

Feasibility of Land Application of Soils **Contaminated with** Pesticide Waste as a Remediation Practice

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Feasibility of Land Application of Soils Contaminated with Pesticide Waste as a Remediation Practice

by

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FEASIBILITY OF LAND APPLICATION OF SOILS CONTAMINATED

WITH PESTICIDE WASTE AS A REMEDIATION PRACTICE

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ABSTRACT

The feasibility of cleaning up soil contaminated with pesticide waste by removing it from the contaminated site and applying it to cropland was examined at the Galesville Chemical Company (GCC) in Piatt Co., Illinois. Soil contaminated with the herbicides alachlor, atrazine, metolachlor, and trifluralin was excavated and applied to an adjacent field divided into corn and soybean plots. Soil was applied in amounts equivalent to an application rate of 3, 7.5, or 15 lbs alachlor per acre (lX, 2.5X, and 5X recommended rates, respectively). Dissipation of residues, phytotoxicity to crops and weeds, bioaccumulation in grain, and quality of shallow groundwater were monitored after application of the contaminated soil. These data were compared to data obtained when herbicides were freshly sprayed at similar concentrations. Dissipation of herbicides in plots treated with contaminated soil was slower than previously reported in the literature. No dissipation of herbicides was seen in waste piles 6 months after Some phytotoxicity to soybean was noted as a result of 5X treatments of waste soil, but herbicide freshly applied in the same amounts caused more damage. Greenhouse bioassays with diluted waste soil showed little phytotoxicity to corn or soybeans; however, a very high bioactivity against weed species was found. Residues did not bioaccumulate significantly in grain, and no difference in recovery of herbicides from samples of shallow groundwater was found among treatments.

EXECUTIVE SUMMARY

An estimated 1500 agrochemical retail outlets are scattered throughout Illinois. These facilities provide farmers with a variety of services, including the custom application of fertilizers and pesticides. Incidental spillage of products during handling is common and results in the accumulation of hazardous chemicals in the soil. Chemicals also accumulate in the soil when tanks are rinsed with water and the waste is not disposed of or recycled properly. Few facilities have methods for collecting and recovering spilled materials. Thus, spilled agrochemicals pose a threat of contamination to ground and surface waters or property of adjacent residents.

The current technology for cleaning up pesticide spills and waste is to excavate the contaminated soil and dispose of it in a landfill or hazardous waste site. The costs associated with transporting to and dumping at a licensed waste facility are prohibitive for small agrochemical outlets. Furthermore, land burial of contaminated materials consumes the limited capacity of hazardous waste landfills without guaranteeing degradation of the waste, and potential leakage
from these facilities poses a threat to water resources. Thus, from these facilities poses a threat to water resources. excavation and burial of contaminated soil is not a permanent solution for cleanup. Safe, efficient, and cost-effective alternatives are therefore needed.

This project was designed to investigate the feasibility of cleaning up a site at the Galesville Chemical Co. by excavating the contaminated soil and applying it to adjacent cropland. We hypothesized that the pesticide contaminants, which were commonly used herbicides, would naturally dissipate without harming the soybean or corn crop.

Four criteria were developed for judging the feasibility of land application of pesticide waste as a remediation practice:

(1) No significant toxicity to crops would occur after land application;

(2) No significant bioaccumulation of pesticide residues would be found in grain;

(3) The rate of dissipation of pesticide residues in the contaminated soil would not differ from that normally found in soil after pesticides had been applied at recommended levels.

(4) Land application of pesticide-contaminated soil would not cause contamination of shallow groundwater above recommended human health advisory levels.

Experiments were designed to test each criterion. Field assays showed no significant toxicity to corn or soybeans, but bioactivity against weed species was very high. Greenhouse assays indicated that

dilution of pesticide-contaminated soil with uncontaminated soil reduced bioactivity. Grain yields were not affected by application of waste soil, and bioaccumulation of herbicide residues did not occur.

Herbicide dissipation was slow to nondetectable when the contaminated soil was applied to cropland. However, there were large variations in herbicide residues recovered within a plot and between plots. Either improved methods of mixing the contaminated soil prior to its application to cropland were needed, or a much longer monitoring time (e.g., years) was needed to characterize more accurately the longevity of the the herbicide residues.

Herbicides did not degrade when the pesticide-contaminated soil was excavated and left in large piles. On the other hand, no evidence of herbicide migration to groundwater was found as a result of applying contaminated soil to cropland.

We concluded that land application may be a cost-effective and safe method for disposing of pesticide-contaminated soil found at agrochemical retail sites. However, the nature of the pesticide waste and the specific crop must be carefully assessed to prevent phytotoxicity to the crop. Although, the pesticide waste from Galesville Chemical Company was not significantly phytotoxic to corn and soybeans in the field, we were concerned that the rate of dissipation of the contaminants proceeded very slowly, if at all.

The following recommendations for future study were made:

(1) The level of herbicide residues in waste piles and on cropland should be monitored to determine if dissipation eventually occurs.

(2) The leachability of pesticides from waste piles, as opposed to cropland, should be studied.

(3) A standardized protocol for greenhouse bioassays should be developed to assess quickly the safety of a specific mixture of pesticide wastes in soil to be applied to cropland.

(4) The feasibility of using microbial cultures to decontaminate a pesticide-waste site in situ should be investigated.

(5) The monitoring of shallow groundwater quality to evaluate fully the effect of all modes of pesticide application should be undertaken.

1. INTRODUCTION

1.1 Sources of Pesticide Waste in Illinois

The Illinois Environmental Protection Agency (IEPA) has estimated that 1500 agrochemica1 retail outlets are scattered throughout Illinois. These facilities provide farmers with a variety of services, including the custom application of fertilizers and pesticides. Most of these chemicals are handled at one 10adout location where spillage is common and results in the accumulation of hazardous chemicals. The rinsing of equipment also results in pesticide-contaminated discharges that move off-site as runoff. Few facilities have methods to collect and recover these materials. and therefore, spilled agrochemica1s pose a threat of contamination to ground and surface waters and adjacent properties.

The IEPA receives dozens of complaints each year regarding runoff from agrochemical facilities that has killed fish or damaged vegetation on neighboring properties. For example, during 1986 44 commercial agrochemical applicator facilities experienced some type of incident or were the subject of citizen's complaints (Taylor, IEPA interagency memo dated February 9, 1987). Wastewater created by equipment rinsing in loadout areas had moved off-site in runoff during storms. Over 72 spills of pesticides were reported in 1986 that included storage tank leaks, pipeline ruptures, and transportation accidents. Currently. IEPA is working with four facilities where operations have contaminated groundwater, including adjacent domestic drinking water wells.

1.2 Potential Solutions for Remediation of Pesticide Waste

Ideally. pesticide-containing wastewater resulting from agrochemical rinsing and cleaning operations should be either recycled or collected and stored in containers. These procedures would require the construction of state-of-the-art rinsing and recycling facilities. However, collected waste must be disposed of subsequently. Furthermore, pesticide contamination of soil from spills. leaks, and uncontrolled runoff must be remediated by cleanup procedures followed by disposal. Since technology for in-situ treatment is not proven for decontamination of soils and water at spill sites, disposal in a hazardous or special waste facility is the conventional alternative. Unfortunately, the costs associated with transportation and dumping at a licensed waste facility are prohibitive for many agrochemica1 outlets. Furthermore, land burial of contaminated materials may prevent degradative processes, consumes the limited capacity of hazardous waste landfills, and poses a leakage threat to ground and surface water resources. In short, excavation and burial of pesticide-contaminated soil is not a permanent solution for cleanup. Efficient but cost-effective alternative disposal or treatment methods must be investigated.

A potential solution for treating soil highly contaminated with pesticide wastes is to spread the soil on cropland and allow natural dissipation processes to reduce the concentration of contaminants to acceptable levels. Land application would be comparatively inexpensive if transportation costs could be minimized by applying the contaminated soil to nearby cropland. Another advantage of land treatment is the expected biological or chemical degradation of the pesticide after mixing the contaminated soil with the native soil. In contrast, soil taken to a hazardous waste facility is likely to be stored under conditions unfavorable to maximal degradative processes. Furthermore. the volumes of soil to be removed might cause handling problems at waste facilities.

