6-1-1989

Minimizing the Potential for Groundwater Contamination from Agricultural Point Sources

Joseph H. Massey
University of Arkansas, Fayetteville

Terry L. Lavy
University of Arkansas, Fayetteville

John D. Mattice
Unversity of Arkansas, Fayetteville

Citation

Massey, Joseph H.; Lavy, Terry L.; and Mattice, John D.. 1989. Minimizing the Potential for Groundwater Contamination from Agricultural Point Sources. Arkansas Water Resources Center, Fayetteville, AR. PUB139. 40
https://scholarworks.uark.edu/awrctr/213

MINIMIZING THE POTENTIAL FOR GROUNDWATER CONTAMINATION FROM AGRICULTURAL POINT SOURCES

J.H. Massey, T.L. Lavy and J.D. Mattice
Department of Agronomy

University of Arkansas
Fayetteville, Arkansas 72701

Publication No. 139

June, 1989

Technical Completion Report Research Project G-1549-03

Arkansas Water Resources Research Center
University of Arkansas
Fayetteville, Arkansas 72701

AWRRC

Arkansas Water Resources Research Center

Prepared for
United States Department of the Interior

MINIMIZING THE POTENTIAL FOR GROUNDWATER CONTAMINATION FROM AGRICULTURAL POINT SOURCES

J.H. Massey, T.L. Lavy and J.D. Mattice
Department of Agronomy
University of Arkansas
Fayetteville, AR 72701

Research Project Technical Completion Report
Project G-1549-03

The research on which this report is based was financed in part by the United States Department of the Interior as authorized by the Water Research and Development Act of 1987 (P.L. 95-467).

Arkansas Water Resources Research Center
University of Arkansas
113 Ozark Hall
Fayetteville, AR 72701

Publication No. 139
June, 1989

The activities on which this report is based were financed in part by the United States Department of the Interior, Geological Survey, through the Arkansas Water Resources Research Center.

ABSTRACT

MINIMIZING THE POTENTIAL FOR GROUNDWATER CONTAMINATION FROM AGRICULTURAL POINT SOURCES

An activated charcoal filtration unit was designed to remove pesticides from leftover pesticide solutions and rinsates generated under farm-like conditions. The system, fabricated for less than $1400 using readily available components, effectively removed the pesticides atrazine, benomyl, carbaryl, fluometuron, metolachlor, and trifluralin from wastewater generated on the University of Arkansas Agronomy Farm located in Fayetteville, AR. A total of 2253 L of wastewater were treated using the system. Of these 1768 L were generated from washing out the spray tank (rinsates) while 485 L stemmed from leftover pesticide solutions that were mixed, but not applied. Typical initial pesticide concentrations in the wastewater were on the order of 500 to 1000 parts per million (ppm). The final pesticide concentrations remaining after charcoal filtration were generally less than 10 ppm. Approximately 1514 L of wastewater was treated with 23 kg of charcoal before the charcoal was replaced. This resulted in an estimated pesticide loading rate on the charcoal of 0.05 to 0.10 kg pesticide active ingredient per kg activated charcoal. Incubation of alachlor-treated charcoal with a mixed culture of microorganisms resulted in approximately a 30% loss of alachlor after 21 d. These results suggest that on-site degradation of spent charcoal may be a feasible alternative to incineration, however more research is needed to fully determine its potential. A reduced adsorption of methylene blue dye with increasing amounts of trifluralin sorbed to charcoal occurred. Activated charcoal treated with 222 mg/g trifluralin sorbed only 19% of the amount sorbed by the control with no trifluralin present. These results suggest that methylene blue or other dyes might be used to indicate the remaining adsorptive capacity of a charcoal used for removing pesticides from wastewater.

Joseph H. Massey, Terry L. Lavy, and John D. Mattice

Completion Report to the U.S. Department of the Interior, Geological Survey, Reston, VA, June 1989.

Keywords: Groundwater/Pesticides/Rinsates/Activated Charcoal/Adsorption/Biodegradation

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the research assistance of Dr. Briggs Skulman and Mrs. Michelle Fitzgerald. The financial support of the U.S. Department of the Interior, and the Arkansas Water Resources Research Center, University of Arkansas, are also appreciated.

INTRODUCTION

With the 1978 discovery of aldicarb in New York's groundwater (Zaki et al., 1982), the quality of the nation's groundwater has become a national issue. In a nationwide survey, the United States Environmental Protection Agency found that 4% of rural domestic drinking-water wells and 10% of the community drinking-water wells contain detectable amounts of at least one pesticide (EST, 1991). It is still widely debated as to whether point verses non-point source contamination is the major contributor to groundwater pollution. Nonetheless, studies by Habecker (1989) and Long (1989) have shown that point-source contamination via pesticide mixing/loading facilities can be significant. Currently, the contamination of groundwater underlying pesticide mixing/loading sites in Arkansas is being evaluated (Senseman et al., 1990).

Groundwater beneath 18 of 20 pesticide mixing/loading facilities monitored in Wisconsin contained quantifiable levels of pesticides (Habecker, 1989). Forty-three of fifty-six mixing/loading facilities monitored in Illinois were found to have groundwater containing trace-levels of at least one pesticide (Long, 1989). In both of these studies, groundwater contamination was partially attributed to the improper disposal of leftover pesticide solutions and contaminated rinse water generated from washing pesticide application equipment.

In Arkansas there were more than 250 commercial pesticide applicator licenses issued by the State Plant Board in 1989 (ASPB, 1989). These commercial applicators included both aerial and ground application operations. Given this large number of commercial pesticide mixing/loading sites, combined with those located on private farms, agricultural research stations, and at urban lawn-care operations, significant contamination potential exists in Arkansas from improper pesticide waste disposal. While widespread contamination of Arkansas' groundwater by agricultural pesticides has not been observed, the herbicides alachlor, atrazine, and metolachlor were detected in a well once used as a water source for mixing pesticides (Cavalier et al., 1989). Proper treatment of pesticide-laden wastewater could significantly reduce or eliminate the contamination source associated with the improper disposal of pesticide wastes at mixing/loading facilities.

A. Purpose and Objectives

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

B. Related Research and Activities

There are several federal regulations that pertain to pesticide waste disposal. In addition to the Clean Water Act of 1977, the Resource Conservation and Recovery Act of 1976 regulates the disposal of wastes to assure minimum effects on human health and the environment. This act pertains to any pesticide which might create a hazard if not properly disposed. Moreover, the Federal Insecticide, Fungicide and Rodenticide Act (1947) regulates pesticide commerce and use. Once a pesticide application is made, excess pesticide concentrate, leftover spray solutions, and discarded pesticide containers may be regulated as hazardous wastes. Through this legislation, there exist legal ramifications that may result from the improper disposal of pesticide wastes. These are in addition to a host of environmental and health problems that might occur.

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

In each of these systems, pesticides were filtered from wastewater using granular activated charcoal. After filtration the wastewater could be reused as a diluent or returned to the environment with minimal impact. Some consider activated charcoal adsorption to be the "accepted best technology" for pesticide waste disposal purposes (Environment Today, 1990). Although activated charcoal has proven to be quite effective at removing pesticides from wastewater, more research is needed in order to optimize the charcoal adsorption process.

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

A potential disposal treatment involves the degradation of sorbed pesticides by microorganisms. The degradation of organic pollutants in soil is frequently the result of microbial activity. However, the sorption of some organics by soil constituents has been found to reduce the availability of organic molecules to microorganisms and, therefore, slow the rate of degradation (Miller and Alexander, 1991). Given that the typical diameters of activated charcoal micropores range from 10 to 1000 angstroms and that most bacterial cells have diameters ranging from 5000 to > 10,000 angstroms, it is probable that bacteria cannot physically migrate into the micropore structure of activated charcoal (Perrotti and Rodman, 1974). For this reason it is not clear that microbial degradation of pesticides sorbed to spent charcoal will be feasible. However, successes with soil (Kilbane et al., 1983; Somich et al., 1990) and peat moss (Mullins et al., 1989) suggest that microbial degradation of sorbed pesticides might be possible.

