ACIDIC AND ALKALINE TRICKLING FILTER SYSTEMS WERE ASSESSED FOR BIOLOGICAL AND CHEMICAL DECOMPOSITION OF PESTICIDES. A DISPOSAL PIT (6.1 m x 6.1 m x 1.2 m) WAS FILLED WITH COARSE GRADE LIMESTONE FOR PROMOTION OF ALKALINE HYDROLYSIS, ANOTHER WITH ACID MATERIAL FROM A STRIP MINE OPERATION TO PROMOTE ACID HYDROLYSIS. A NETWORK OF 2-IN PERFORATED PVC PIPE SUSPENDED OVER THE FILTER MATERIAL AND A CIRCULATION PUMP FACILITATE DISTRIBUTION OF THE TEST SOLUTIONS. THE TREATMENT SYSTEMS WERE INOCULATED WITH INDIGENOUS PESTICIDE-DECOMPOSING BACTERIA TO ENHANCE DEGRADATION.

MICROBIAL COUNTS HAVE BEEN DETERMINED OVER TIME AND COMPARED WITH PESTICIDE CONCENTRATIONS (VIA GAS CHROMATOGRAPHY). COMPOUNDS TESTED INCLUDE ALACHLOR, ATRAZINE, BUTYLATE, CYANAZINE, LINURON, METOLACHLOR, METRIBUZIN, PENDIMETHALIN, AND TRIFLURALIN. ALL BUT GRANULAR FORMULATIONS HAVE BEEN USED. GREATER DEGRADATION RATES WERE GENERALLY OBSERVED IN THE ACID SYSTEM (UP TO 30% PER DAY). DEGRADATION RATES FOR THE ALKALINE DISPOSAL SYSTEM AVERAGED 2.5% PER DAY.

INTRODUCTION

PESTICIDE APPICATORS AND DEALERS ARE FACED WITH A WASTE DISPOSAL PROBLEM WHICH MAY VARY ACCORDING TO THE SIZE AND TYPE OF OPERATION. WASTE-WATER FROM VEHICLE WASHING, SPRAY OR NURSE TANK RINSE-WATER, HAULBACK SOLUTIONS, FACILITY RUNOFF, SPILLED MATERIALS, OBSOLETE OR UNIDENTIFIABLE CHEMICALS, CONTAINERS AND INCOMPATIBLE MIXTURES ARE ALL RECOGNIZED SOURCES OF WASTE PESTICIDE SOLUTIONS (6).

LITERATURE REVIEW

THE USE OF TOXIC CHEMICAL COMPOUNDS IN AGRICULTURE HAS CREATED PROBLEMS OF BIOLOGICAL AND ENVIRONMENTAL CONCERN SINCE THE PESTICIDES EMPLOYED MAY NOT BE TOTALLY SPECIFIC AND DEGRADED TO A HARMLESS STATE. THE CONCERN FOR POTENTIAL BIOHAZARDS WHICH MAY EXIST FROM YEARLY APPLICATION WAS ACKNOWLEDGED IN A STUDY CARRIED OUT BY THE ASSOCIATION OF STATE UNIVERSITIES AND LAND GRANT COLLEGES AND UNITED STATES DEPARTMENT OF AGRICULTURE (20).

The Fate of Pesticide in the Soil

PESTICIDES APPLIED TO THE SOIL OR WHICH ULTIMATELY REACH THE SOIL MAY BE ACTED UPON PHYSICALLY, CHEMICALLY, OR BIOLOGICALLY. ALL RESULT IN A CHANGE OF STRUCTURE AND/OR TOXICITY (2, 17). PHYSICAL LOSSES OF PESTICIDES FROM THE SOIL INCLUDE: WIND AND WATER EROSION, ADSORPTION TO SOIL PARTICLES SUCH AS ORGANIC MATTER, LEACHING, AND VOLATILIZATION. CHEMICAL MECHANISMS OF TRANSFORMATIONS ARE MUCH LESS UNDERSTOOD AND ONLY RECENTLY ARE BEING PROPOSED AS MAJOR PATHWAYS OF PESTICIDE DEGRADATION. IN ADDITION, CHEMICAL TRANSFORMATIONS MAY CONTRIBUTE ESSENTIAL STAGES TO PRINCIPALLY BIOLOGICAL DECOMPOSITION PATHWAYS (16). ALKALINE HYDROLYSIS, REDUCTION, ELIMINATION, DECARBOXYLATION, OXIDATION, AND ISOMERIZATION ARE AMONG THE REACTIONS THAT MAY OCCUR (12). PHOTODECOMPOSITION IS A COMBINATION OF PHYSICAL AND CHEMICAL TRANSFORMATIONS. THE MAJORITY OF PESTICIDES ARE SUBJECT TO PHOTODECOMPOSITION AND THIS MAY BE THE PROMINANT DEGRADATIVE MECHANISM OF PESTI-
icide vapors. However, it is not significant when the material is soil incorporated or on crops and crop residues (14).