Land treatment of hazardous wastes is defined in the Resource Conservation and Recovery Act (RCRA) as "the hazardous waste management technology pertaining to application/incorporation of waste into upper layers of the soil for the purpose of degrading, transforming, and/or immobilizing hazardous constituents contained in the applied waste." Land application of sewage sludge has been intensively studied and reported in the scientific literature; however, land application of
pesticide-contaminated materials has been given little attention. There pesticide-contaminated materials has been given little attention. was a recent report that investigated under laboratory conditions the feasibility of land treatment of creosote/pentachlorophenol wastes. but field studies of feasibility have not been attempted (Sims et a1. 1987). Winter1in et a1. (1986) investigated the land application of composted cotton gin wastes containing pesticide residues. They concluded that pesticide residues were very low to undetectable after incorporation of the waste into the soil.

Before a large scale program for land applying pesticide and fertilizer-contaminated soils from agrochemical spills can be implemented, several important variables must be investigated. First, most land that would be suitable as a candidate for land treatment of pesticide waste is cropland. Thus. potential problems of phytotoxicity to crops must be elucidated. Even though most of the contaminants that would be found at facilities in Illinois are registered for either soybeans, corn, or both crops, concentrations in waste material may be quite high. Also, additive effects at low herbicide levels are unknown. Second, the rate of dissipation and translocation of the pesticides must be studied to ensure that normal processes of biodegradation or chemical degradation are occurring in the presence of relatively high chemical and nutrient concentrations. Availability of the contaminants to surface runoff or subsurface leaching should be studied to prevent contamination outside the land treatment area. Third, harvested grain must be analyzed to determine if pesticide residues exceed established tolerances.

If pesticides at high concentrations in contaminated soil are found to behave similarly to pesticides freshly applied at lower, conventional amounts, then land spreading (i.e., land treatment) of contaminated soil is feasible. The following report describes a one-year project for cleanup of soil contaminated with pesticide waste. The project was undertaken to complement the Hazardous Waste Research and Information Center's objective of developing treatment and remediation methods for reducing the volume and toxicity of hazardous waste and to mitigate existing contamination problems.

1.3 Problem Background

We assessed the feasibility of cleaning up soil contaminated with pesticide waste by applying it to nearby cropland. At the suggestion of the IEPA, we investigated a contaminated site at the Galesville Chemical Company (GCC) in Piatt Co., Ill. An adjacent area (approximately 55 yds by 15 yds) on railroad right-of-way property was formerly used as a discharge site for pesticide wastewater from rinsing and cleanup operations. IEPA had found this site to be devoid of vegetation IEPA had found this site to be devoid of vegetation and highly contaminated with the herbicides alachlor, atrazine. metolachlor, and trif1uralin. Analyses of contaminated soil taken from within an area measuring 100 yds by 15 yds showed the presence of alachlor in concentrations ranging from 24,000 ppm at a 3-inch depth to 1100 ppm at a 1-foot depth. Our analyses of a composite sample collected from the upper 2 ft of the soil profile near the former discharge point indicated average concentrations of 100 ppm alachlor, 62 ppm atrazine, and 20 ppm meto1achlor (triflura1in was not checked). Surface residues of herbicides after normal application practices should be less than 5 ppm.

In addition to the contamination of soil along the railroad right-of-way, IEPA determined that ditches in the community of Galesville were contaminated with all of the herbicides at ppm levels. A house well just west of the discharge site was contaminated with the herbicides alachlor (14 ppb), atrazine (47 ppb), and metolachlor (120 ppb). Alachlor is currently under special review by the u.s. EPA as a suspected carcinogen in humans.

IEPA ordered GCC to change its tank rinsing facilities and excavate the contaminated site along the railroad right-of-way. GCC complied with the former request by building a state-of-the-art wastewater collection and storage system. However, excavation of the pesticide-contaminated soils would require long-term storage in a landfill. This type of remediation effort would have been very costly to GCe, and long-term storage of the contaminated soil would not have solved potential toxicity problems. With collaboration from IEPA. we designed an experiment to test the cleanup potential of applying the contaminated soils to adjacent cropland. Thus, we were testing the feasibility of natural degradation processes for treating the pesticide waste.

1.4 Experimental Strategy

Our strategy for testing the feasibility of land applying waste was to compare the dissipation of herbicides and their phytotoxicity in soil derived from waste piles at GCC with the dissipation of herbicide freshly sprayed at similar application rates. We were also interested in comparing bioaccumulation of residues in grain and possible translocation of herbicides to groundwater. Thus, a major criterion for assessing feasibility would be differences in environmental and biological behavior between pesticides that had remained in soil as a concentrated waste for years and pesticides that had been freshly sprayed pesticides.

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2. GOALS AND OBJECTIVES

Our goal was to determine the feasibility of decontaminating pesticide spill sites at agrochemica1 retail outlets by removing and land-applying contaminated soils. Several objectives were designated that would determine the feasiblity of this method of waste-site remediation and the optimal rates of application. The optimal rate would minimize the space needed for land treatment, not cause phytotoxicity to the crop, not contaminate water resources, and not leave illegal pesticide residues in harvested grain. Therefore, the objectives of this study were as follows:

(1) To determine if crop phytotoxicity occurs when waste soil containing high levels of herbicides is applied to corn or soybean fields;

(2) To determine if dissipation rates of pesticides from contaminated soils and their translocation to shallow groundwater are similar to those of conventionally applied pesticides;

(3) To monitor residues of pesticides in harvested grain for violations of legal tolerances.

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3. METHODOLOGY

3.1 Excavation of Contaminated Soil

An area measuring 210 ft by 45 ft along the railroad tracks immediately east of GCC was designated by the Illinois EPA as the site to be excavated (Figure 1). In previous years, GCC had used the east side of the tracks as a discharge site for pesticide rinse water by pumping wastewater under the track onto the right-of-way land. As a result of localized flooding and ponding of water, herbicide contamination had spread from the discharge point across the site. Based on earlier IEPA monitoring, three zones were designated for excavation within the site (Figure 1). Zone A had the highest residues of herbicides and measured 45 ft by 30 ft around the discharge point. Zone B was 90 ft by 15 ft on either side of Zone A and had significantly less residues. Zone C encompassed an area 90 ft by 30 ft on either side of Zone A and lay on the western edge of Zone B. Residues were not characterized in this zone. An agreement was made between GCC and IEPA to excavate zones A, B, and C to a depth of 3 ft, 2 ft, and 0.5 ft, respectively.

Excavation was subcontracted by GCC and began on 21 May 1986. Soil was removed using bulldozers and a dredge scoop and placed into one of 4 piles (Figure 1). Soil from the top 2 feet of Zone A was placed into a pile designated as no. 2. The 3rd foot of soil from Zone A was placed into pile no. 3. A bulldozer was used to displace the soil from Zones B and C into piles no. 1 and 4 on the south and north sides, respectively, of Zone A. The contaminated soil in the piles was referred to as "waste-pile soil."

After excavation, the site was backfilled with soil from an adjacent fence row that was at a higher elevation and not considered to be contaminated.

3.2 Sampling and Analysis of Waste-pile Soils

Waste-pile soils were sampled twice before application (22 and 27 May) to determine appropriate loading rates on adjacent cropland. Waste piles were sampled again in November to determine whether residue concentrations had declined as a result of mixing and aeration of soil throughout the summer. Sampling on May 22 involved taking random 2-inch diameter soil cores at the surface and at a depth of about 1 foot. On 27 May and in November, a 2-inch diameter bucket auger was used to sample the piles to a maximum depth of 4-feet. Soils were analyzed for herbicide concentrations within one week after collection. Average herbicide concentrations recovered from pile no. 2 during the May collections were used to calculate the weight of soil needed to give the desired concentrations of herbicides in the crop plots.