Simple techniques for assessing the adsorptive capacity of activated charcoal are needed to ensure the proper filtration of pesticide wastes. Although a thin-layer chromatography method was developed to detect pesticides in filtered effluent (Dennis, 1988), this is likely impractical for use under farm conditions. The use of dyes to assess the adsorptive capacity of activated charcoal has proven to be helpful in many industrial operations. To qualify for use, the dyes should have adsorptive characteristics similar to those of the chemicals being adsorbed (Hassler, 1974). Thus, the ability of a dye to reflect the remaining adsorptive capacity of a charcoal being used to treat pesticide-laden wastewater must be determined.

METHODS AND PROCEDURES

A. Activated Charcoal Filtration Unit

A schematic diagram of the activated charcoal filtration unit (ACFU) is given in Figure 1 and a parts listing in Table 1. The system was fabricated using readily available materials and was simple in design. At the heart of the ACFU was a 0.23 m x 1.02 m fiberglass tank filled with 23 kg of Cullar-D granular activated charcoal. Table 2 provides properties of Cullar-D granular activated charcoal (GAC). The 1/2 hp electric centrifugal pump

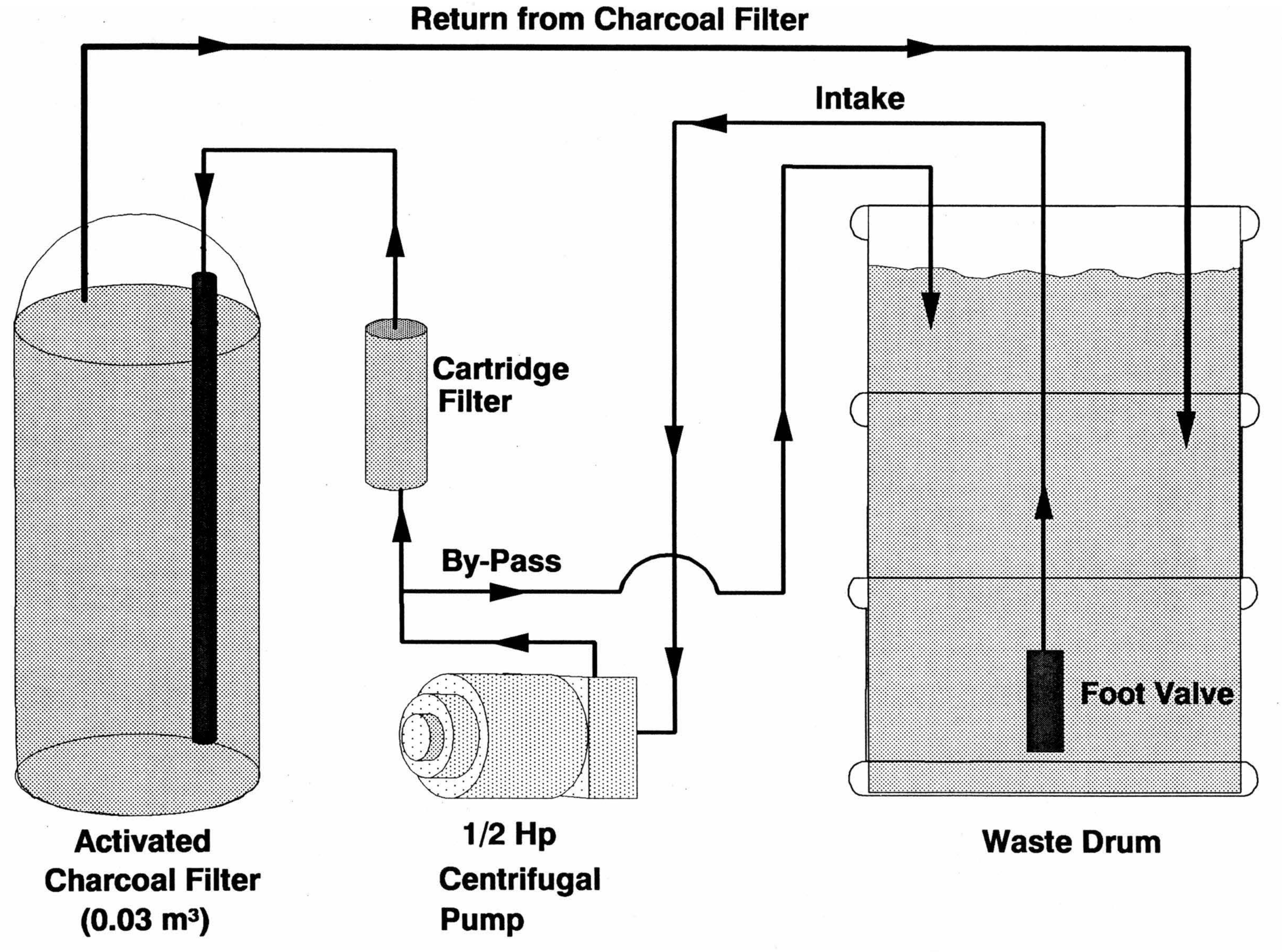

Figure 1. Schematic diagram of the activated charcoal filtration unit

Table 1. Parts listing for the activated charcoal filtration unit.

(1)	1/2 hp electric motor w/centrifugal pump
(1)	9" x 40" fiberglass tank with brass fittings
(1)	1 1/4" foot valve
15′	3/4" (i.d.) high pressure hose
(1)	10" filter cartridge
(1)	1 3/4 x 3/4" SxT bushing reducer
(2)	1 1/4 x 1" SxT bushing reducer
(4)	3/4" nylon hose barb
(6)	stainless steel hose clamps
(1)	1 1/4" PVC male adapter
(1)	3/4" high-impact ball valve
(1)	3/4" pipe x hose thread adapter
(1)	1" male adapter
(1)	1 x 3/4" all-thread
(1)	1" PVC Tee
(1)	3/4 x 1" SxT bushing adapter
(1)	3/4" pipe x hose thread adapter (female)
(1)	low-pressure cut-off switch for electric motor
(1)	manual reset switch for electric motor

Table 2. Technical data for DARCO Cullar-D granular activated charcoal.[1]

ORIGIN: Lignite-based

ACTIVATION: Steam activated at 900 to 1000 degrees C

TYPICAL PROPERTIES:

--iodine number (mg/g)	1050
--Abrasion number	80
--apparent density (kg/m3)	470
--effective size (mm)	0.60
--total surface area (m^2/g)	1000 to 1100

[1] Source: Bulletin No. 5312
American Norit Company, Inc.
402 Agmac Av.
Jacksonville, Fl. 32205

produced a flow rate through the charcoal filter of 0.65 L/s. A 0.25 m cartridge filter (30 lm) was placed before the charcoal filter to remove any sediment or debris which might clog the more expensive charcoal filter. By mounting the pump and cartridge filter housing onto a wagon and using a hand-truck for the fiberglass tank, the unit was easily transported to the pesticide mixing/loading site.

Two modifications were made to the electric water pump of the ACFU. First, a low-pressure cutoff switch was added. This safety switch shut the system down when the water pressure dropped below 10 psi. This helped to protect the water pump from damage that might occur if water is denied the ACFU. Also, a manual reset button was installed which would not allow the ACFU to automatically restart after overheating without the assistance of the operator. These modifications increased the level of equipment protection and eliminated the need for constant supervision of the ACFU while in use. The retail cost of the ACFU was about $1400 (1990 dollars). Pesticide-laden wastewaters generated during 1990 on the University of Arkansas Main Agricultural Experiment Station, Fayetteville (MAES) were stored in 208 L teflon-lined drums. The wastewater stemmed from two primary sources: leftover pesticide solutions and rinsates from cleaning out the inside of a tractor-mounted spray rig. No effort was made to collect the leftover pesticides or rinsates located within the boom or nozzles of the spray rig. The leftover pesticide solutions and rinsates were transferred to the containment drums via a hand-gun spray apparatus attached to the tractor-mounted spray rig. Wastewater generated from each individual application was stored separately. Records were kept concerning the pesticide applications made during the 1990 growing season. Visual estimates, to the nearest gallon, were made of the leftover solution and rinsate volumes collected (Table 3).

Prior to filtration, the wastewater was mixed for one minute with vigorous hand stirring using a wooden rod. Next, the waste solution pH was determined using a dip-stick test and solution temperature measured to the nearest C. A 175 mL sample of the waste solution was collected in order to determine the initial pesticide concentration.

During filtration, effluent from the charcoal filter was returned to the containment drum. This recirculation kept the solution well mixed. At various time intervals, subsequent samples were collected from the bulk solution inside the containment drum. As a general rule, filtration was continued until the wastewater was clear and odorless. This typically occurred after 3 to 5 h of filtration.

