39.69%	65.72%
420	NC	Low	Low	LWick	Silty	120	4	5295.96	41.17%	72.27%
421	SC	High	High	LWick	Silty	120	1	13740.21	48.19%	83.04%
422	SC	High	High	LWick	Silty	120	2	13182.46	38.24%	69.10%
423	SC	High	High	LWick	Silty	120	3	15506.76	25.77%	57.96%
424	SC	High	High	LWick	Silty	120	4	12347.34	53.94%	79.71%
425	S	High	Low	LWick	Silty	120	1	7584.76	50.39%	71.68%
426	S	High	Low	LWick	Silty	120	2	7467.16	42.18%	67.65%
427	S	High	Low	LWick	Silty	120	3	7741.98	36.16%	60.42%
428	S	High	Low	LWick	Silty	120	4	6978.59	48.12%	75.84%
429	N	Low	High	LWick	Silty	120	1	10070.70	60.43%	89.72%
430	N	Low	High	LWick	Silty	120	2	9299.04	56.92%	84.30%
431	N	Low	High	LWick	Silty	120	3	9310.01	46.98%	87.88%
432	N	Low	High	LWick	Silty	120	4	9376.08	53.27%	88.09%
433	NC	Low	Low	LWick	Silty	180	1	8296.37	54.20%	83.86%
434	NC	Low	Low	LWick	Silty	180	2	6321.44	35.32%	83.14%
435	NC	Low	Low	LWick	Silty	180	3	7397.52	44.71%	85.16%
436	NC	Low	Low	LWick	Silty	180	4	8514.81	55.58%	85.75%
437	SC	High	High	LWick	Silty	180	1	16033.23	54.46%	85.08%
438	SC	High	High	LWick	Silty	180	2	16576.63	53.12%	88.89%
439	SC	High	High	LWick	Silty	180	3	15646.43	42.45%	91.33%
440	SC	High	High	LWick	Silty	180	4	18487.82	53.48%	91.88%
441	N	Low	High	LWick	Silty	180	1	10567.65	48.41%	88.21%
442	N	Low	High	LWick	Silty	180	2	11726.15	52.22%	89.14%
443	N	Low	High	LWick	Silty	180	3	15204.66	59.28%	91.62%
444	N	Low	High	LWick	Silty	180	4	12998.40	49.58%	86.51%
445	S	High	Low	LWick	Silty	180	1	11701.66	50.88%	79.25%
446	S	High	Low	LWick	Silty	180	2	10880.54	54.46%	84.09%
447	S	High	Low	LWick	Silty	180	3	11092.52	47.35%	82.94%
448	S	High	Low	LWick	Silty	180	4	9418.97	55.89%	85.04%