Figure 1. Schematic diagram of waste discharge site and waste-pile locations at Galesville Chemical Co.

3.3 Description of Cropland

A 4-acre site adjacent to the railroad right-of-way and to the north of the waste piles was divided into two 2-acre fields for land application of the waste pile soil. The southern-most field was designated for corn production and the northern-most field was designated for soybean. The entire field was planted to corn in 1985, and it had been chisel plowed the previous fall.

TWo soil types were present in the experimental field: Ipava silt loam (fine. montmori110nitic. mesic, Aquic Argiudo11s) and Sable silty clay loam (fine silty mixed. mesic Typic Haplaquo11s). Natural soil drainage class is poor for both soil series. Organic matter content ranges from 4-5% and 5-6%, respectively in the Ipava and Sable soils. Parent materials consist of >60 inches of loess over loamy glacial outwash containing sand and gravel lenses. The field gently sloped (~2%) from north to south.

3.4 Experimental Design

Initially, six treatments were randomly assigned to each of 4 blocks numbered I through IV (Figures 2,3). Block I. which was adjacent to railroad right-of-way, was highly compacted owing to vehicular traffic. This block was dropped from the experiment owing to a lack of time necessary to till and loosen it. Each treatment replicate consisted of a 1600 sq ft plot (40 ft by 40 ft) surrounded by a 20 ft by 20 ft untreated buffer zone. Amounts of waste pile soil and herbicide needed for land application were calculated on the basis of alachlor concentration since it was the most prevalent herbicide contaminant.

The following treatments were tested:

- (1) untreated check $(code = check)$;
- (2) herbicide spray mixture applied at the rate normally recommended for alachlor, 3 lbs a.i./acre (code = 1X-N); the mixture consisted of alachlor, atrazine. metolachlor, and triflura1in in proportion to the concentrations found in the waste piles;
- (3) herbicide spray mixture applied at 15 lbs $a.i./acre$ i.e., 5 times the recommended alachlor rate $(code = 5X-N);$
- (4) waste soil applied at the equivalent a1achlor rate of 3 1bs $a.i./acre$ (code = 1X-S);
- (5) waste soil applied at the equivalent alachlor rate of 7.5 1bs $a.i./acre$ (code = $2.5X-S$);

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Corn Plot

Figure 2. Experimental design of the corn plot.

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Soybean Plot

 (6) waste soil applied at the equivalent alachlor rate of 15 1bs $a.i./acre$ (code = $5X-S$);

3.5 Application of Waste-pile Soils and Herbicide Spray Mixture

On 3-4 June 1986. soil was applied to the appropriate plots from a manure spreader pulled by a tractor. The spreader was filled by using a front loader. The bucket of the front loader was calibrated by weighing the entire loader with and without a full load of soil. Based on the mean alachlor concentration found during the analysis of waste pile no. 2 samples collected 22 and 27 May (Table 1). 1. 2.4. and 4.8 tons of soil were required to vield alachlor rates of application of 3 $(1x-**S**)$. 7.5 (2.5X-S). and 15 (5X-S) lbs active ingredient/acre. respectively.

A herbicide spray mixture was made to contain concentrations of alachlor, atrazine, metolachlor, and trifluralin in proportions similar to those found in the waste pile no. 2 (Table 1). The spray mixture was applied using a boom linked to a backpack sprayer.

After waste-pile soil and herbicide spray applications. all plots were disked twice in two directions to incorporate the pesticides and soil. Buffer zones were also disked. which served to clean equipment and minimize cross-contamination between treatment plots.

3.6 Planting

On 10 June 1986 corn and soybeans were planted across plot treatments and buffers in a north-south direction. Each plot contained 16 crop rows spaced 30 in apart.

3.7 Soil Sampling

3.7.1 Sampling Methods

To compare the dissipation of herbicides derived from waste pile soil with freshly applied chemical, soil from the top 12 inches of the field was sampled in 6-inch increments employing a 2-inch diameter bucket auger. Soil was collected immediately after application and 41. 82. and 140 days later. The auger was rinsed between samples with methanol. For the O-day sampling period. three subsamples of each depth were taken per treatment replicate and analyzed individually to determine the spatial variability of residues. On subsequent sampling days. two subsamp1es per plot were collected from both the 0-6-inch and 6-12-inch soil depths. The subsamples for each treatment within a block were combined in the field. Soils were returned to the lab on the same day, stored at $0-4$ C, and sieved through a screen $(3.5-mm)$ openings) prior to analysis.

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1/ Concentration expressed on the basis of oven-dry soil. Soil moisture was 31.3% and 34.2% in May and November. respectively.

2/ Fisher's Least Significant Difference test with p=0.05.

3.7.2 Storage

Owing to a lack of freezer space, soils were stored at 4°C in a walk-in cold room. To determine the effect of refrigerated storage on degradation and subsequent recovery of herbicide residues, 50-g aliquots of untreated soil from the corn and soybean plots were fortified with a mixture of alachlor, atrazine, metolachlor, and trifluralin (AMAT) at a rate of either 1, 5, or 10 ug/g. At various time intervals, individual samples from each treatment concentration were removed for analysis.

3.8 Well Information

3.8.1 Well Installation and Description

To determine whether the herbicides might leach from the various soil treatments, wells were drilled by an IEPA subcontractor. Wells were located in blocks II and III of the corn plot, and one well was placed in a check plot within block II of the soybean field (Figures 2,3). Two wells were placed in two of the $1X-N$, $5X-N$, and $1X-S$
treatments. Two wells were drilled for the $5X-S$ treatment, but Two wells were drilled for the 5X-S treatment, but the one
lid not vield water above 19 feet and was abandoned. Table in block II did not yield water above 19 feet and was abandoned. 2 describes the depth of each well.

The wells were constructed of polyvinyl chloride pipe containing a slotted screen on the lower end. A sand pack was placed around the well to a depth of several feet above the screen. A one-to-two-foot bentonite seal was placed on top of the sand pack, and the well was encased in grout to the soil surface. A protective metal casing was placed on top of the well head which protruded about 3 feet from the soil surface.

3.8.2 Monitoring

Wells were sampled 2, 41, 85 and 148 days after application of waste soils. A PVC bailer was used to collect a 500 mL sample of water and sediment. Wells were not purged before the first two sampling events because we found that bailing was inadequate to accomplish purging. However, a battery-powered pump became available later in the study and the wells were purged before the 85- and 148-day sampling.

3.9 Phytotoxicity Assays

3.9.1 Field Assays

Assessment of the bioactivity of waste pile-soil treatments was compared to freshly applied herbicide treatments by monitoring crop injury and weed growth. Visual assessment of weed control and crop

Block Number/Crop	Treatment Code $1/$	Water Table Level (ft) 2/	Depth Range of Screen (ft)
II soybean	No pesticide	5.5	$5 - 9$
II corn	1X-N	6	$6 - 10$
III corn	$1X-N$	11.7	$8 - 13$
II corn	$1x-S$	14	$10 - 15$
III corn	$1X-S$	5.5	$5 - 9.5$
II corn	$5X-N$	3.3	$5.5 - 10.5$
III corn	5x-n	4	$5.5 - 10.5$
II corn	5X-S	$\frac{3}{ }$	
III corn	$5x-S$	7	$6.5 - 11$

Table 2. Descriptions of wells drilled by Envirodyne Engineers, Inc. under subcontract to Illinois EPA.

1/ See text and Figures 2 and 3 for explanation of treatment codes and well locations.

2/ Level at which water table was encountered during drilling of well.

3/ No well; groundwater was not encountered above 19 ft.

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injury was made on 25 June and 4 August, 1986 . Coverage of the plots by weeds was assessed using a scale of 0 (no control of weeds) to 100% (total absence of weeds). This method is a standard technique sanctioned by the Weed Science Society of America. Crop injury was assigned a percentage between 0 and 100 based upon symptomatology and plant stand. Signs of herbicide injury included chlorosis, stunting, root deformities, and deformed leaves. This percentage represented an estimate of the total plants injured per treatment. Fresh weight of soybeans was measured during August after severing plants from their roots in 1 m of row. Fresh corn weight was not measured because the crop showed insignificant injury in all treatments.