Analyses of wastewater filtered through the ACFU have been made. The analytical methodologies for some pesticides applied on the MAES, however, were not available. For the herbicide AAtrex Nine-O (atrazine, CIBA-GEIGY Corp., Greensboro, NC 27409) and insecticide Sevin (carbaryl, Union Carbide Co. Inc., Res. Triangle Park, NC 27709) a high pressure liquid chromatography (HPLC) method

Table 3. Technical data for DARCO Cullar-D granular activated charcoal.

Pesticide Name		Formulation	Application	Leftover	Mass in	Rinsate	Total		
Trade	Common	(g/L)	Rate (g/L)	Vol (L)	Soln (g)	Vol (L)	Vol (L)	pH	Temp (C)
Gramoxone	paraquat	180	1.45	11.4	16.5	75.7	87.1	7	26
Furadan +	carbofuran +	480	13.0						
Bicep	atrazine	400	2.18						
	metolachlor	320	2.73	10.0	178.1	161	171	7	24
Furadan +	carbofuran +	480	0.67		28.1				
AAtrex	atrazine	400	2.33	42.0	97.9	72	114	7	25
Treflan	trifluralin	480	3.82	19.0	72.7	75.7	94.7	7	20
Treflan	trifluralin	480	3.82	56.8	216.9	83.3	140.0	7	22
Treflan +	trifluralin +	480	3.82		14.5				
Sencor	metribuzin	75%	1.5	3.8	5.7	75.7	79.7	7	22
Cotoran	fluometuron	192	4.13	30.3	125.2	75.7	106	7	22
Treflan	trifluralin	480	3.82	22.7	86.8	75.7	98.4	6	29
Treflan	trifluralin	480	3.82	18.9	72.3	181.7	200.6	7	30
Gramaxone	paraquat	180	1.45	1.0	1.5	113.6	114.6	NA	NA
Prowl	pendimethalin	480	7.25	15.1	109.5	75.7	90.8	NA	NA
Orthene	acephate	75%	0.80	22.7	18.2	94.6	117.3	NA	NA

continued

Table 3. (cont.)

Pesticide Name		Formulation	Application	Leftover	Mass in	Rinsate	Total		
Trade	Common	(g/L)	Rate (g/L)	Vol (L)	Soln (g)	Vol (L)	Vol (L)	pH	Temp (C)
Poast	sethoxydim	180	1.44	68.1	98.1				
Basagran	bentazon	480	4.29	22.7	97.4				
Fusilade	fluazifop	120	0.80	22.7	18.2	75.7	166.5	NA	NA
Sencor	metribuzin	75%	1.69	56.8	95.8	75.7	132.5	NA	NA
Fusilade	fluazifop	119.9	0.80	30.3	24.2	83.3	113.6	NA	NA
Ambush	permethrin	240	0.56	3.8	2.14	75.7	79.5	7	24
Sevin	carbaryl	50%	6.00	7.6	45.4	68.1	75.7	7	24
Ambush	permethrin	240	1.05	22.7	23.8	106	128.7	NA	NA
Orthene	acephate	75%	5.40	15.1	81.5	75.7	90.8	NA	NA
Ambush	permethrin	240	0.56	3.8	2.1	75.7	79.5	NA	NA

was employed. Due to the high initial concentrations, appropriate dilutions of the samples were made with water. Either 25 or 50 1L of sample were placed in a 25 mL volumetric flask, and the contents diluted with distilled water. The diluted samples were injected directly without further clean-up into an ISCO model 2350 liquid chromatograph equipped with a variable wavelength UV detector. General operational conditions for the HPLC were as follows:

Column: Whatman C-18 Parti-Sphere
Flow rate: 1.5 mL/min
Detector: 220 nm
Chart: 15 cm/h
Sensitivity: 0.01
Peak Duration: 1/3
Flush Time: 20 s
Atrazine Mobile Phase: 40/45/15 MeOH/H20/K buffer (pH 7)
Atrazine Retention Time: 15 min
Carbaryl Mobile Phase: 40/1 AcCN/AcOH in d. H_2O
Carbaryl Retention Time: 3 min

Under these conditions, deflections for a 1 ppm standard of atrazine and carbaryl were 56 and 102 mm, respectively.

Analyses for the herbicides Bicep 4.5L (metolachlor, CIBA-GEIGY Corp., Greensboro, NC 27409) and Treflan EC (trifluralin, Elanco Products Co., Indianapolis, IN 46285) were made by shaking 10 mL of sample with 10 mL of hexane for 1 minute. Dilutions were made of the hexane extract by placing either 25 or 50 1L of the extract into a 25 mL volumetric flask and diluting to the mark with hexane. These dilutions were injected into a Tracor 550 gas chromatograph under the following conditions:

Column: 6′x 2 mm glass column packed with 1.5% SP-2250 and 1.95% SP-2401 on 100/120 Supelcoport

Flow rate: 55 mL/min
Detector (nm): 350 C
Injector: 125 C
Injection Volume: 2 lL
Flow rate: 55 mL/min
Oven temp: 170 C (trifluralin); 220 C (metolachlor)
Retention time: 2.5 min (trifluralin); 5.4 min (metolachlor)

Under these conditions a 1 ppm trifluralin standard averaged 143 mm of deflection while 1 ppm of metolachlor averaged 110 mm of deflection. Recoveries of the trifluralin from water using a hexane partition averaged 111% while that of metolachlor averaged 74% at a 1 ppm fortification level.

External quantification was employed for all determinations using a 1 ppm standard. The peak heights were measured by hand to the nearest 0.5 mm. All data presented were corrected for dilution and partition efficiency when appropriate.

Two additional studies were conducted to evaluate the ability of the ACFU to remove Benlate 50% WP fungicide (benomyl, DuPont Co. Inc., Wilmington, DE 19898) and Cotoran herbicide (fluometuron, CIBA-GEIGY Corp., Greensboro, NC 27409) from wastewater. Synthetic benomyl-wastewater was made by adding 189 g of 50% DF Benlate Fungicide to 189 L of tap water. After mixing, the solution had a pH of 7 and a temperature of 24 C. Samples were collected in 175 mL Nalgene containers prior to filtration and at various times thereafter.

The synthetic fluometuron wastewater was prepared by adding 197 mL of Cotoran 4 L Herbicide to 189 L of tap water. After mixing, the pH and temperature of the solution were found to be 7 and 23 C, respectively.

The HPLC conditions for fluometuron and benomyl were as follows:

Column: Whatman C-18 Parti-Sphere
Flow Rate: 1.5 mL/min
Detector (nm): 225 fluometuron; 285 benomyl
Chart Speed: 30 cm/h
Injection Volume: 50 μL
Mobile Phase: 40/50/10 MeOH/H_2O/K-buffer (pH 7)
Sensitivity: 0.01
Peak Duration: 1/3
Flush Time: 20 s
Retention Time: 7.0 min (fluometuron); 2.8 min (benomyl)

Under these conditions a 0.25 ppm benomyl standard averaged 52 mm of deflection while 1 ppm of fluometuron averaged 40 mm of deflection.

After these and the actual wastewater generated on the farm were filtered, a final sample was collected from each solution. The filtered wastes were then applied to grass-covered areas located on the MAES.

B. Microbial Degradation of Spent Charcoal

A system was designed to aid in determining the feasibility of microbial degradation of pesticides sorbed to spent charcoal. The system was similar to that reported by Wolf and Legg (1984) except than no CO_2 trapping was involved (Figure 2). Air was bubbled through charcoal samples stored in a water bath kept at 33 ± 1 C. The degradation of Lasso 4EC herbicide (alachlor, Monsanto Co., St. Louis, MO 63167) sorbed to activated charcoal was measured by using an analytical rather than a radioisotopic technique.