Column #	Chamber	Airflow	Temp.	Applic.	Soil	Time	Reps	Total Water Evaporated Volume (ml)	Total % FLMT Degraded	Total % ATRAZ Degraded
449	SC	High	High	SWick	Silty	30	1	4315.24	32.00%	66.80%
450	SC	High	High	SWick	Silty	30	2	3479.04	31.16%	59.06%
451	SC	High	High	SWick	Silty	30	3	3562.45	31.71%	58.75%
452	SC	High	High	SWick	Silty	30	4	3478.56	25.56%	56.42%
453	NC	Low	Low	SWick	Silty	30	1	1143.63	29.13%	59.90%
454	NC	Low	Low	SWick	Silty	30	2	1669.48	34.91%	59.62%
455	NC	Low	Low	SWick	Silty	30	3	1879.68	28.61%	56.38%
456	NC	Low	Low	SWick	Silty	30	4	1345.28	35.55%	60.81%
457	S	High	Low	SWick	Silty	30	1	1917.13	37.60%	63.99%
458	S	High	Low	SWick	Silty	30	2	2250.11	28.48%	56.97%
459	S	High	Low	SWick	Silty	30	3	2528.44	32.45%	55.83%
460	S	High	Low	SWick	Silty	30	4	2792.99	22.50%	51.21%
461	N	Low	High	SWick	Silty	30	1	1530.60	39.76%	68.08%
462	N	Low	High	SWick	Silty	30	2	3220.11	25.61%	69.47%
463	N	Low	High	SWick	Silty	30	3	2316.21	40.42%	67.11%
464	N	Low	High	SWick	Silty	30	4	1789.00	28.08%	57.08%
465	S	High	Low	SWick	Silty	60	1	3589.69	26.66%	60.13%
466	S	High	Low	SWick	Silty	60	2	3764.37	28.85%	59.01%
467	S	High	Low	SWick	Silty	60	3	3609.13	17.92%	56.37%
468	S	High	Low	SWick	Silty	60	4	3547.02	21.95%	56.68%
469	SC	High	High	SWick	Silty	60	1	6149.40	32.07%	62.31%
470	SC	High	High	SWick	Silty	60	2	8876.98	21.00%	61.27%
471	SC	High	High	SWick	Silty	60	3	7434.83	32.89%	72.00%
472	SC	High	High	SWick	Silty	60	4	6758.19	36.03%	66.30%
473	N	Low	High	SWick	Silty	60	1	5183.41	27.79%	69.27%
474	N	Low	High	SWick	Silty	60	2	3466.50	38.15%	68.80%
475	N	Low	High	SWick	Silty	60	3	4998.39	38.77%	72.92%
476	N	Low	High	SWick	Silty	60	4	3530.87	35.86%	69.99%
477	NC	Low	Low	SWick	Silty	60	1	2370.05	19.56%	60.85%
478	NC	Low	Low	SWick	Silty	60	2	3312.98	38.07%	67.26%
479	NC	Low	Low	SWick	Silty	60	3	2242.99	13.88%	60.48%
480	NC	Low	Low	SWick	Silty	60	4	2691.50	24.15%	62.30%
481	NC	Low	Low	SWick	Silty	120	1	4763.30	50.01%	74.94%
482	NC	Low	Low	SWick	Silty	120	2	4003.32	49.75%	78.08%
483	NC	Low	Low	SWick	Silty	120	3	4822.01	46.97%	67.10%
484	NC	Low	Low	SWick	Silty	120	4	4155.64	40.56%	70.91%
485	SC	High	High	SWick	Silty	120	1	16910.38	53.36%	70.43%
486	SC	High	High	SWick	Silty	120	2	15633.12	55.84%	70.13%
487	SC	High	High	SWick	Silty	120	3	14366.71	58.98%	76.20%
488	SC	High	High	SWick	Silty	120	4	12992.55	59.68%	71.71%
489	S	High	Low	SWick	Silty	120	1	7614.75	55.46%	66.29%

Column #	Chamber	Airflow	Temp.	Applic.	Soil	Time	Reps	Total Water Evaporated Volume (ml)	Total % FLMT Degraded	Total % ATRAZ Degraded
490	S	High	Low	SWick	Silty	120	2	10049.91	39.27%	49.20%
491	S	High	Low	SWick	Silty	120	3	7925.34	53.00%	65.51%
492	S	High	Low	SWick	Silty	120	4	11385.83	46.76%	54.10%
493	N	Low	High	SWick	Silty	120	1	3840.98	60.41%	89.99%
494	N	Low	High	SWick	Silty	120	2	11809.21	51.15%	70.95%
495	N	Low	High	SWick	Silty	120	3	9086.26	44.05%	71.67%
496	N	Low	High	SWick	Silty	120	4	6731.57	62.03%	79.93%
497	NC	Low	Low	SWick	Silty	180	1	6911.24	57.87%	79.56%
498	NC	Low	Low	SWick	Silty	180	2	7434.88	59.24%	78.73%
499	NC	Low	Low	SWick	Silty	180	3	9288.70	58.28%	73.72%
500	NC	Low	Low	SWick	Silty	180	4	9621.40	55.60%	73.07%
501	SC	High	High	SWick	Silty	180	1	18304.68	49.79%	70.55%
502	SC	High	High	SWick	Silty	180	2	20115.16	57.05%	79.39%
503	SC	High	High	SWick	Silty	180	3	25222.26	59.39%	74.94%
504	SC	High	High	SWick	Silty	180	4	18178.51	69.33%	68.65%
505	N	Low	High	SWick	Silty	180	1	12030.73	56.29%	82.96%
506	N	Low	High	SWick	Silty	180	2	10230.29	68.52%	86.08%
507	N	Low	High	SWick	Silty	180	3	9955.53	50.91%	75.89%
508	N	Low	High	SWick	Silty	180	4	10247.83	57.52%	80.92%
509	S	High	Low	SWick	Silty	180	1	15592.94	97.06%	71.59%
510	S	High	Low	SWick	Silty	180	2	10290.61	58.43%	72.02%
511	S	High	Low	SWick	Silty	180	3	13781.88	56.93%	77.07%
512	S	High	Low	SWick	Silty	180	4	14406.05	56.37%	74.97%