3.9.2 Greenhouse Bioassays

Phytotoxicity was studied under greenhouse conditions using waste-pile soil diluted with uncontaminated soil. Assays were conducted in July and December 1986 using soil collected in June and November, respectively. December, 1986. The source of uncontaminated soil for dilution was either that collected from the untreated experimental plots (July assay) or a Flanagan silt loam-Drummer silty clay loam mix routinely used in the greenhouse (December assay). Soil from waste pile no. 2 was diluted with various amounts of uncontaminated soil to make a mixture containing either 50, 25, 12.5, 6.25, 3, 1.5, or 0% contaminated soil by weight. Uncontaminated soil was freshly treated with a mixture of herbicides in the same proportion to that found in waste pile no. 2
(Table 1). This soil mixture was also diluted with untreated. (Table 1). This soil mixture was also diluted with untreated,
uncontaminated soil. The soil mixtures were placed in aluminu The soil mixtures were placed in aluminum trays, and each soil treatment was replicated three times. Corn, soybean. velvet leaf, foxtail, and pigweed seeds were planted in each tray. Growth of seedlings was monitored for 10 days. At the end of this incubation period, surviving plants were harvested and weighed. During the first assay only, a visual injury rating index was also employed. This index was based on the number of dead or injured plants using a scale ranging from 0 (all plants dead or no emergence) to 5 (no observable effect).

3.9.3 Yields

During October, corn and soybeans were harvested to determine the effect of the various waste soil and herbicide treatments on yield. Soybeans were harvested by collecting plants from 17 feet of row. Plants were returned to the laboratory, and the beans separated in a thresher. Beans were weighed, moisture content determined, and then stored at -15 C for later chemical analysis. Corn was harvested by collecting ears from 17 feet of row. Whole ears were returned to the lab, and the kernels were separated from the cobs using a sheller. The kernels were then treated like the soybeans.

3.10 Analytical Methods

3.10.1 Extraction of Residues from Soil

Fifty-gram aliquots of moist soil were extracted twice with 90 mL of ethyl acetate after first preparing a slurry with 20 mL of water. Soil-solvent mixtures were mixed on a magnetic stirrer for 45 minutes between each extraction. The ethyl acetate was decanted and concentrated on a steam bath. After concentration, the volume of ethyl acetate was adjusted to 10 mL, which was either diluted or concentrated as needed prior to analysis. Ten-gram aliquots of unextracted soil were oven-dried for determination of moisture content.

Well samples were filtered through glass microfiber filters to separate water and sediment. Sediments were left intact on the filter papers and extracted with ethyl acetate by adding 5 mL of water to the sediment and 90 mL of ethyl acetate. The extraction was repeated twice, and the decanted extract was concentrated as above.

3.10.2 Extraction of Residues from Well Water

Three hundred-milliliter aliquots of filtered water were extracted twice with 100 mL of ethyl acetate in a separatory funnel. The organic phase was saved and concentrated as described above for soil.

3.10.3 Extraction of Residues from Grain

Grain samples were ground in a blender. Twenty-five grams were mixed with 100 mL of acetonitrile for 2 mintues in a Sorvall mixer. The acetonitrile was decanted through filter paper. The grain was extracted with an additional 100 mL of acetonitrile. The acetonitrile was evaporated to dryness with a rotary evaporator. The residue was rinsed into a separatory funnel with 25 mL of hexane followed by 25 mL of acetonitrile. The hexane was partitioned twice with acetonitrile, and the acetonitrile phase was saved. The acetonitrile was evaporated to dryness. The residue was rinsed into a column containing 10 g of activated Florisil. The column was washed with 50 mL of hexane, which was then discarded. The herbicides were eluted with 100 mL of 2% acetone in hexane followed by 100 mL of 5% acetone in hexane. The solvents were evaporated to near dryness and the final extract dissolved in ethyl acetate. Extraction efficiencies for alachlor. metolachlor, atrazine and trifluralin at 1.0 ppm levels of fortification to corn were 80, 77, 92, and 95%, respectively. Extraction efficiencies from soybean at 1.0 ppm were 57, 56, 60, and 64%, respectively. At a 0.1 ppm fortification level, efficiencies were 64. 59, 69, and 54% from corn and 78, 62, 70, and 56% from soybean for alachlor, metolachlor, atrazine, and trifluralin, respectively.

3.10.4 Quantitation of Herbicide Residues

All herbicides were qualitatively and quantitatively analyzed by packed column gas-liquid chromatography (GLC) with nitrogen-phosphorus specific detection. A gO-cm x 0.2 cm i.d. glass column of 5% Apiezon + 0.125% DEGS maintained isothermally at either 180 or 190 C was used to separate residues. A $10-m \times 0.22$ mm i.d. capillary column (CP-SIL-5 CP) and electron capture detector was employed to tentatively confirm the identity of suspected herbicide peaks identified by analysis on the packed column.

3.11 Statistical Analysis

Herbicide residue and phytotoxicity data were analyzed by the Statistical Analysis System (SAS) General Linear Means (GLM) procedure (Ray 1982). which is the same procedure as an analysis of variance for unbalanced experimental designs. Probabilities that the calculated F statistic was greater than the table value for the appropriate degrees of freedom were shown in each data table where the GLM procedure was carried out. Comparisons between means for a series of treatments within an experiment were tested by Fisher's Least Significant Difference (LSD) test at the 5% probability level. If any two means were different by the value of the LSD and the above analysis of variance procedure showed a significant F statistic at the 5% probability level. then the means were considered signficantly different.

4. RESULTS

4.1 Concentration of Herbicides in Waste-pile Soils

The concentrations of herbicides in waste pile soils were expressed on an oven-dry soil basis as averages throughout the pile (Tables 1, 3). These concentrations were derived from samples collected from depths up to 4 feet into the waste pile. Waste pile no. 2, which was derived from the upper 2 feet of the most contaminated site east of the chemical plant (Zone A, Figure 1), had the highest concentrations of alachlor, metolachlor, atrazine, and trifluralin (Tables 1,3). Pile no. 3, which represented the 2-3 foot depth excavated from Zone A, contained the lowest herbicide concentrations compared to the other piles. Concentrations of herbicides in pile no. 1 were not significantly different than those in pile no. 4.

Soil from pile no. 2 was applied to the corn and soybean plots because it had the highest concentrations of herbicides, and therefore less soil would be required to produce the desired range of herbicide application rates. To calculate the amount of soil needed, concentrations on a wet soil weight basis were used based on the average of the 22 and 27 May samplings. For alachlor, atrazine, metolachlor, and trifluralin these concentrations were 56.6, 31.1, 9.6, and 1.5 ppm, respectively. We made the assumption that the average concentrations would not change significantly as different portions of the pile were taken for application.

Concentrations of herbicides in soil collected in May were compared to concentrations collected in November to determine whether natural biodegradative processes would occur once the soil was excavated, mixed, and aerated (Table 1). No significant differences were noted in recovery of alachlor and atrazine from pile no. 2 between sampling months. The concentrations of meto1achlor and trifluralin were higher in November than in May. These observations indicated that no degradation of the herbicides had occurred, and the difference in residue values represented sampling variations. Less variation in herbicide residues was observed between the May and November samplings of pile no. 4, and no degradation of the herbicides seemed to occur during the summer months. It is pertinent that visual inspection of the waste piles throughout the summer of 1986 and in the spring of 1987 indicated little or no vegetative growth on the piles, but abundant growth was seen on adjacent areas along the railroad right-of-way.

1/ Piles no. 2 and 4 represent the mean concentration in samples collected in May and November. 1986. The data for piles no. 1 and 3 were derived from samples collected in November. Parts per million (ppm) were calculated on an oven-dry soil basis. See text for definition of pile identifying numbers.