Alachlor-amended charcoal was prepared to have a concentration

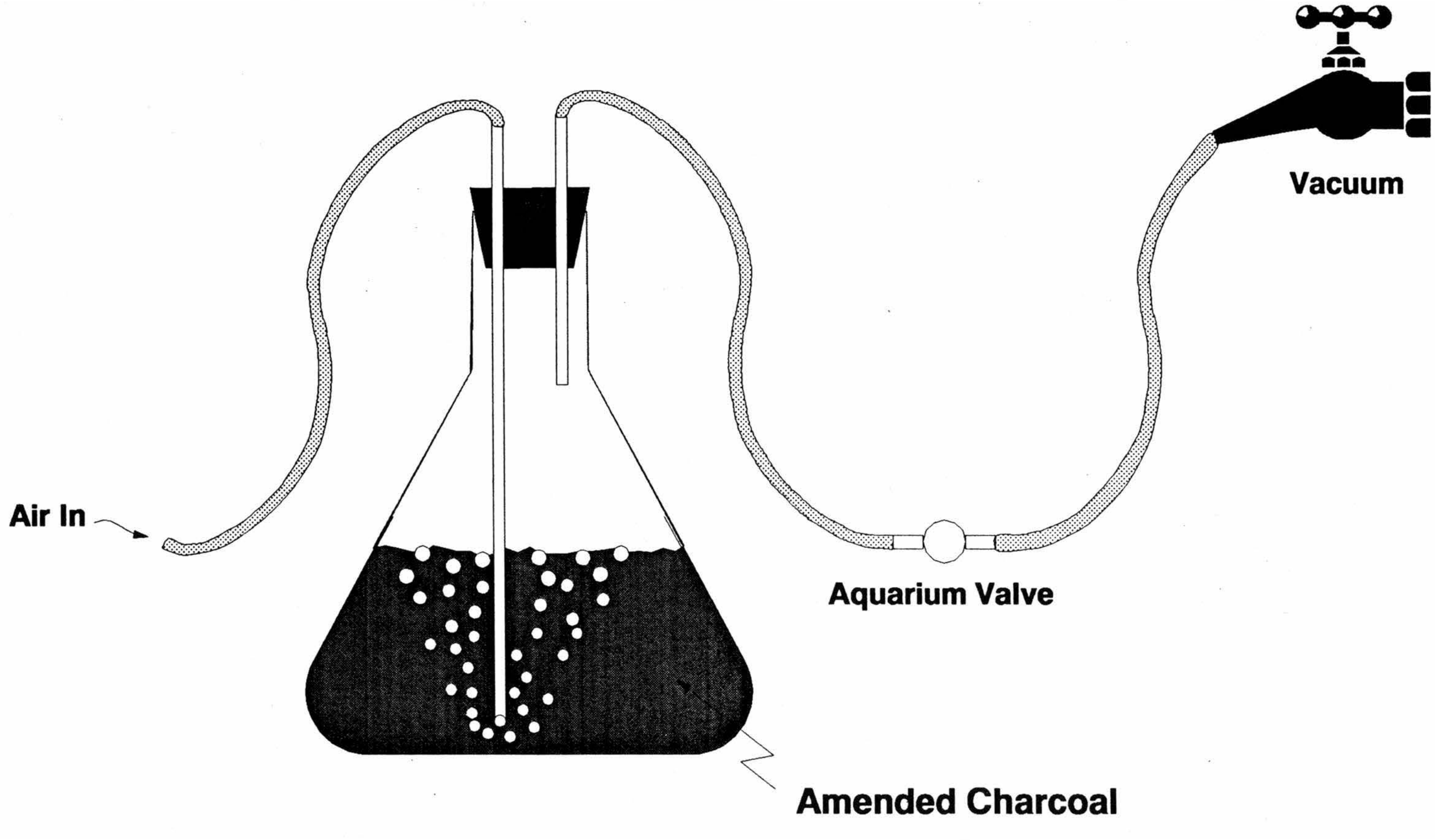

Figure 2. Apparatus used for studying the degradation of alachlor on granular activated charcoal

of 23,707 ± 1816 ug alachlor/g GAC. Approximately 60 g (wet weight) of this treated charcoal was placed into a 125 mL erlenmeyer flask containing 25 mL of nutrient broth solution. The nutrient broth solution, added to aid microbial growth, was made by adding 4 g of BBL Nutrient Broth (Becton Dickinson Microbiology Systems, Cockeysville, MD 21030) to 1 L of distilled water. Next, 1 mL of a 10^5 soil dilution was added to the flask. Six replications of the amended charcoal treatment were employed.

Two controls were also incubated with the amended charcoal samples. One was a charcoal control which contained similar amounts of charcoal, nutrient broth, and soil inoculant but had no alachlor added. These were placed in a 125 mL erlenmeyer flask and served as a check to determine the existence of any interfering compounds that might cause errors in detecting the alachlor molecule. Five repetitions of this control were employed.

The second control sample consisted of 30 mL of water containing 620 ± 89 ppm of alachlor with 25 mL nutrient broth and 1 mL of soil inoculant with no charcoal present. This served to ensure that the incubation conditions were actually suited for microbial growth as well as a test to determine if the microbial degradation of alachlor in solution was possible. Five repetitions of this control were incubated with the amended charcoal samples and the no-alachlor controls.

The moisture inside each flask was replenished daily. On Monday and Thursday of each week, the 16 flasks were sampled for alachlor content. For the charcoal-containing treatments, 1.5 g (moist weight) was placed into a 1 x 12.5 cm glass culture tube and dried under N_2 at room temperature until the charcoal granules were dry. Next, 5 mL of toluene was added, the culture tube capped, and placed into a boiling water bath for 1 h. After boiling, the toluene was decanted into a 10 mL calibrated test tube. The charcoal was thrice rinsed with 1 mL of toluene, the rinses combined in the 10 mL test tube, and the final volume adjusted to 10 mL. Average recovery of alachlor from charcoal (N = 24) was 61 ± 10%. Dilutions of the samples were made when the concentrations fell outside the linear range of the gas chromatograph. The sample weights were corrected for % moisture (determined by drying 1 g moist charcoal 105 to 110 C for 24 h.)

For the non-charcoal water samples, sampling consisted of removing 100 µL of solution from each flask and placing each into a 10 mL volumetric flask. The samples were diluted to the mark with ethyl acetate. The contents were mixed by placing the flasks on a Vortex mixer for approximately 1 min. This technique resulted in the total dissolution of alachlor into the ethyl acetate.

Alachlor concentrations were determined using a Perkin Elmer Sigma 2 gas chromatograph equipped with an electron capture detector. The operating conditions were 210, 400, and 250 C for the oven, detector and injection port, respectively. The column was a

Supelco 15 m x 0.53 mm (i.d.) SPB-608 with a 5:95 CH_4/Ar carrier flow rate of 4 mL/min. Retention time for alachlor was about 3.8 min.

C. Adsorptivity Assays for Used Charcoal

For the first series of tests Treflan herbicide and methylene blue dye (85%, Matheson Coleman & Bell, Norwood, OH) were used. Methylene blue ($C_{16}H_{18}ClN_3S$) is commonly used as a stain in histology and bacteriology, has a molecular weight of 319.85, an absorbance maximum at 668 nm, and a water solubility of 40,000 ppm (Merck Index, 1989).

An adsorption isotherm study involving Treflan herbicide and Cullar-D activated charcoal was conducted using the batch technique described by Webber (1986). To 1 g of oven-dried charcoal, 5 mL of herbicide solution containing 0, 30, 60, 95, 135, 205, or 275 mg trifluralin was added. For each concentration 3 repetitions were used. The 1 x 10 cm glass culture tubes containing the charcoal and solution were capped and shaken at 12 rpm for 5 h. The 5 h contact time was required for the solution concentration to reach equilibrium at room temperature, as determined in a time-series study.

After shaking, the equilibrium solutions were removed, diluted with ethyl acetate as required, and analyzed using gas chromatography with conditions similar to those described in part A. The amount of trifluralin adsorbed per gram charcoal (mg/g) was determined by the difference in the initial and final solution concentrations.

Next the treated charcoal was rinsed with 5 mL of distilled water to remove any trifluralin remaining in solution. To each culture tube was added 5 mL of 0.46 ug/g methylene blue dye. The tubes were capped and shaken at 12 rpm for 3.5 h at 18 ± 1 C. The absorbance of the dye in solution was measured using a Hewlett Packard 8451A Diode Array spectrophotometer. A standard curve, using methylene blue concentrations ranging from 0 to 2.58 μM, was prepared. The concentration of dye remaining in solution was estimated using the standard curve equation ($r^2 = 0.99$)

$$[\mu M] = ((Abs_{664}) + 0.00365)/1.508.$$

PRINCIPAL FINDINGS AND SIGNIFICANCE

A. Field Evaluation of the ACFU

A total of 11 different herbicides and 4 insecticides were treated by the ACFU. Of the 2252 L of wastewater generated on the MAES, 1548 L and 704 L were attributed to herbicides and insecticides, respectively. The most frequently applied herbicide was Treflan while the most common insecticide was Ambush.