APPENDIX E:

STATISTICAL RESULT TABLES

Table E-1: Listing of SAS® Type III Sum of Squares for significant variables and combinations from the normalized evaporation model (at $\alpha = 0.05$).

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Airflow	1	27.50914	27.50914	1079.35	0.0001
Temp	1	30.25773	30.25773	1187.20	0.0001
Airflow*Temp	1	0.47250	0.47250	18.54	0.0001
Applic	3	0.84902	0.28301	11.10	0.0001
Airflow*Applic	3	0.07995	0.02665	1.05	0.3723
Temp*Applic	3	0.23549	0.07850	3.08	0.0275
Airflow*Temp*Applic	3	0.02511	0.00837	0.33	0.8048
Soil	1	1.15116	1.15116	45.17	0.0001
Airflow*Soil	1	0.00756	0.00756	0.30	0.5863
Temp*Soil	1	0.03061	0.03061	1.20	0.2738
Airflow*Temp*Soil	1	0.01971	0.01971	0.77	0.3797
Applic*Soil	3	0.16954	0.05651	2.22	0.0857
Airflow*Applic*Soil	3	0.18119	0.06040	2.37	0.0702
Temp*Applic*Soil	3	0.03124	0.01041	0.41	0.7469
Airflow*Temp*Applic*Soil	3	0.05867	0.01956	0.77	0.5129
Time	3	223.61070	74.53690	2924.54	0.0001
Airflow*Time	3	0.14279	0.04760	1.87	0.1346
Temp*Time	3	0.29229	0.09743	3.82	0.0101
Airflow*Temp*Time	3	0.17646	0.05882	2.31	0.0761
Applic*Time	9	0.61272	0.06808	2.67	0.0051
Airflow*Applic*Time	9	0.48526	0.05392	2.12	0.0274
Temp*Applic*Time	9	0.32138	0.03571	1.40	0.1856
Airflow*Temp*Applic*Time	9	0.35917	0.3991	1.57	0.1236
Soil*Time	3	0.11062	0.03687	1.45	0.2288
Airflow*Soil*Time	3	0.28582	0.09527	3.74	0.0114

Table E-1. Continued.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Temp*Soil*Time	3	0.07281	0.02427	0.95	0.4154
Airflow*Temp*Soil*Time	3	0.04416	0.01472	0.58	0.6300
Applic*Soil*Time	9	0.10253	0.01139	0.45	0.9089
Airflow*Applic*Soil*Time	9	0.11412	0.01268	0.50	0.8761
Temp*Applic*Soil*Time	9	0.14949	0.01661	0.65	0.7524
Airflow*Temp*Applic*Soil*Time	9	0.09017	0.01002	0.39	0.9383

Table E-2: Listing of SAS® Type III Sum of Squares for significant variables and combinations from the fluometuron degradation model (at $\alpha = 0.05$).