- 2/ The probability that the value of the F statistic calculated by the SAS General Linear Means procedure (GLM) is greater than the table value for the appropriate degrees of freedom.
- 3/ Fisher's Least Significant Difference value at the 5% probability level.

4.2 Concentrations of Herbicides in Field Soils after Application of Waste-pile Soils or Sprayed Herbicides

4.2.1 Extraction Efficiency and Storage Recovery

Greater than 80% of each herbicide was recovered from field-collected soil that was fortified in the laboratory with a mixed acetone solution of analytical grade alachlor, metolachlor, atrazine, and trifluralin. Soil samples had to be stored under refrigeration rather than frozen owing to a lack of storage space. The effect of cold storage on herbicide stability was monitored for 112 days after fortification of soils that had been weighed into flasks. Degradation of herbicides was not detected during cold storage (Figures 4-7). Field-collected soil samples were usually extracted within 2 months of collection, and therefore no adjustment in residue values was necessary in subsequent analyses of the data.

4.2.2 Variation in Sampling Immediately after Application

We indirectly determined the uniformity of coverage of waste-pile soil on the field plots by examining the coefficient of variation (CV) for herbicide concentration that resulted from subsampling each block replicate. These coefficients were compared to those of check and sprayed herbicide treatments in both corn and soybean plots (Tables 4,5). We noted a wide range of CV's among pesticides and between blocks sampled. In many cases, CV's for plots in which waste-pile soil had been applied did not differ numerically from CV's for check and sprayed plots. These results indicated that although variations among subsamp1es were large. variations in plots covered with waste-pile soil were generally no greater than in plots that had been sprayed.

We were also interested in the initial concentration of herbicides found in all experimental plots compared to the theoretical amounts we had calculated. We focused our attention mainly on a1achlor because it was the major contaminant and of the greatest environmental concern. On the basis of a 3 1b a.i./acre application rate (i.e., lX treatment), the soil to a depth of 6 inches should have contained theoretically 1.71, 4.28 , and 8.55 ppm for a 1X, $2.5X$, and 5X application rate, respectively. Tables 6 and 7 show the actual recoveries of alachlor in the top 6 inches of soil. The percentage of theortetical recovery ranged from 33.6% for the SX-S soybean treatment to 113% for the 1X-N corn treatment. Percentage of theoretical recovery for all treatments combined was $66.5 + 23.0\%$.

Another concern was the initial concentration of herbicides in soil-treated plots compared to the corresponding treatments in the

Figure 4. Effect of cold storage on recovery of alachlor from untreated soil collected in the corn and soybean plots and fortified at 1, 5. or 10 ppm.

Figure 5. Effect of cold storage on recovery of atrazine from untreated soil collected in the corn and soybean plots and fortified at 1. 5. or 10 ppm.

Effect of Storage on Metolachlor Recovery, Soybean Soil

Figure 6: Effect of cold storage on recovery of metolachlor from untreated soil collected in the corn and soybean plots and fortified at 1. 5. or 10 ppm.

Figure 7. Effect of cold storage on recovery of trifluralin from untreated soil collected in the corn and soybean plots and fortified at 1, 5, or 10 ppm.

Table 4. Coefficients of variation for subsamples taken from the top 6 inches of soil in corn plots after application of waste-pile soil.

1/ Three subsamples were collected from the 0-6 inch depth of each replicate plot in each block during 24-48 hours after application of waste soil and sprayed herbicide.

Table 5. Coefficients of variation for subsamples taken from the top 6 inches of soil in soybean plots after the application of waste-pile soil.

1/ Three subsamples were collected from the 0-6 inch depth of each replicate plot in each block during 24-48 hours after application of waste soil and sprayed herbicide.

Table 6. Concentration of alachlor in the upper 12 inches of soil collected from corn plots at various intervals after application of waste-pile soil and the spraying of herbicides.

				ug herbicide/g soil	(ppm)			
Days After				Treatment Code				
Application	Check	$1X-N$	$5X-N$	$1X-S$	$2.5x-S$	$5x-S$	p ₁	LSD 2/
					---------0-6 inch depth-----------			
$\mathbf 0$	0.13	1.93	5.13	1.15	2.51	4.65	0.043	3.31
41	0.04	0.39	4.05	1.00	0.81	2.71	0.013	2.15
82	0.06	0.40	1.81	0.92	3.81	7.60	0.000	2.25
140	0.04	0.29	1.64	2.34	1.75	6,63	0.032	3.82
$p \frac{3}{ }$ LSD 4/	0.133 0.09	0.001 0.64	0.157 3.71	0.609 2.70	0.410 3.97	0.214 5.19		
					-6-12 inch depth --------------			
$\mathbf 0$	0.02	0.26	0.44	0.09	0.18	0.98	0.117	0.72
41	0.01	0.04	0.21	0.07	0.10	0.17	0.049	0.13
82	0.01	0.02	0.06	0.02	0.14	0, 33	0.009	0.17
140	0.01	0.02	0.05	0.14	0.07	0.12	0.621	0.20
$p \frac{3}{ }$	0.803	0.001	0.175	0.707	0.509	0.196		
LSD 4/	0.02	0.10	0.41	0.23	0.18	0.92		

- 1/ p is the probability that the value of the calculated F statistic (by the SAS General Linear Means procedure) is greater than the table value for the appropriate degrees of freedom. The analysis of variance was performed across soil treatments as the class variable.
- 2/ Fisher's Least Significance Difference test (p=0.05) across soil treatment variables.
- 3/ p value from analysis of variance performed across days after application as the class variable.
- 4/ Fisher's Least Significance Difference test across days after application.

Table 7. Concentration of alachlor in the upper 12 inches of soil collected from soybean plots at various intervals after application of waste-pile soil and the spraying of herbicides. 1/

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1/ See table 6 for explanation of statistical data (i.e., p and LSD values) •

sprayed plots. With the exception of the 5X-S and 5X-N alachlor treatments (Table 7) in the soybean plots, there were no significant differences ($p \leftarrow 0.05$) in recovery of herbicides between soil-applied and sprayed herbicide on 0 day in the top 6 inches of the profile (compare 0 day data in Tables 6-13). Nearly twice as much alachlor was recovered from the 5X-N treatment in the soybean plot as from the *SX-S* treatment (Table 7). This difference may reflect sampling error because concentrations of alach10r recovered later from the SX-S treatment were much higher.

Low levels of herbicides were recovered from corn and soybean check plots to a depth of 12 inches immediately after application of waste soils and herbicides to the other plots. These residues probably represented undegraded herbicides resulting from past farming practices. Generally, the amount of residue recovered from the check plots was much lower numerically than the waste soil and sprayed treatments, but statistically significant differences at the S% level by GLM procedures could not be detected owing to the extremely high sampling variability in some cases. However, significant differences at the 10% probability level were generally detected between initial day herbicide concentrations recovered from the check plots and from the treated plots.

4.2.3 Dissipation of Herbicides from Field Soils, 0-6 inch

Concentrations of all herbicides recovered from the top 6 inches of soil 41, 82, and 140 days after application were compared among treatments and among days sampled within a treatment. No significant trend toward loss of a1achlor from plots receiving waste-pile soil could be detected at the 5% probability level (Tables $6, 7$, treatments $1x-S$, 2.SX-S, SX-S). There was a significant decrease in alachlor residues in the lX-N corn plot and the SX-N soybean plot after the O-day sampling. In general, however, a1achlor residues in the sprayed treatments declined much more slowly than expected. Owing to high sampling variability, it was difficult to detect clear trends in decline of alachlor residue when comparisons were made across treatments. However, significantly more alachlor was recovered in the corn plots at 0-6 in depths from the 5X-S treatment than from the SX-N treatment on days 82 and 140 (Table 6). Initial concentrations recovered were similar in those two treatments.