About 485 L of leftover pesticide solutions and 1768 L of rinsates were treated. These figures reveal that 79% of the wastewater treated stemmed from the cleaning of the spray tank. There were 3785 L of pesticide solutions mixed during the 1990 growing season. Of these, 485 L (13%) of the pesticide solutions were returned unused to the waste drum. The average volume of the leftover solutions was 23 ± 23 L while that of the rinsates was 87 ± 34 L.

The ACFU effectively removed the commonly applied herbicides atrazine, metolachlor, and trifluralin (Figure 3) and other pesticides including benomyl fungicide, carbaryl insecticide, and fluometuron herbicide (Figure 4). Typical initial pesticide concentrations were on the order of 500 to 1000 ppm while final concentrations after filtration were < 10 ppm. Using the initial and final concentrations and the volume of the wastewater, the amount of pesticide removed from solution was determined. The grams of each pesticide removed from solution were: 215 g atrazine, 83 g metolachlor, 61 g trifluralin, 12 g benomyl, 28 g carbaryl, and 51 g fluometuron. These values do not reflect any of the inert materials removed by filtration which can range from 50 to 98% (w/w) of the pesticide formulation.

Assuming that the other wastewater, which was filtered but not analyzed, had similar initial and final pesticide concentrations, an estimated 0.05 to 0.10 kg of pesticide active ingredient could be adsorbed by each kg of GAC. These values were based on the fact that after 1514 L of wastewater had been filtered, the 22 kg of GAC no longer effectively removed pesticides from solution. At this point the spent GAC was replaced with new GAC and the adsorbing performance of the ACFU was reestablished.

Other than adsorption onto GAC, there exist at least two other

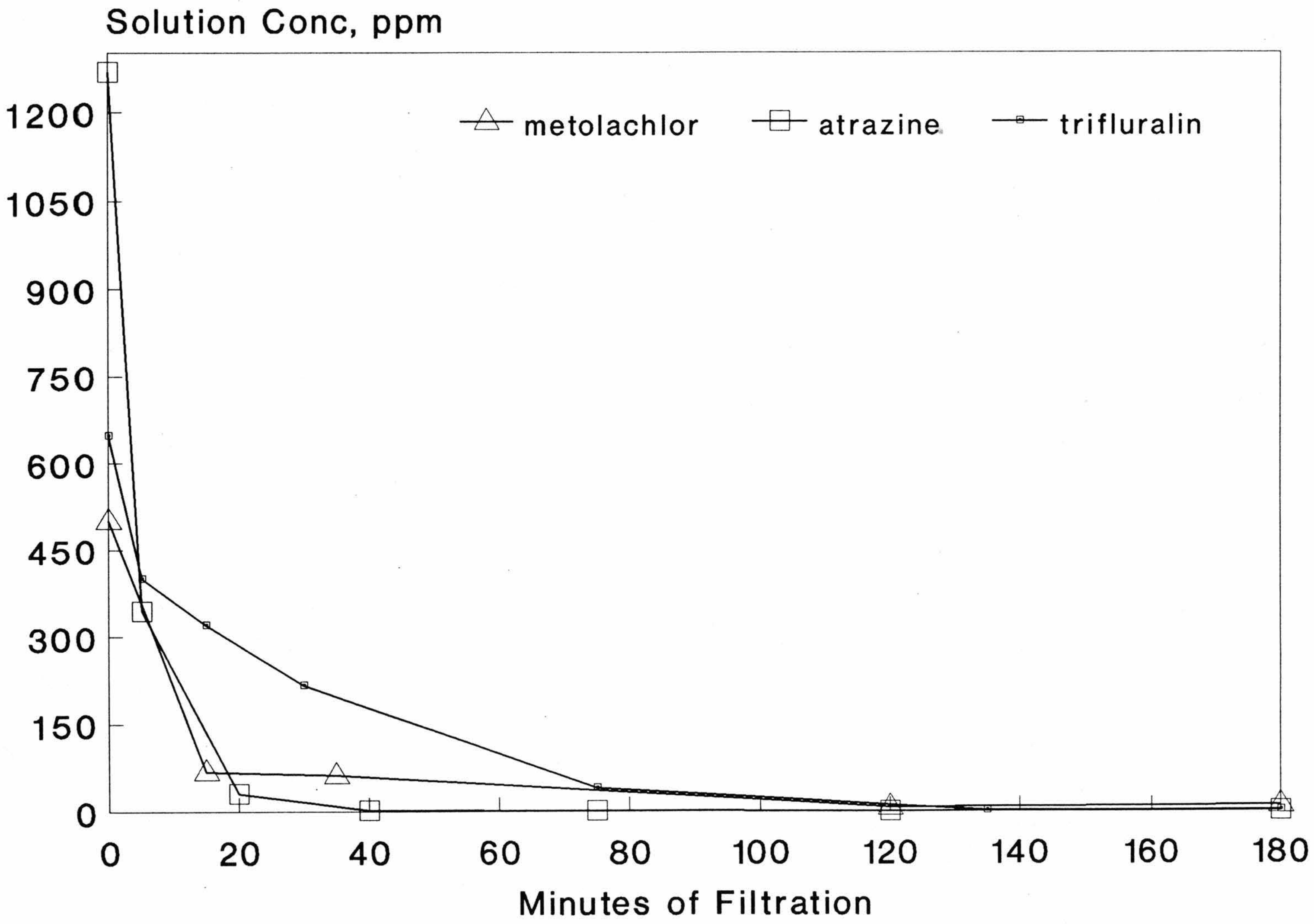

Figure 3. Removal of three herbicides from wastewater via activated charcoal filtration