Soil microorganisms and plants are responsible for biological pesticide transformations. Transformations by plants (such as plant uptake of herbicides) result in a decrease of pesticide concentrations (1, 13). Indigenous microbial populations of bacteria and fungi play a key role in pesticide biodegradation (2). Alexander (2) and Atlas and Bartha (8) have categorized microbial transformations of pesticides on the basis of the end-product formed: detoxification, degradation, conjugation, complex formation, activation, defusing, and a change in the spectrum of toxicity.

Rates and mechanisms of pesticide degradation are dependent on the environmental conditions (15). Biological, chemical, and physical transformations cannot be separated since exclusion of one will alter rates and pathways of the decomposition process (15, 17).

The pesticides used in this study were selected on the basis of their popularity in Illinois agriculture systems. For information on the degradation of alachlor (2-chloro-2',6'-diethyl-N-[methoxymethyl]acetonilide), atrazine (2-chloro-4-[ethylamino]-6-[isopropylamino]-s-triazine), butylate (s-ethyl diisobutylthiocarbamate), cyazine (2-[[4-chloro-6-(ethylamino)-s-triazin-2-yl]amino]-2-methylpropionitrile), linuron (3-[3,4-dichlorophenyl]-1-methoxy-1-methylurea), metolachlor (2-chloro-N-[2-ethyl-6-methylphenyl]-N-[2-methoxy-1-methylethyl]acetamide), metribuzin (4-amino-6-tert-butyl-3-[methylthio]-as-triazin-5(4H)-one), pendimethalin (N-[1-ethylpropyl]-3,4-dimethyl-2,6 dinitrobenzenamine), and trifluralin (2,6-dinitro-N,N-dipropyl-4-trifluoromethylaniline) please consult the following sources: Brown (9), Cripps and Roberts (11), Herbicide Handbook of the Weed Science Society of America (7), and Knuesel et al. (18).

Pesticide Disposal Practices

The mismanagement of generated waste pesticide materials may cause potential environmental problems: the contamination of ground and surface water via runoff from the site of pesticide mixing, and/or discharge of chemical spray tank rinsates into streams (4, 6). The difficulty of implementing regulatory measures for the proper disposal of waste pesticide materials has resulted in certain illegal disposal practices such as rinsing spray tanks on open lots without providing containment, improper disposal of the rinsate solutions, dumping excess spray solutions and tank rinsings along fence rows, and discharging pesticide-contaminated waste-waters into ditches and streams (6).

Various methods of treatment and disposal of waste pesticide solutions have been proposed and evaluated. Such methods include land disposal (land cultivation, soil mounds and pits), evaporation basins and lagoons, chemical treatments, physical treatments (adsorption and reverse osmosis), biological treatment (trickling filters and activated sludge) and incineration (4).

From 1977 to 1979, Iowa State University conducted an experimental study of pesticide decay by using 56 minipits (plastic garbage cans), 2 macropits, and 4 micropits (5). The macropits were designed for the more practical aspect of waste pesticide disposal. Essentially, they were soil pits with a top or middle layer of rock. Neither circulation nor aeration occurred, thus representing static systems. These pits were also uncontrolled since timing, amount, and type of waste materials to be disposed were not planned, but merely monitored over time. The pH, chemical constituents, and microbial populations were determined. However, the role of the microbial populations in pesticide decomposition was not delineated.