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Airflow	1	167.57	167.57	3.12	0.0780
Temp	1	1839.09	1839.09	34.28	0.0001
Airflow*Temp	1	324.01	324.01	6.04	0.0144
Applic	3	3749.38	1249.79	23.30	0.0001
Airflow*Applic	3	469.49	156.50	2.92	0.0341
Temp*Applic	3	234.23	78.08	1.46	0.2264
Airflow*Temp*Applic	3	193.81	64.60	1.20	0.3080
Soil	1	1708.18	1708.18	31.84	0.0001
Airflow*Soil	1	98.96	98.96	1.84	0.1752
Temp*Soil	1	56.64	56.64	1.06	0.3048
Airflow*Temp*Soil	1	22.80	22.80	0.43	0.5148
Applic*Soil	3	687.72	229.24	4.27	0.0055
Airflow*Applic*Soil	3	226.77	75.59	1.41	0.2397
Temp*Applic*Soil	3	34.84	11.61	0.22	0.8850
Airflow*Temp*Applic*Soil	3	93.86	31.29	0.58	0.6264
Time	3	101470.63	33823.54	630.46	0.0001
Airflow*Time	3	177.14	59.05	1.10	0.3488
Temp*Time	3	633.65	211.22	3.94	0.0087
Airflow*Temp*Time	3	520.33	173.44	3.23	0.0224
Applic*Time	9	2796.26	310.70	5.79	0.0001
Airflow*Applic*Time	9	488.91	54.32	1.01	0.4292
Temp*Applic*Time	9	449.74	49.97	0.93	0.4975
Airflow*Temp*Applic*Time	9	595.45	66.16	1.23	0.2729
Soil*Time	3	145.34	48.45	0.90	0.4397
Airflow*Soil*Time	3	120.37	40.12	0.75	0.5241
Temp*Soil*Time	3	594.03	198.01	3.69	0.0121

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Airflow*Temp*Soil*Time	3	134.05	44.68	0.83	0.4764
Applic*Soil*Time	9	654.62	72.74	1.36	0.2066
Airflow*Applic*Soil*Time	9	968.74	107.64	2.01	0.0375
Temp*Applic*Soil*Time	9	312.29	34.70	0.65	0.7568
Airflow*Temp*Applic*Soil*Time	9	704.04	78.23	1.46	0.1617

Table E-3: Listing of SAS® Type III Sum of Squares for significant variables and combinations from the atrazine degradation model (at $\alpha = 0.05$).

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Airflow	1	426.22	426.22	15.51	0.0001
Temp	1	2218.89	2218.89	80.72	0.0001
Airflow*Temp	1	26.18	26.18	0.95	0.3297
Applic	3	5957.65	1985.88	72.25	0.0001
Airflow*Applic	3	910.47	303.49	11.04	0.0001
Temp*Applic	3	281.40	93.80	3.41	0.0176
Airflow*Temp*Applic	3	292.60	97.53	3.55	0.0147
Soil	1	203029.70	203029.70	7386.21	0.0001
Airflow*Soil	1	10.26	10.26	0.37	0.5416
Temp*Soil	1	774.05	774.05	28.16	0.0001
Airflow*Temp*Soil	1	40.90	40.90	1.49	0.2233
Applic*Soil	3	1795.23	598.41	21.77	0.0001
Airflow*Applic*Soil	3	129.26	43.09	1.57	0.1968
Temp*Applic*Soil	3	434.29	144.76	5.27	0.0014
Airflow*Temp*Applic*Soil	3	48.66	16.22	0.59	0.6218
Time	3	24130.82	8043.61	292.63	0.0001
Airflow*Time	3	127.22	42.41	1.54	0.2030
Temp*Time	3	217.76	72.59	2.64	0.0492
Airflow*Temp*Time	3	138.06	46.02	1.67	0.1721
Applic*Time	9	3422.82	380.31	13.84	0.0001
Airflow*Applic*Time	9	375.18	41.69	1.52	0.1399
Temp*Applic*Time	9	240.66	26.74	0.97	0.4621
Airflow*Temp*Applic*Time	9	718.74	79.86	2.91	0.0024
Soil*Time	3	4050.83	1350.28	49.12	0.0001
Airflow*Soil*Time	3	125.07	41.69	1.52	0.2097
Temp*Soil*Time	3	721.94	240.65	8.75	0.0001

Table E-3. Continued.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Airflow*Temp*Soil*Time	3	129.44	43.15	1.57	0.1963
Applic*Soil*Time	9	1404.60	156.07	5.68	0.0001
Airflow*Applic*Soil*Time	9	394.45	43.83	1.59	0.1149
Temp*Applic*Soil*Time	9	606.04	67.34	2.45	0.0101
Airflow*Temp*Applic*Soil*Time	9	424.64	47.18	1.72	0.0835

APPENDIX F:

COLUMN SPATIAL VARIABILITY

Table F-1. Summary of results from preliminary tests on spatial variability of soil herbicide concentrations within the columns.