By 140 days after application, atrazine residues in the upper 6 inches of soil were much lower in all treatments in both corn and soybean plots than were atrazine residues at that depth recovered on 0 day (Table 8, 9). High sampling variability precluded the detection of significant differences at the 5% probability level. Although initial concentrations of atrazine ranged up to 5 ppm, final concentrations were below 1 ppm in all treatments.

Table 8. Concentration of atrazine in the upper 12 inches of soil collected from corn plots at various intervals after application of waste-pile soil and the spraying of herbicide. 1/

				ug herbicide/g soil (ppm) Treatment Code				
Days After								
Application	Check	$1X-N$	$5X-N$	$1X-S$	$2.5x-S$	$5x-S$	p 1/	LSD ¹
					-----0-6 inch depth-------------			
$\mathbf 0$	0.22	1.05	2.96	0.77	0.87	2.24	0.064	1.87
41	0.08	0.27	1.51	0.29	0.27	0.61	0.000	0.36
82	0.07	0.24	0.65	0.18	2.80	3.49	0.398	4.44
140	0.04	0.21	0.63	0.24	0.24	0.51	0.189	0.50
\mathbf{p}	0.029	0.000	0.009	0.074	0.462	0.317		
LSD	0.11	0.23	1.30	0.48	4.05	3.95		
					------6-12 inch depth-------------			
$\mathbf 0$	0.03	0.17	0.29	0.05	0.10	0.37	0.130	0.289
41	0.02	0.04	0.15	0.04	0,06	0.08	0.002	0.05
82	0.01	0.02	0.05	0.01	0.04	0.07	0.015	0.03
140	0.04	0.05	0.05	0.15	0.05	0.06	0.719	0.18
p	0.174	0.000	0.192	0.477	0.298	0.127		
LSD	0.02	0.04	0.27	0.21	0.07	0.31		

1/ See table 6 for explanation of statistical data (i.e., p and LSD values) •

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Table 9. Concentration of atrazine in the upper 12 inches of soil collected from soybean plots at various intervals after application of waste-pile soil and the spraying of herbicide. 1/

				ug herbicide/g soil (ppm)				
Days After				Treatment Code				
Application	Check	$1X-N$	5X-N	$1X-S$	$2.5X-S$	$5X-S$	p ¹	LSD ¹
					--------0-6 inch depth--------------			
$\mathbf 0$	0.10	0.84	2.94	0.60	1.49	5.23	0.493	6.22
41	0.05	0.28	0.88	0.28	0.59	0.61	0.032	0.48
82	0.05	0.38	0.45	0.38	2.83	0.61	0.098	2.02
140	0.02	0.32	0.28	0.17	0.36	0.46	0.12	0.32
$\, {\bf p}$	0.000	0.100	0.000	0.16	0.212	0.46		
LSD	0.02	0.49	0.43	0.40	2.67	7.77		
					---6-12 inch depth------------			
$\mathbf 0$	0.03	0.11	0.16	0.08	0.23	0.10	0.014	0.10
41	0.04	0.04	0.18	0.06	0.05	0.07	0.182	0.13
82	0.01	0.03	0.04	0.04	0.06	0.16	0.082	0.11
140	0.01	0.03	0.03	0.01	0.07	0.03	0.389	0.06
\mathbf{p}	0.341	0.088	0.103	0.005	0.015	0.173		
LSD	0.032	0.07	0.15	0.03	0.11	0.13		

1/ See table 6 for explanation of statistical data (i.e., p and LSD values) •

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Trends in recovery of metolachlor residues from the plots treated with waste-pile soil were similar to those observed for alachlor (Table 10, 11). Residue levels in the upper 6 inches of soil varied without a clear trend in the 5X-S treatments, and 5.3 and 2.3 ppm were recovered in corn and soybean plots, respectively, at 140 days after application. In contrast to a1achlor, metolachlor in sprayed plots was consistently below 1 ppm on all sampling days, and there was a numerical trend toward lower concentrations recovered on day 140.

Trifluralin concentrations in the upper 6 in of soil were less than
pm in all treatments on all sampling days (Table 12, 13). The 0.5 ppm in all treatments on all sampling days (Table 12 , 13). highest concentrations were recovered from the plots treated with waste soil at all rates. There was no clear trend for dissipation of triflura1in residues in any of the plots.

4.2.4 Herbicide Residues below the 6-inch Depth

Residues of each herbicide were recovered in the soil samples taken at a depth of 6-12 in on all sampling days (Tables 6-13). Some residues were probably transported to this depth by disking and not by contamination during sampling. (We discarded the top inch of the 6-12 inch layer during sampling to avoid contamination from soil falling into the augered hole.) Residues at the 6-12-inch depth may also represent residual herbicides from pesticide applications in prior years. There was no trend toward downward movement of any herbicide from day 0 to day 140. Indeed, in most cases, herbicide concentrations were numerically lower on day 140 than on previous sampling days.

4.3 Herbicide Residues in Well Water and Sediment

Herbicide residues in well water were reported only if they could be detected by GLC analysis employing both a packed column linked to a nitrogen-phosphorus detector and a capillary column linked to an electron capture detector (Table 14). Low concentrations of atrazine and a1ach10r were found in some wells, including the check well, 2 days after the application of the waste-pile soil and the spraying of herbicides. Since the wells were not purged before sampling at this time, these residues may have translocated over time owing to past farming practices. No signficant differences in atrazine or a1achlor concentrations were found among soil treatments. Lower concentrations of atrazine and a1achlor were recovered at day 85 and 148 coincident with a change in sampling procedure. At that time we began to purge the wells with a pump and allowed them to recharge before sampling with the PVC bailers. Trifluralin and meto1achlor were not detected in any well sample.

Table 10. Concentration of metolachlor in the upper 12 inches of soil collected from corn plots at various intervals after application of waste-pile soil and the spraying of herbicide. 1/

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1/ See table 6 for explanation of statistical data (i.e., p and LSD values) •

Table 11. Concentration of metolachlor in the upper 12 inches of soil collected from soybean plots at various intervals after application of waste-pile soil and the spraying of herbicide. 1/

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1/ See table 6 for explanation of statistical data (i.e., p and LSD values) •

Table 12. Concentration of trifluralin in the upper 12 inches of soil collected from corn plots at various intervals after application of waste-pile soil and the spraying of herbicide. 1/

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1/ See table 6 for explanation of statistical data (i.e., p and LSD values).

Table 13. Concentration of trifluralin in the upper 12 inches of soil collected from soybean plots at various intervals after application of waste-pile soil and the spraying of herbicide. 1/

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1/ See table 6 for explanation of statistical data (i.e., p and LSD values) •

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- 1/ Four hundred mL of water were extracted twice with ethyl acetate. Extracts were assayed by packed column GLC with confirmation of positive samples by capillary GLC. The limit of detection for well water samples was 0.2 ppb and the limit of quantitation was 0.5 ppb. The limit of detection for sediment samples varied depending on the weight of the sediment sample recovered and extracted.
- $2/$ W = water samples; S = sediment samples
- $3/$ $p =$ probability of calculated F-statistic greater than table value for appropriate degrees of freedom as calculated by the SAS General Linear Means Procedure.
- 4/ $LSD = Fisher's Least Significant Difference (p = 0.05)$.

Detections of alachlor, atrazine. metolachlor, and trifluralin in well sediment were more frequent than in water (Table 14). In some cases. pesticides were detected in sediment but not in water. Several treatments. including the check. showed sediment concentrations of trif1ura1in. atrazine. and alachlor in the parts per million range (e.g•• data for day 41 and 148 data). Herbicide residues in sediment were determined by packed column GLC but not confirmed by capillary GLC.