In a recent project at Southern Illinois University-Carbondale, the disposal of atrazine and trifluralin was assessed in an acid and alkaline trickling filter system (21). Trifluralin phytotoxicity was observed to decline to 3% and 5% in the acid and alkaline disposal pits, respectively, following 21 days of incubation. Atrazine phytotoxicity fell to 23% in the acidic pit after 21 days of incubation but remained constant (68 to 70%) in the alkaline pit. However, herbicide concentrations were not determined. Population counts of herbicide decomposers demonstrated a one to two log increase in the alkaline pit following 5 to 9 days of incubation. The acidic pit showed two peaks in the counts of herbicide decomposers after
1 and 14 days of incubation. Significant cubic and quadratic functions were determined for herbicide phytotoxicity and decomposer counts versus time in the acid and alkaline disposal pits, indicating a direct effect by the microbial population on herbicide activity.

The objectives of this study were:
to evaluate a variety of herbicides commonly used in high volumes in Illinois for disposal in acid and alkaline trickling filter systems and to compare numbers of pesticide degrading microorganisms with pesticide degradation.

MATERIALS AND METHODS

Description of Pesticide Disposal Pits

During the summer of 1981, trickling filter disposal pits were constructed at the Southern Illinois Fruit Station, Carbondale, Illinois in an argillic (Bt) horizon of a Weir silt loam (fine, montmorillonitic, mesic typic ochraqualf) (Figures 1 and 2). The dimensions of the pits are 6.1 m x 6.1 m x 1.2 m or 44.7 m³. The pits are side by side but separated by a 1 m clay barrier and surrounded by a 61 centimeter (cm) berm. In one pit, the filtering medium is coarse grade limestone (alkaline pit). This creates a neutral to alkaline environment facilitating chemical hydrolysis and microbial growth. In the adjacent pit, the medium is acid mine gob obtained from a nearby coal strip mine, creating a highly acidic and strongly anaerobic system (acid pit). Each pit has a single well equipped with a 248 kilogram meter squared per cubic second (kg. m² S⁻³) sump pump discharging the dilute pesticide solutions through a network of 5.1 cm PVC perforated pipe. The flow rate of the pumps was rated at 10.4 (m³ hr⁻¹). Because of high porosity of the limestone, the pesticide solutions were discharged in a continuous mode in the alkaline pit. The very low porosity of the gob material only permitted intermittent discharging (at 30 minute (min) cycles) of the pesticide solutions.

Isolation of Pesticide Decomposing Microorganisms

Soil samples, as a source of herbicide decomposing microorganisms, were taken from the soils adjacent to the acid/alkaline trickling filter system. The soil samples were composited and sieved to a two to five millimeter (mm) particle size followed by storage at 4 degrees celsius (C) until used.

The isolation of herbicide decomposers utilized the soil perfusion method described by Collins and Simms (10). This system was used as an enrichment technique. Super Floc 127 (American Cyanimid), a soil stabilizer, was added (0.8% dry weight basis) to each 100 gram (g) soil sample. Tap water was added to bring the mixture to a smooth paste consistency. The soil-paste was sieved, obtaining five to seven mm crumb-like particles. The particles were air dried for two days at room temperature.

Following drying, 20 g of the stabilized particles were placed in a perfusion flask containing 250 milliliters (ml) of tap water. A total of 18 flasks were perfused for 24 hours. The perfusates were discarded and replaced with 200 milligrams per liter (mg L⁻¹) solution of alachlor, atrazine, butylate, cyanazine, linuron, pendimethalin, metolachlor, metribuzin, or trifluralin, plus 30 ml of pesticide grade methanol (two flasks per treatment). The experimental units were run for 14 days in the dark at room temperature under optimal aeration and suction.

The perfusates were analyzed initially and every four days thereafter for herbicide degrading microorganisms employing a differential medium (19) modified from Thornton's agar. Each of the herbicides being tested was the sole carbon source in the growth media. A 0.1 ml sample from each perfusion flask was plated on the
appropriate differential medium. The appearance of red or blue colonies allowed for the identification and subsequent culturing of the desired microorganisms.