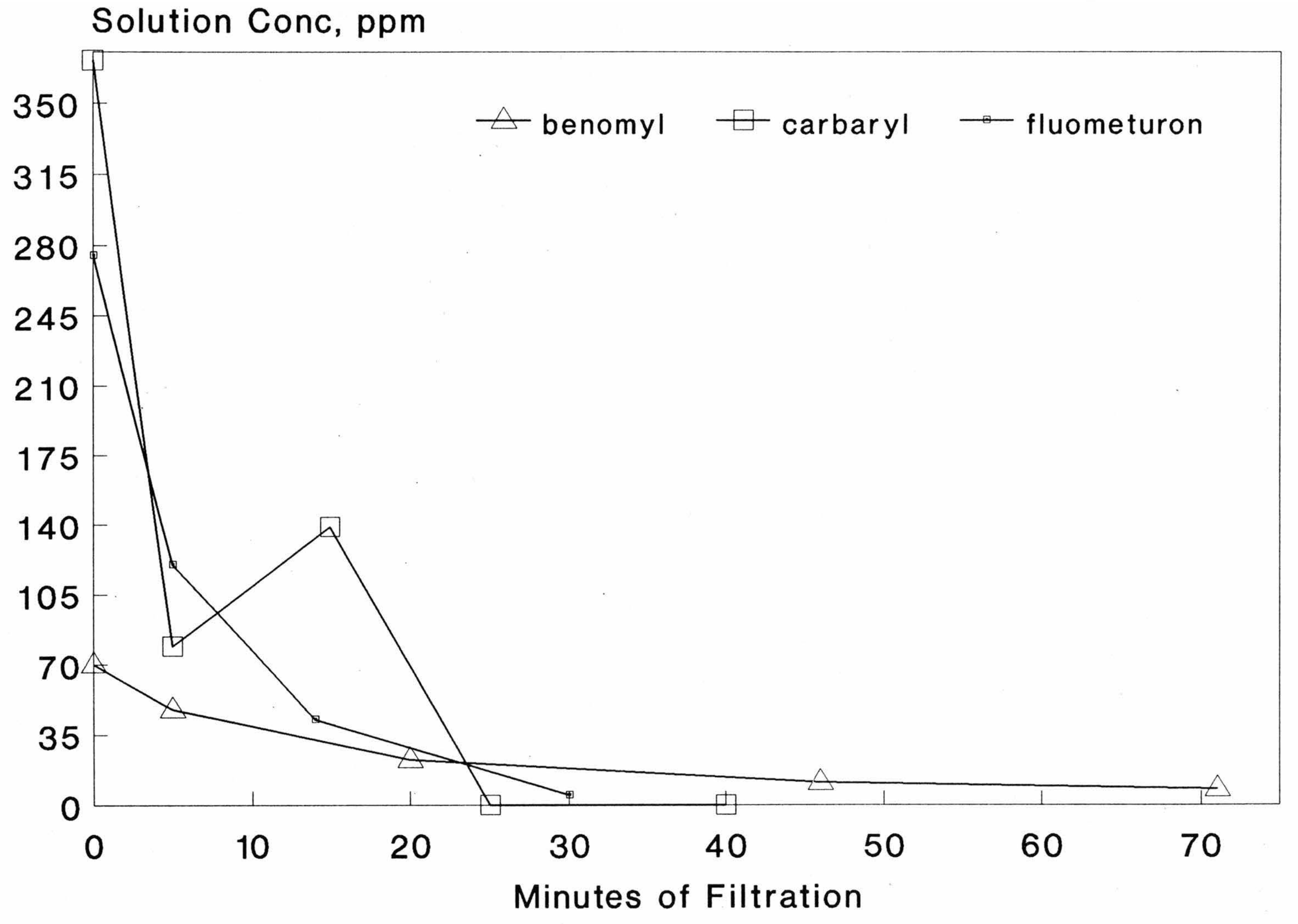

Figure 4. Removal of various pesticides from wastewater via activated charcoal filtration

avenues for pesticide dissipation not explored in this study. First, some of the pesticide may be either trapped or adsorbed onto the 30 um filter used to protect the GAC filter. Wettable powder and other solid-carrier pesticide formulations (e.g. AAtrex Nine-O) will be trapped to some degree by the filter. Moreover Treflan, formulated as an emulsifiable concentrate, was seen to sorb onto the paper filter. This was evident by the bright yellow stains produced on the filter. These contaminated filters will have to be disposed of in a proper manner.

Volatilization from solution is a potential avenue of dissipation for some pesticides such as Treflan. Controlling factors of volatilization from water include the solubility, molecular weight, and vapor pressure of the pesticide and the nature of the air-water interface through which it must pass. The turbulence generated during the recirculation of the wastewater would likely enhance volatilization. The Henry's Law Constant or air-water partitioning coefficients are often used to predict the direction and rate of vapor exchange between water and the atmosphere (Fendinger and Glotfelty, 1988).

The coagulation of a non-adsorbed material in a batch of wastewater was required once. A 208 L solution of Basagran (bentazone, BASF Wyandotte Corp., Parsippany, NJ 07054) Fusilade (fluazifop-p, ICI Americas Inc., Wilmington, DE 19897) , and Poast (sethoxydim, BASF Wyandotte Corp., Parsippany, NJ 07054) herbicides contained a milky-white material which remained in solution after

5.5 h of filtration. This material, believed to be a crop oil adjuvant, was successfully coagulated with 0.23 kg of alum (aluminum sulfate). The supernatant was clarified following the alum treatment. Other common coagulants include lime, ferric chloride, ferric sulfate, copperas, and sodium aluminate (Faust and Aly, 1983). Under less controlled situations, such as where a rinse pad is used to collect the rinsates, clay and other debris would likely be present in the wastewater. Coagulation of this suspended material prior to GAC filtration would increase the effectiveness and longevity of the GAC and would be highly recommended under these conditions.

B. Microbial Degradation of Spent Charcoal

Figure 5 presents data generated during the incubation of alachlor amended charcoal under conditions which should favor microbial growth. The degradation of alachlor on charcoal appeared to occur at a steady, slow rate. After 21 d of incubation slightly less than 70% of the originally applied alachlor still remained on the charcoal. The degradation of alachlor in the water control samples was variable and suggested little to no degradation until about day 14. Losses of alachlor by siphoning out of the sample flask during the last two sampling dates is a possible explanation for the sudden drop in concentration. Generally, no interfering substances were produced in the charcoal control samples.

These data are preliminary and no significant generalizations can yet be made from them. However, that the degradation of

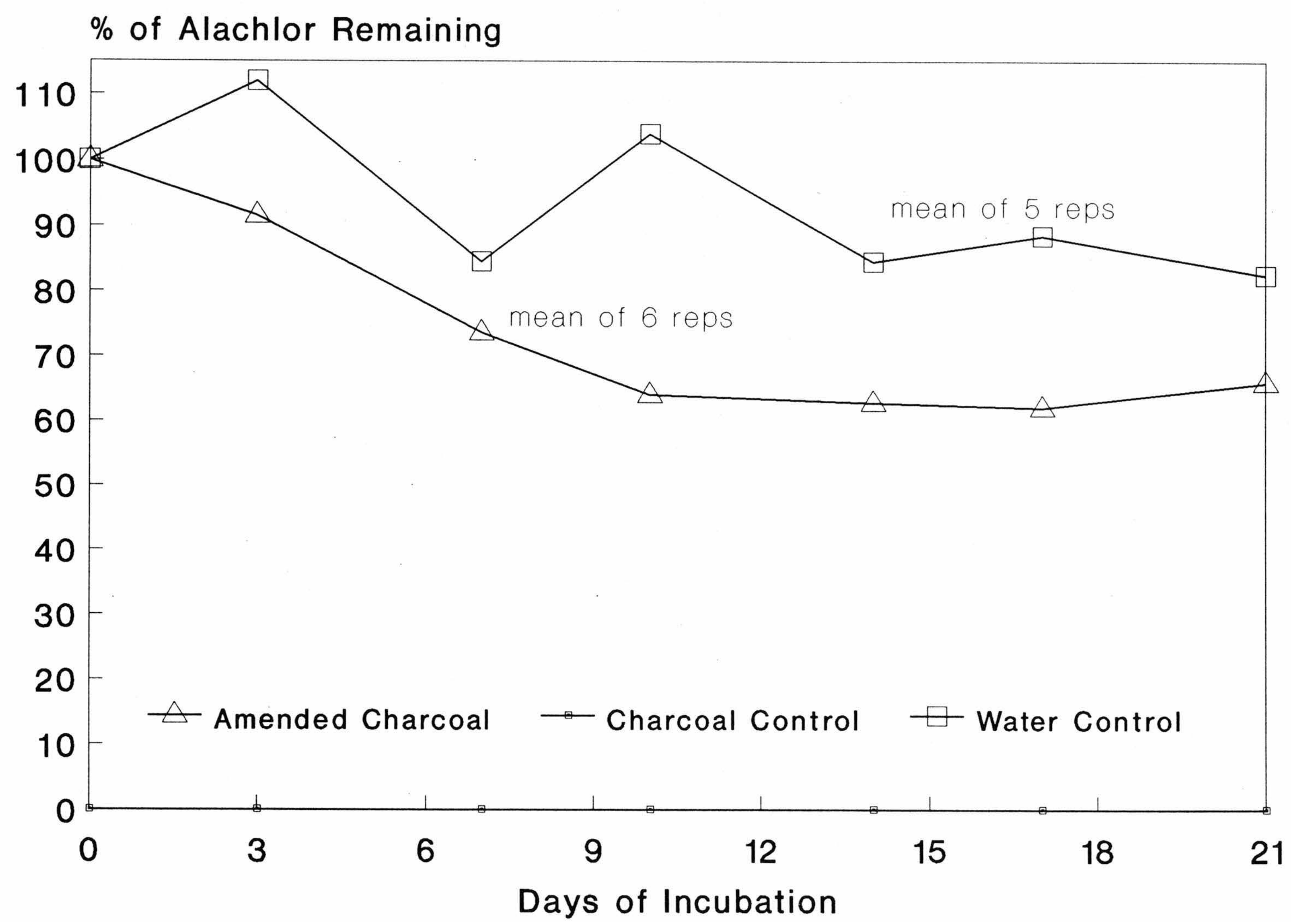

Figure 5. Degradation of alachlor sorbed to Cullar-D activated charcoal

alachlor appeared to be enhanced by the charcoal is similar to results presented by Perrotti and Rodman (1974). In their research Perrotti and Rodman demonstrated a synergistic effect of activated charcoal on total organic carbon removal during the aerobic oxidation of glucose and phenol. The exact mechanism for this phenomenon was not determined.