4.4 Phytotoxicity

4.4.1 Field Results

Weed control and crop phytotoxicity were used as indicators of potential bioactivity of herbicide residues in contaminated soil. High levels of weed control occurred in plots treated with waste-pile soil as well as in those freshly sprayed with herbicide (Table 15). Soybeans were noticeably injured in 2.5X-S and 5X-S treatments, but phytotoxicity in plots treated with waste-pile soil was generally lower than phytotoxicity in plots freshly sprayed with herbicide (lX-N and 5X-N treatments). Fresh weights of soybean biomass from all treatments except 5X-N did not differ significantly. Severe phytotoxicity occurred to soybeans in the 5X-N treatment with symptoms characteristic of atrazine injury; consequently. biomass was significantly lower in that treatment than in other treatments. Insignificant injury to corn was observed and did not seem related to rate of herbicide application.

Corn and soybean yields were used as another indicator of phytotoxicity. No difference in corn yields among soil treatments was detected, but the 5X-N treatment in soybeans caused nearly total loss of bean yield owing to the high levels of atrazine (Table 16). A corresponding yield loss was not seen in the 5X-S treatment. Yields in the checks were numerically lower than in the treatments because plots were not hand-weeded. and therefore, the crops in the check suffered from severe competition with weeds. In contrast, the excellent weed control provided by the waste-pile soil treatments resulted generally in the highest corn and soybean yields. However, overall yields were low due to the late planting date.

4.4.2 Greenhouse Bioassays

Two bioassays in the greenhouse were conducted with soil collected in May and November from waste pile no. 2. The visual injury rating index for the first bioassay (Table 17) indicated some phytotoxicity to corn at the lowest dilution rate (50%), but the injury was more pronounced with freshly treated soil even at higher dilution rates. Soybeans were more susceptible to injury than corn as was observed in the field. but no injury was observed with dilutions of waste-pile soil

Table 15. Weed control and crop injury ratings for corn and soybeans treated with waste-pile soil or sprayed with herbicides. Ratings are the means of observations taken 25 June and 4 August 1986.

		$-----%$ Control $2/------$				
Treatment 1/	Foxtail	Velvet Leaf	Crop Injury 3/			
		Soybeans------------				
1xN	87	76	33			
1xS	79	72	10			
2.5xS	75	65	23			
5xN	100	100	95			
5xS	84	83	20			
Check	9	26	0			
		Corn-				
1xN	95	96	10			
1xS	74	81	$\boldsymbol{0}$			
2.5xS	79	87	3			
5xN	99	99	10			
5xS	93	91	7			
Check	35	49	3			

 $1/$ 1xN, $5xN =$ herbicide spray mixture equivalent to 3 1bs and 15 lbs/acre of alachlor, respectively;

 $1xS$, $2.5xS$, $5xS$ = waste-pile soil applied in amounts to approximate 3, 7.5, and 15 lbs/acre of alachlor, respectively;

 $Check = no herbicide treatment$

- $2/ 0 =$ no control; $100 =$ complete control (based on visual ratings)
- $3/$ 0 = no injury; 100 = crop kill (based on symptomatology and plant stand)

Table 16. Effect of soil treatment on yields of corn and soybean.

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below 25%. Severe phytotoxicity to the three weed species at nearly all dilution rates of contaminated and freshly treated soil confirmed field observations of good weed control.

Visual ratings for the first test were further corroborated by examining fresh weights of plants after the 10-day incubation period (Table 18). Significant reductions in weights of all weed species occurred at all dilutions of waste-pile and freshly treated soil. Compared to the untreated soil controls, corn and soybean were affected by the 50% dilution of waste-pile soil and by most of the dilutions of freshly treated soil.

Results of the second greenhouse bioassay were less conclusive than the first. Seed germination for all plant species was poor in this test. Toxicity against weed species was significant for all soil dilutions to 1.5% when compared with the untreated control (Table 19). In contrast to the first bioassay, corn was not injured (as measured by plant numbers and fresh weights) in any of the waste-pile soil treatments. However, significant injury was observed with the freshly treated soil down to a level of 6%. The yield of soybean biomass in the untreated control was unusually low, and therefore significant differences between the controls and the freshly treated or waste-pile soil were not observed, even when the soils were left undiluted. On the other hand, there was a significant difference in fresh weights between the undiluted (100% TRT) or 50% diluted (50% TRT) freshly treated soil and the highest dilutions of that soil (i.e., 0.75% TRT).

4.5 Herbicide Residues in Grain

Herbicide residues in harvested corn and soybean were quite low (Table 20). No residues were detected in grain from the untreated checks, and atrazine was not detected in any treatment. Residues of trif1ura1in and meto1achlor were too low to be precisely quantitated. Only alachlor was above the limit of quantitation $(e.g., the 2.5X-S)$ treatment for corn and the 1X-N treatments for corn and soybean). Herbicide residues in grain were not related to soil treatment.

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Table 17. Phytotoxicity Assay No.1 (July 1986): Visual injury ratings for corn, soybean, velvetleaf, foxtail, and pigweed grown in soil mixed either with waste-pile soil from Galesville or with soil freshly treated with herbicides.

1/ Soil treatment expressed as the percentage of waste-pile or freshly treated soil mixed with uncontaminated soil from the Galesville study site.

2/ Mean visual injury rating scale: $0 =$ plants dead; $5 =$ no observable effect Table 18. Phytotoxicity Assay No.1 (July 1986): Fresh weights of corn, soybean, velvetleaf, foxtail, and pigweed grown in uncontaminated soil mixed either with waste-pile soil or with soil freshly treated with herbicides.

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1/ Percentage of waste-pile or freshly treated soil mixed with uncontaminated soil.

Table 19. Phytotoxicity Assay No.2 (January 1987): Mean fresh weights of corn and soybean and number of plants of corn, soybean. velvetleaf, foxtail, and pigweed grown in uncontaminated greenhouse soil mixed either with waste-pile soil (CON) or soil freshly treated with herbicides (TRT).

1/ Soi1		corn		soybean	velvetleaf	foxtail	pigtail
Treatment		# $2/$ wt $3/$	#	wt	#	$\#$	∦
100% TRT	$\mathbf{2}$	0.38	3	1.80	0	0	0
100% CON	6	17.06	3	3.82	$\overline{7}$	Ω	$\mathbf 0$
50% TRT	6	2.56	3	2.05	1	$\mathbf 0$	0
50% CON	$\overline{7}$	16.57	$\mathbf{3}$	3.68	9	0	0
25% TRT	6	4.97	5	3.38	4	$\mathbf{0}$	0
25% CON	8	20.75	4	5.08	6	$\mathbf 0$	0
12.5% TRT	8	7.80	4	3.25	7	0	0
12.5% CON	9	18.99	5	6.26	$\overline{7}$	0	3
6% TRT	9	11.64	5	5.87	4	0	3
6% CON	8	14.54	$\overline{7}$	9.34	9	1	9
3% TRT	9.	15.02	4	4.49	9	0	8
3% CON	8	14.54	$\overline{7}$	9.34	9	$\mathbf{1}$	9
1.5% TRT	8	14.33	3	3.59	13	$\mathbf{1}$	10
1.5% CON	8	13.95	5	6.69	6	6	9
0.75% TRT	8	12.60	4	5.91	5	20	19
0.75% CON	8	12.14	5	6.16	6	16	12
UNTREATED	8	16.74	3	4.41	14	12	12
LSD (0.05)	$\mathbf{2}$	3.75	3	3.89	4	7	6

1/ Percentage of freshly treated soil or waste-pile soil from Galesville mixed with uncontaminated greenhouse soil. Herbicides were sprayed onto greenhouse soil to provide concentrations equivalent to those in soil collected from waste pile no. 2. Experiment was conducted between 2 March - 2 April, 1987.

 $2/$ # = no. of plants harvested at the end of the bioassay.

3/ wt = mean fresh weight (grams) of corn or soybean.

Table 20. Herbicide residues recovered from harvested corn and soybean.

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1/ Limit of quantitation was 8 ppb.

2/ Detected but not quantitated.

2/ Insufficient grain was harvested for analysis owing to severe phytotoxicity.

