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Use of Landfarming to Remediate Soil Contaminated by Pesticide Waste

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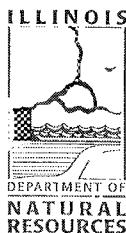
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Abstract

Landfarming is an old technology used to clean up municipal sludges, wastewater, and petroleum refinery sludges, it has been applied recently to remediate herbicide contaminated soils excavated from agrochemical retail facilities in the Corn Belt. This project tested the effectiveness and environmental safety of landfarming by using 30 m² plots outfitted for collection of runoff and leachate. Degradation and phytotoxicity of herbicides following landfarming of waste-contaminated soil (=landfarmed plots) was compared to degradation and phytotoxicity of the same compounds following spraying (=sprayed plots). The landfarmed soil was taken from the site of a pesticide warehouse fire; the soil contained alachlor, trifluralin, atrazine, and metolachlor. Three rates of application were made based on a nominal 1X, 5X, and 10X rate of alachlor application, which was the most prevalent herbicide contaminant. Herbicide residues in landfarmed plots degraded at a similar rate to residues in sprayed plots within the first 100 days after application, but degradation slowed appreciably thereafter. No excessive phytotoxicity was noted if landfarmed herbicides were applied at 1X rates. Cumulative runoff and erosion of residues at the 1X rate of application was similar between treatments, but at the 5X and 10X rates, higher loads of herbicides were generated by the landfarming plots than by the sprayed plots. Detections of herbicides in lysimeter collected soil-water were infrequent, concentrations were very low and did not correspond to mode of application. The concentrations of herbicides in the runoff water were not high enough to produce adverse toxic effects in two types of aquatic bioassays. With the exception of trifluralin, herbicide residues in soybeans were well below established tolerances, trifluralin residues did violate the established tolerance in some samples but were unrelated to treatment. Corn meal affords the opportunity to enhance the degradation of herbicide residues during landfarming.

Executive Summary

Rationale for Landfarming

Agrochemical retail facilities provide farmers with a variety of services including the custom application of fertilizers and pesticides. Chemicals are often mixed and loaded at one location where occasional spillage may result in the accumulation of high concentrations. Rinsing of equipment and of empty containers also produces contaminated discharges that can move off-site as runoff if not handled properly. Similar conditions of spillage and rinse out may occur on individual farms, especially when the same site is used repeatedly for loading and cleanup. Another waste-generating problem common to commercial operations and individual farms is the storage of fuels in leaky tanks either above or below ground. Fuel may also be spilled during loading or discharged during maintenance of equipment. When present in the soil at unusually high concentrations, biodegradable chemicals can be extremely persistent, which increases the risk of surface and ground water contamination, thus, contaminated soils at agrochemical facilities require quick, efficient and economical cleanup.

The ubiquity of pesticide and fuel waste, the need for cost-control, and the lack of adequate landfill space has stimulated a prolific research interest in decontamination of soils by microbial systems. Several strategies, which are currently used or are being studied include (1) spreading of waste on agricultural or noncropped land to stimulate degradation, transformation, and/or immobilization of contaminants (variously known as landfarming, land treatment, land application, or land spreading), (2) pretreatment of contaminants with various reagents to produce degradates more amenable to microbial mineralization, (3) treatment of soil with microbial enzymes, (4) amendment of soils and groundwater with nutrients and/or alteration of physical conditions to stimulate indigenous microbial metabolism (biostimulation), (5) inoculation of wastes with contaminant-adapted microorganisms (bioaugmentation). The latter four strategies are largely experimental or under development. Landfarming, on the other hand, has been used for several decades to dispose of municipal sludge and oily wastes.

Some states have passed legislation enabling certain agencies to permit landfarming, the motivation for these actions are the urgent need to clean up sites and the comparative low cost and ease of landfarming. The technique would seem particularly suitable for pesticide-contaminated soils because the practice involves a technology that has been used for many years. Furthermore, at many sites, the pesticides in contaminated soils are usually registered by the U.S. EPA for application to soil.

In the Corn Belt, candidate land to receive contaminated soils will likely be fields that cannot be taken out of production. Unresolved questions from previous landfarming experiments funded by the Illinois Hazardous Waste Research and Information Center included the translocation of pesticides from the receiving land, prolonged persistence of pesticides in contaminated soils, and potential for crop phytotoxicity. Because landfarming is a leading candidate for treatment of pesticide-contaminated soils, these questions must be accurately assessed to help define appropriate guidelines and regulations.

Chapter 5, Paragraph 819.9 of the Illinois Legislative Act PA86-1172 gave the Illinois Department of Agriculture (IDOA) authority to permit landfarming of pesticide-contaminated soils at agronomic rates. The authorization allowed IDOA to prescribe operational control practices to protect the site of application. This project was designed to provide IDOA with reliable information upon which technical criteria can be developed to refine the permitting process. The project also addresses the possibilities for enhancing degradation of pesticides during the landfarming process. The objectives are

- (1) Determine the effects of soil loading rate, especially beyond the maximum permissible agronomic rate, on degradation of landfarmed pesticides,
- (2) Determine if organic nutrient amendments can stimulate the degradation of landfarmed pesticides,
- (3) Determine the safety of landfarming with respect to off-site movement of pesticides, toxicity of residues, and contamination of on-site crops.