Disposal Pit Inoculation

Isolates of herbicide decomposing bacteria were maintained on fresh plates containing 200 mg L\(^{-1}\) of the appropriate herbicide. One to two isolates of each type of herbicide decomposer were grown in 1 L of Thorton's medium and used to inoculate each disposal pit prior to herbicide additions. Samples of the inoculum were plated on the differential media as previously described for an initial herbicide decomposer count.

Loading of the Disposal Pits

On October 4, 1985, each disposal pit was loaded with 4.7 L Astrex (40.8% a.i.), 4.4 L Bladex 4L (43% a.i.), 1.9 L Dual 8E (86.4% a.i.), 1.6 L Lasso (45.1% a.i.), and 1.7 L Sutan+ (6 lb/gal a.i.). The water level was maintained at approximately 51 cm in the alkaline pit and 40 cm in the acid pit.

A second inoculation and herbicide loading of the disposal pits were made on November 7, 1985. Each pit received 1 kilogram (kg) Lexone DF (75% a.i.), 0.4 L Prowl (42.3% a.i.), and 4.8 L Treflan (41.2%). Due to extreme amounts of rainfall throughout November, the pump was removed from the alkaline pit on November 12 and from the acid pit November 17.

Sampling and Biological/Chemical Analyses

Composite water samples were taken from each PVC pipe at a schedule of 1, 4, 7, 10, 13, 16, 19, 22, 25, and 28 days. Duplicate 125 ml samples were collected in sterile plastic bottles. Total bacteria counts, herbicide decomposer counts, herbicide concentration, and pH were determined for each sample.

Total bacteria counts were made by plating the water samples on Thorton's medium. Herbicide decomposer counts were determined by employing the various differential media as previously described.

The pH of the water samples was determined with a Fisher accumet pH meter, model 620.

To extract the herbicides, ten milliliters of sample were added to a 50 ml Erlenmeyer flask followed by the addition of 20 ml diethyl ether. The mixture was shaken for 5 min on a rotary shaker and transferred to a 250 ml separating funnel and allowed to stand for 15 min. The water layer was then removed and the ether fraction was collected for analysis via gas-liquid chromatography.

For the determination of each herbicide, a 1 microliter (\(\mu\)l) sample was injected into a Varian 3700 series gas chromatograph equipped with a flame ionization detector. Nitrogen was used as the carrier gas (flow rate 30 ml min\(^{-1}\)) while air (flow rate 300 ml min\(^{-1}\)) and hydrogen (flow rate 30 ml min\(^{-1}\)) provided for flame ionization. The herbicides were separated on a 1.8 m x 4 mm glass column packed with PT 5% SE-30 on Chrom W-HP, 80 to 100 mesh (Alltech Associates, Deerfield, IL). The column temperature was maintained at 180 C while the injector temperature was maintained at 210 C and the detector temperature was set at 230 C. Range and attenuation setting was set at 4 x 10\(^{-6}\). A 200 microgram per milliliter (\(\mu\)g ml\(^{-1}\)) standard of each herbicide was used as a reference. The concentration of each herbicide in the water samples was then determined as described by Standard Methods of Water Analysis (3).

Statistical Analysis

An analysis of variance and trend analysis of total and herbicide decomposer bacteria counts over time were conducted. Percent decay curves were determined for applied-herbicides. Statistical analysis was performed by an IBM 370 computer using the SAS statistical package.

RESULTS AND DISCUSSION

Disposal of Corn Herbicides

Total bacteria and average herbicide decomposer population counts for corn herbicides applied to the alkaline and acid disposal systems are summarized in Figures 3 and 4, respectively. Total bacteria numbers represent the mean of seven samples. Decomposer counts represent the mean of alachlor-, atrazine-, butylate-, cyanazine-, and metolachlor-
decomposers. The value for each type of herbicide decomposer is the mean of seven samples. Herbicide concentrations (microgram per liter, \( \mu g \, L^{-1} \)) for alachlor + metolachlor, atrazine, and butylate in the alkaline and acid systems are presented in Figures 5 and 6, respectively.