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5. DISCUSSION

Before beginning our studies we developed four criteria for successful remediation of the herbicide-contaminated soils:

(1) No significant toxicity to crops as measured by phytotoxicity assays in the field or greenhouse and by comparison to yields from the untreated checks;

(2) No significant residues in grain;

(3) Residues in soil within 9 months are not significantly different than expected from typical applications of the herbicides;

(4) No wells contaminated above the levels recommended by human health advisories.

First, strong evidence indicates that the herbicide residues in the waste piles are biologically active. Weeds were well controlled in the field by applications of waste-pile soil, and significant toxicity was
observed in greenhouse bioassays even when the soil was diluted. The observed in greenhouse bioassays even when the soil was diluted. weed species chosen for the assay and those present in the field were very susceptible to the herbicides studied. although velvetleaf is not affected by recommended use rates of alachlor.

The phytotoxicity of the waste-pile soil to corn and soybean was more obscure than its phytotoxicity to weeds. Corn injury in the field was insignificant and was not manifested in greenhouse studies when the soil was diluted below 50%. Soybean injury as determined by comparison of fresh plant weights in the 50% waste-pile soil treatment to the untreated control was observed but not statistically significant at the 5% level of probability. When the soil was further diluted, phytotoxicity did not appear. Interestingly, soil containing freshly applied herbicide with nominal concentrations similar to those in waste-pile soil produced significant corn and soybean phytotoxicity at the lowest levels of dilution. We did not analyze the mixtures of diluted soil to determine actual herbicide concentrations. However, if we assume that the concentrations in waste-pile and freshly treated soil were the same, then it seems that the residues in the freshly treated soil were biologically more available than were residues in the waste-pile soil.

Whether or not farmers would accept application of waste soil to their cropland depends ultimately on whether low levels of crop phytotoxicity decrease yield. Our data show no differences in yield between corn grown in waste-pile soil and in soil with freshly applied herbicides. Indeed, soybean yields were highest in the 5X-S treatments. However. due to the late date of planting. overall yields were low and

additional crop year data are needed to adequately evaluate effects on yield. The results of the phytotoxicity assays from the field and greenhouse suggest that sufficient dilution of soil containing pesticide waste would render it relatively harmless to crops. However, the kinds of pesticides present in the soil and the crop species must be given careful consideration. For example, corn is extremely sensitive to injury by trif1uralin. Higher trif1uralin concentrations might have altered our conclusions about phytotoxicity to corn.

Our second criteria of no herbicide residues in grain was met with surprising success. Few residues were found in grain from any Few residues were found in grain from any treatment, and no trend in residue recovery between treatments was found. Federal tolerances for residues of a1achlor, atrazine, metolachlor, and triflura1in on corn are 0.20, 0.25, 0.10, and 0.05 ppm, respectively (Code of Federal Regulations 40, Parts 150-189, 1985). The corresponding tolerances on soybeans are, respectively, 0.20, none, 0.10, and 0.05 ppm. Thus, we conclude that applications of contaminated soils similar to the waste-pile soil used in this study are unlikely to result in violations of pesticide tolerance regulations, as they pertain to the parent pesticide. However, we did not analyze for metabolites of a1ach1or and meto1achlor, which are also covered by the tolerance regulations.

Determining whether the results support the third criterion of successful remediation is somewhat more problematic than the former two criteria. Alachlor. metolachlor, and trif1ura1in are known to be biologically degraded, and atrazine is initially chemically degraded. Much of the scientific literature shows that these compounds are degraded much more rapidly than the rates we observed. Reported half-lives have been variable but generally range from one to two months when moisture is adequate (Baker and Johnson 1979, Walker and Brown 1985, Savage 1978). Although there was a numerical trend for lower recovery of the herbicides 140 days after sprayed applications compared to the initial recoveries, with the exception of atrazine, no trend for dissipation was seen in treatments with waste-pile soil.

One problem we encountered in analyzing the soil data was the high variability of residues in all treatments. This variability precluded detection of significant differences between soil treatments at the 5% probability level. This high variability may suggest that different procedures for mixing the waste-pile soil prior to application were needed. However, coefficients of variation for residues initially recovered from plots where waste-pile soil had been applied did not noticeably differ from those for plots sprayed with herbicides. The variation also indicates that a much longer period was needed to assess the true degradation rate of the herbicides in the waste-pile soil treatments.

Problems with spatial variability of pesticide residues in soil has been discussed previously in the scientific literature (Walker and Brown 1983). Our studies with insecticides have indicated that variability is greater when residues are not rapidly degrading but instead remain comparatively stable. Results in this study showed that alachlor did not seem to degrade in the waste-pile soil treatments at rates comparable to those observed by other workers. On the basis of differences in bioactivity that we observed in phytotoxicity assays and the lack of dissipation within 140 days. we concluded that alachlor and metolachlor residues in soils had different physicochemical and biological interactions with the waste pile soil than with the freshly treated soil. Fortunately. the apparent strong binding to the waste-pile soil and the comparative lack of biological availability to crop plants resulted in low phytoxicity and no accumulation of herbicide residues in the crops. On the other hand. the paradoxically high toxicity to weeds can be explained by their extreme susceptibility to the herbicides studied.

The comparison of alachlor and metolachlor concentrations between the May and November collections of soil from waste pile nos. 2 and 4 support our observation of very slow degradation in the field soil. Simple excavation and mixing of the soil seemed insufficient to stimulate biodegradation of these herbicides. Our results indicate the need for intensive microbiological studies to determine the limitations of natural biodegradative processes operating in soils contaminated with high amounts of herbicides.

Although we observed comparatively high concentrations of alachlor and atrazine in sediments separated from well water, residues in the water itself were very low and similar to concentration ranges reported elsewhere (Holden 1986). The soils in the plots were classified as having slow permeability. but the wells were quite shallow. Shallow wells have been shown to be at risk for pesticide contamination (Cohen et a1. 1984). Fortunately, the wells were not tapping a potable water supply. Unfortunately. uniform criteria for human health advisories have not been set at this time. and we cannot judge whether our fourth criteria was met. However. our results did not show differences among soil treatments in recovery of residues from wells.

In conclusion. at least two of our initial criteria for determining the feasibility of disposing of pesticide waste by applying it to cropland were successfully met, i.e., no significant toxicity to crops and no violative residues in grain. We are concerned about the lack of degradation of alach10r and meto1achlor in the waste-pile soils after 5 months in the field. This observation supports our earlier statement that land filling of pesticide waste may lead to further problems and at best merely displaces a current problem. Land application may be the most cost effective and the safest method for disposing of

pesticide-contaminated soils from agrochemical retail sites. However, the nature of the pesticide waste and the specific crop must be carefully assessed to prevent phytotoxicity. At the very least, land application is a method of disposing of pesticide-contaminated soils that should be more intensively investigated.

6. RECOMMENDATIONS

Our study showed that land application of pesticide waste may be a feasible method of remediation at agrochemica1 retail sites. However, several questions raised by the study should be answered before proceeding generally with this method. Furthermore, alternative methods for remediation should be explored to minimize cost and avoid the possibly adverse consequences of applying complex pesticide mixtures. We recommend the following studies:

(1) Monitor the pesticides in the waste piles at the Galesville Chemical Co. and in the adjacent field plots for an additional growing season to characterize more accurately the dissipation rate of the herbicides and to document the longevity of the herbicide residues.

(2) Determine the leachability of pesticides from waste piles to document possible consequences of 1andfi1ling the waste soil in addition to simply letting the waste piles sit unattended for a prolonged period of time.

(3) Develop a standardized protocol that uses a greenhouse bioassay of contaminated soils to determine whether the land application of pesticide-contaminated soil is safe for a given crop.

(4) Conduct additional monitoring of the quality of shallow groundwater to evaluate more fully the effect of all modes of pesticide application.

(5) Determine the feasibility of using microbial cultures to decontaminate a pesticide-waste site in situ. Although this type of study would not yield immediate results, it might eventually offer an alternative that would avoid the problems associated with landfi11ing or transporting waste from one location to another. Such a study would have to be preceeded by a thorough investigation of the microbial ecology of soils contaminated with high levels of pesticide waste.

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