Sample Number	Percent Moisture	Atrazine				Fluometuron			
		Conc. (ppb)	Mean Conc. (ppb)	STD	CV	Conc. (ppb)	Mean Conc. (ppb)	STD	CV
9A	15.324	7611.64	6188.67	0.114	1.843	8245.47	6809.33	0.365	5.363
9B	0.599	6091.46				6515.26			
9C	0.414	6160.51				6695.44			
9D	0.792	6314.11				7217.97			
73A	0.639	6402.49	6527.5	0.153	2.342	7002.45	7300.75	0.454	6.219
73B	0.616	6711.02				7975.61			
73C	0.399	6401.75				7147.1			
73D	0.639	6596.31				7078.2			
137A	0.568	8377.14	8248.5	0.186	2.255	9181.45	9535.25	1.289	13.52
137B	0.683	8433.07				11444.6			
137C	0.599	8137.62				8740.60			
137D	0.421	8046.38				8773.93			
201A	0.531	10107.4	9717.25	0.277	2.849	11475.2	1078.78	0.472	4.380
201B	0.372	9453.29				10409.6			
201C	0.364	9642.92				10691.4			
201D	0.465	9665.83				10575.4			
265A	1.309	4830.29	4953.25	0.089	1.804	7887.09	8026.75	0.101	1.262
265B	1.586	4945.25				8064.31			
265C	1.300	5024.24				8029.56			
265D	1.459	5013.55				8125.57			
329A	1.662	4683.22	4744.25	0.121	2.558	7833.00	8952.00	2.091	23.36
329B	1.696	4721.71				7769.72			
329C	1.925	4921.30				8125.47			
329D	1.786	4651.12				12080.1			

Sample Number	Percent Moisture	Atrazine				Fluometuron			
		Conc. (ppb)	Mean Conc. (ppb)	STD	CV	Conc. (ppb)	Mean Conc. (ppb)	STD	CV
393A	1.698	5751.24				9416.33			
393B	1.753	5818.50	5740.50	0.067	1.159	9491.54	9388.50	0.121	1.288
393C	1.807	5735.43				9431.80			
393D	1.904	5657.12				9213.90			
457A	1.327	6312.71				9871.07			
457B	1.023	6053.20	6117.33	0.173	2.824	9311.32	9503.00	0.319	3.355
457C	12.941	7680.74				11741.5			
457D	1.407	5985.54				9327.11			

* All columns were from the 30-day time period and were pulled from the South chamber (i.e., low temperature and high airflow).

** Columns # 9, 73, 137, and 201 contained sandy soil; columns # 265, 329, 393, and 457 contained silty soil.

*** Columns #9 and 265 ⇒ 5-day flood/dry (SF)
Columns #73 and 329 ⇒ 10-day flood/dry (LF)
Columns #137 and 393 ⇒ 10"-wicking (LW)
Columns #201 and 457 ⇒ 7"-wicking (SW)

VITA

Brian K. Corwin was born November 7, 1968 in Birmingham, Alabama. He is the son of Mr. Wilson P. Corwin Jr., and the late Marjorie C. Corwin. He resided in Jefferson County and attended its public school system until graduation from W.A. Berry High School in May, 1987. At the age of 17 he received the Eagle Scout Award from the Boy Scouts of America.

In September, 1987, he entered The University of Tennessee, Knoxville, and received a Bachelor of Science degree with a major in Agricultural Engineering in December, 1992. The following month he enrolled in the Graduate School at The University of Tennessee, Knoxville, and accepted a research assistantship with the Agricultural Engineering Department. In August, 1996, he earned a Master of Science degree with a major in Agricultural Engineering and a minor in Environmental Engineering.

During his collegiate tenure he was active in numerous professional societies including the American Society of Agricultural Engineers, the Soil and Water Conservation Society, the Tennessee Agricultural Chemical Association, and the Tennessee Section of the American Water Resources Association. He is a member of Tau Beta Pi and Gamma Sigma Delta honor societies. During his undergraduate career he was also active in Alpha Tau Omega Fraternity.