These results suggest that the disposal of spent charcoal via microbial degradation may be feasible. This study did not address, however, the possibility that some degradation may have occurred via other means such as through chemical reactions or volatilization. Such questions will be addressed in future research.

Until the feasibility of microbial degradation of spent charcoal is more fully determined, the spent charcoal can be successfully disposed through incineration. For this reason, an estimated cost of disposing the spent charcoal via incineration at the Environmental Systems Company (ENSCO) El Dorado, AR plant was calculated. According to Mrs. Holly Wall of ENSCO (504-927-9600), pesticides sorbed to charcoal can be incinerated for $2.10/kg. Transportation costs normally run $25/drum with a $50 stop-fee. An analytical determination of the drum contents is also required ($300/sample).

The 23 kg of spent charcoal generated by filtering 1514 L of wastes would occupy about 1/4 of a 208 L drum. Given a minimum invoice of 1000 dollars, at least 2 drums would be required for economical reasons. At this rate, two drums might handle about 8 seasons worth of charcoal used to treat pesticides applied to a 81 ha farm.

Assuming an apparent density of 470 kg/m^3 (Table 2), a 208 L drum of charcoal would weigh about 97 kg. Two drums would contain 200 kg of charcoal. At $2.10/kg disposal fee, this would cost about $420, plus $100 for shipping and $600 for analytical costs. This results in a total cost of $1120 to dispose of 8 seasons worth of charcoal for a 81 ha farm or 1 season for a 810 ha farm.

In the event that the microbial degradation of pesticides or some other on-site treatment are not viable means by which to dispose of the spent charcoal, these estimates suggest that incineration would not represent a major cost to the larger pesticide application operations in Arkansas.

C. Adsorptivity Assays for Used Charcoal

The adsorption isotherm for Treflan adsorption onto Cullar-D activated charcoal is given in Figure 6. The isotherm appears to be a C-type isotherm which is characterized by an initial slope that remains independent of the concentration of trifluralin solution until the maximum possible adsorption (Sposito, 1984).

The amount of methylene blue adsorbed by charcoal previously treated with various levels of trifluralin is depicted in Figure 7. For the first four trifluralin concentrations, no observable difference in dye adsorption occurred. However charcoal treated with 122 mg/g trifluralin adsorbed only 77% of the dye adsorbed by

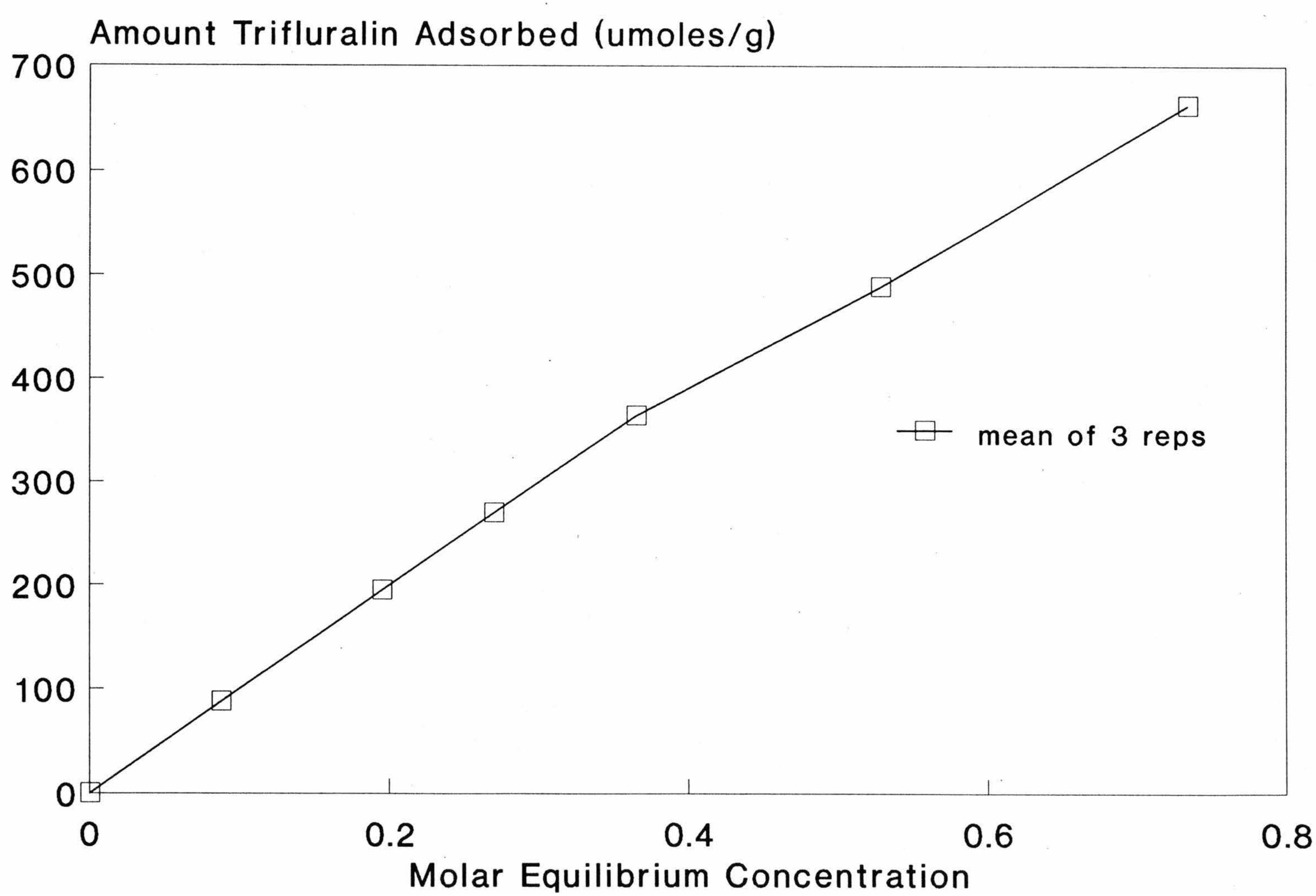

Figure 6. Adsorption isotherm for Treflan EC herbicide on Cullar-D activated charcoal