Figure 3. Total and decomposer counts for corn herbicides applied to the alkaline disposal system.

Figure 4. Total and decomposer counts for corn herbicides applied to the acid disposal system.

Figure 5. Corn herbicide concentrations in the alkaline disposal system.

Figure 6. Corn herbicide concentrations in the acid disposal system.

Total and decomposer counts responded similarly to the addition of herbicides to both pits. The population counts initi-
ally increased, with the highest values occurring between days 4 and 10. In the alkaline pit, counts decreased throughout the remainder of the trial with a slight gain at days 25 and 28 for total bacteria and day 28 for decomposer bacteria. In the acid pit, the overall population counts decreased. However, secondary and tertiary peaks occurred at days 16 and 25 for total bacteria and days 22 and 28 for decomposer bacteria. These non-primary peaks may be the result of several influences. The microbial response to desorbed herbicide from the gob material and/or initial breakdown products as new substrates or changes in pH are likely candidates.

According to analysis of variance, total counts were significant at P<0.05 for the alkaline pit and at P<0.1 for the acid pit. Trend analysis showed these relationships over time to be non-significant in the acid pit and quartic (P<0.05) in the alkaline pit. The analysis of variance of decomposer counts was also significant at P<0.05 and quartic over time (P<0.05) by trend analysis.

In the alkaline system, herbicide concentrations generally decreased throughout this first experiment. Decay rates were 3% per day for alachlor + metolachlor (r=0.904), 2.5% per day for atrazine (r=0.951), and 3% per day for butylate (r=1.133). Herbicides in the acid system degraded more readily. Initial concentrations were two fold that of the alkaline system and final concentrations were nearly non-existant. Minor increases (less than 30 ppb) in concentrations are likely due to either inherent error in the sampling and preparation for gas chromatography analysis, or desorption of the herbicide from the gob material. Decay rates were 30% per day for alachlor + metolachlor (r=1.005), 28% per day for atrazine (r=0.897), and 19% per day for butylate (r=0.824).

**Disposal of Soybean Herbicides**

Total bacteria and average herbicide decomposer bacteria counts for soybean herbicides applied to the alkaline and acid disposal pits are given in Figures 7 and 8 respectively. Total bacteria counts represent the mean of seven samples. Decomposer counts are the average of linuron-, metribuzin-, pendimethalin-, and trifluralin-decomposer bacteria. There were seven samples for each specific herbicide decomposer. Herbicide concentrations (mg L⁻¹) of metribuzin and pendimethalin for alkaline and acid systems are illustrated in Figures 9 and 10, respectively.

![Figure 7](image-url)  
**Figure 7.** Total and decomposer counts for soybean herbicides applied to the alkaline disposal system.

![Figure 8](image-url)  
**Figure 8.** Total and decomposer counts for soybean herbicides applied to the acid disposal system.

Total and decomposer counts demonstrated tri-modal curves for both disposal systems with peaks occurring approximately 10 days apart. This cyclic growth pattern is a likely microbial response to the addition of the herbicides. The secondary and tertiary peaks are the result of the microbial population adjusting to new and perhaps
CONCLUSIONS

The load capacity of these systems is dictated by the size of pits constructed. The estimated capital and operating costs (1985 dollars) are $6,000 and $2,500/yr., respectively. Some advantages to these systems are that they are effective on most commonly used herbicides and insecticides in Illinois, and further disposal of residues is not required. Another desirable aspect is that the skills required to construct and maintain either of these systems are available in any agricultural community. Persistence of triazines in the alkaline system, low infiltration rates of waste solutions through the acid material, and necessity of noncorrodable pumps are the disadvantages to these systems. Life expectancy, identification of major breakdown products contained in the systems and of volatilized compounds should be established prior to use of this technology for the treatment and disposal of pesticide wastewater. Current trends in state regulation of in-ground disposal systems may cause them to become obsolete. However, this technology can be readily incorporated into an above-ground system as illustrated in Figure 11.

Figure 9. Soybean herbicide concentrations in the alkaline disposal system.

Figure 10. Soybean herbicide concentrations in the acid disposal system.

Figure 11. Proposed above-ground pesticide disposal system.
REFERENCES