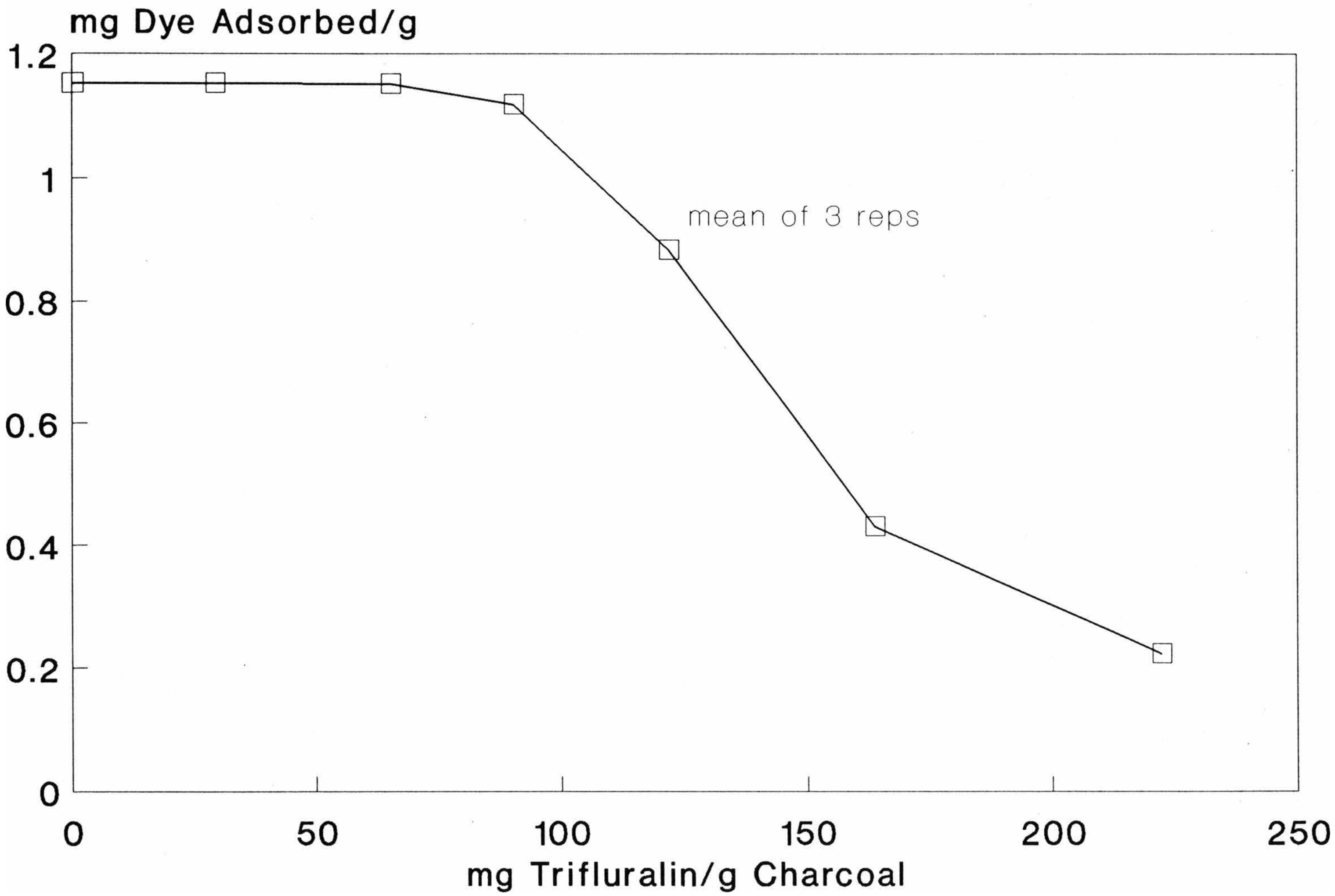

Figure 7. Adsorption of methylene blue dye on Cullar-D activated charcoal treated with Treflan EC herbicide

the control (Table 4). With the addition of 222 mg/g trifluralin the charcoal adsorbed only 19% of that adsorbed by the control.

These results suggest that it might be feasible to use methylene blue dye to assess the remaining pesticide capacity of charcoal. Ongoing research is assessing the adsorption of seven additional dyes onto charcoal treated with pesticides commonly used in Arkansas agriculture.

CONCLUSIONS

An activated charcoal filtration unit, fabricated using readily available components, effectively removed the pesticides atrazine, benomyl, carbaryl, fluometuron, metolachlor, and trifluralin from leftover pesticide solutions and rinsates. Approximately 1500 L of wastewater could be effectively treated using 23 kg of Cullar-D activated charcoal before replacement was necessary.

The disposal of spent charcoal via microbial degradation is still under investigation. Results from an alachlor incubation study suggest that this may be a feasible alternative to incineration but more research is required to fully determine the treatment's potential.

The ability of methylene blue dye to reflect differing amounts of adsorbed trifluralin on charcoal is promising. It is likely that this or other dyes could be used to indicate when the capacity of activated charcoal is exhasted and, therefore, when it is necessary to replace the charcoal filter.

Table 4. Methylene blue dye adsorption on Cullar-D activated charcoal treated with Treflan EC herbicide.

Sample[1] absorbance (664 nm)	Estimated dye concentration (μm)	Dilution factor	Corrected dye concentration (μm)	Adsorbed[2] dye concentration (μm)	Amount[3] dye adsorbed (μ moles)	Amount[4] dye adsorbed (mg/g)	Amount[5] trifluralin adsorbed (mg/g)
0.0477	0.0340	1.67	0.0567	721	3.60	1.15	0
0.0467	0.0334	1.67	0.0556	721	3.60	1.15	29.3
0.105	0.0720	10	0.720	720	3.60	1.15	65.2
0.0620	0.0435	500	21.8	699	3.50	1.12	90.3
0.506	0.338	500	169	552	2.76	0.883	122
1.36	0.904	500	452	269	1.34	0.430	164
1.75	1.16	500	581	140	0.698	0.223	222

[1] Arithemitic means of 3 replications.

[2] 1.44 μM initial dye concentration.

[3] 0.005 L dye solution added.

[4] Molecular weight = 319.85 mg/mmole.

[5] As determined in K_D study.

LITERATURE CITED

Anonymous. 1989. Commercial pesticide applicator licenses issued for 1989 by the Arkansas State Plant Board. Division of Feeds, Fert., & Pest. Little Rock, AR. 11p.

Anonymous. 1990. Are sunny days forecasted for wastewater treatment?. Environment Today. 1(8):1.

Anonymous. 1991. ES&T Currents. Environ. Sci. Technol. **25**(1):10.

Cavalier, T.C., T.L. Lavy, and J.D. Mattice. 1989. Assessing Arkansas ground water for pesticides: Methodology and findings. Ground Water Monitoring J. 9(4):159-166.

Dennis, W.H., Jr. 1988. A practical system to treat pesticide-laden wastewater. In <u>Pesticide Waste Disposal Technology</u>. J.S. Bridges and C.R. Dempsey (eds). Noyes Data Corp. 331 p.

Faust, S.D. and O.M. Aly. 1983. Removal of particulate matter by coagulation. In <u>Chemistry of Water Treatment</u>. Butterworth Publishers, Boston. p. 267-367.

Fendinger, N.J. and D.E. Glotfelty. 1988. A laboratory method for the experimental determination of air-water Henry's Law Constants for several pesticides. Environ. Sci. Technol. **22**(11):1289-1293.

Habecker, M.A. 1989. <u>Environmental contamination at Wisconsin pesticide mixing/loading facilities: Case study, investigation and remedial action evaluation</u>. WI Dept. Agric., Trade, and Consumer Protection, Agric. Res. Mng. Div. 80 p.

Kilbane, J.J., Chatterjee, D.K., and A.M. Chakrabarty. 1983. Detoxification of 2,4,5-trichlorophenoyacetic acid from contaminated soil by Pseudomonas cepacia. Appl. Environ. Microbiol. **45**(5):1697-1700.

Long, T. 1989. <u>Proc. Ill. Agric. Pesticides Conf. '89.</u> Univ. Ill. Coop. Ext. Serv., Urbana-Champaign. pp. 139-149.

Miller, M.E. and M. Alexander. 1991. Kinetics of bacterial degradation of benzylamine in a montmorillonite suspension. Environ. Sci. Technol. **25**(2):240-245.

Merck Index. 1989. Merck and Co., Inc. Rahway, NJ. p.5979.

LITERATURE CITED continued

Mullins, D.E., Young, R.W., Palmer, C.P., Hamilton, R.L. and P.C. Sherertz. 1989. Disposal of concentrated solutions of diazinon using organic absorption and chemical and microbial degradation. Pestic. Sci. **25**:241-254.

Nye, J.C. 1988. Physical treatment options: Removal of chemicals from wastewater by adsorption, filtration, and/or coagulation. In Pesticide Waste Disposal Technology. J.S. Bridges and C.R. Dempsey (eds). Noyes Data Corp. 331 p.

Perrotti, A.E. and C.A. Rodman. 1974. Factors involved with biological regeneration of activated charcoal. AIChE Symposium Series 144 vol.70. p. 316-325.

Senseman, S.A., Lavy, T.L., and T.C. Daniel. 1990. Survey of Arkansas groundwater at pesticide mixing and loading sites. Ark. Agric. Pestic. Assn. Abstract. **29**:15.

Somich, C.J., Muldoon, M.T., and P.C. Kearney. 1990. On-site treatment of pesticide waste and rinsate using ozone and biologically active soil. Environ. Sci. Technol. **24**(5):745-749.

Sposito, G. 1984. The Surface Chemistry of Soils. Oxford Press, New York. pp. 234.

Webber, J.B. 1986. Soils, herbicide sorption and model plant-soil systems. In Research Methods in Weed Science. N.D. Camper, (ed). Southern Weed Science Society. pp. 486.

Wolf, D.C. and J.O. Legg. 1984. Soil microbiology. In Isotopes and Radiation in Agricultural Sciences. M.F. L'Annunziata and J.O. Legg, (eds). Academic Press, New York. p.100-139.

Zaki, M.H., Morgan, D., and D. Harris. 1982. Pesticides in groundwater: the aldicarb story in Suffolk County, New York. Amer. J. Public Health. **72**: 1391-1395.

Zanitsch, R.H. and M.H. Stenzel. 1978. Economics of granular activated carbon water and wastewater treatment systems. In Carbon Adsorption Handbook. P.N. Cherermisinoff and F. Ellerbusch, (eds). p. 215-239.