Experimental Procedures

Soil contaminated with alachlor and three other herbicides, trifluralin, atrazine, and metolachlor were applied at three different loading rates based on the legal application rate of alachlor (i.e., 1X, 4.5 kg ai ha⁻¹, 5X, 22.4 kg ai ha⁻¹, 10X, 44.8 kg ai (active ingredient) ha⁻¹). To assess the efficiency and safety of alachlor degradation during landfarming, similar rates of application were simulated by spraying a herbicide mixture containing the four pesticides on replicate field plots. It was hypothesized that if landfarming were efficacious and safe, then degradation rate of alachlor would be very similar in plots receiving contaminated soil or sprays.

Plots comprised an area 10-m long by 3-m wide and were outfitted for collection of runoff. Thirty such plots were constructed with 24 devoted to pesticide applications either by landfarming or spraying, and six plots devoted to no pesticide applications for determination of background pesticide residues.

Degradation of alachlor was monitored by collecting 10 cm deep soil cores at random within each plot on 0, 30, 96, 187, 335, and 425 days after application. To reduce variability known to occur when sampling field plots, six individual cores from each of four replicated experimental units were analyzed individually before averaging together the residue values. To compare different pesticide loadings, all pesticide residue data was normalized to a percentage based on the initial residues recovered.

Plots were bermed along all sides so that all runoff and erosion would be directed across a trough into collection barrels. Water and sediment were sampled after every runoff-producing rainfall by stirring the contents and immersing a collection bottle. Sediment was separated from the water by filtration and analyzed separately for residues of alachlor. Alachlor concentration was multiplied by runoff volume or eroded sediment weight to obtain total mass of pesticide per runoff event, which was then summed over 37 events from growing season 1991 to August 1992. Data were expressed as a percentage of the initial application mass. In addition to measuring runoff, two lysimeters were installed per plot, and soil-water was sampled on a monthly basis.

Phytotoxicity was determined by measuring soybean plant stand, weed counts, and standing biomass. Yield of beans were also compared among treatments. Toxicity of runoff water was measured by an algal photosynthetic inhibition bioassay and the Microtox assay.

In separate plots (1 m²) adjacent to the runoff plots, contaminated soil and sprays were applied at 1X, 5X, and 10X equivalent alachlor rates, which were similar to rates applied in the larger landfarming plots. These plots were designated "biostimulation plots." Sewage sludge (25 g kg⁻¹ soil based on a 7.5 cm depth) and corn meal (50 g kg⁻¹ soil) were incorporated into the top 5 cm of selected plots to stimulate the degradation of herbicide residues. Unamended, pesticide-treated plots were used as positive controls, and amended, no-pesticide plots were used as controls for determination of analytical background and microbial activity. Three soil cores (7.5 cm deep) were

collected from each plot through 428 days after application of soil and sprays. Microbial activity (soil dehydrogenase activity) was determined on triplicate subsamples of bulked cores from each plot

Results & Conclusions

In an attempt to lessen sampling variance, the number of cores taken per plot in the current experiment was increased to six; furthermore, each core was analyzed individually. Concentrations in the six cores were averaged before an analysis of variance was conducted on the four true experimental units or replicates. Spatial variability in herbicide concentrations for similar treatments across the whole field seemed to have been lowered by averaging out the variability within a plot. Actual field residues following application sometimes varied by as much as two-fold from the mean, such variance could have important implications for crop phytotoxicity. Accurate assessment of sampling variance would therefore be important for predicting environmental safety during landfarming.

Because environmental dissipation results from an interaction of physical, chemical and biological processes, Hamaker (1972) suggested comparing pesticide loss by visual examination of the dissipation curve (i.e., concentration recovered vs time) and determining the point of 50% ($DT_{50\%}$) or 90% ($DT_{90\%}$) disappearance. All curves exhibited a fast degradation phase within the first 100 days after application, followed by a much slower degradation over the next year. With the exception of metolachlor, which was subject to much variation in recoveries, landfarmed herbicides applied at an equivalent load of 1X (based on alachlor concentrations) dissipated in the first 100 days within time frames similar to that of the sprayed material. However, the $DT_{90\%}$ for alachlor, atrazine, and metolachlor residues was prolonged in the landfarming plots, suggesting a very slow degradation beyond 100 days.

Although dissipation of herbicide residues in the landfarmed plots at the 1X rates of application were prolonged compared to dissipation in the sprayed plots, plant stand counts and biomass during 1992 showed no differences between the two application modes. Thus, higher residues in the landfarmed soils did not automatically translate to higher phytotoxicity. The latter concern would be an important consideration in deciding when a site for landfarming could be brought back into production. The data suggested that a two year period may be necessary to avoid liability problems as a result of unexpected toxicity to subsequent crops.

Residues of herbicides recovered in soybeans were quite low, although during 1991, all samples contained trifluralin residues. In some samples, the residues violated the 0.05 ppm tolerance for soybeans, but this level was also violated in the unweeded Check treatment. Trifluralin was occasionally detected in Check soils at levels <100 ppb, thus, it could have been absorbed by soybean plants and as a result of its very low water solubility, concentrated in the oily fraction of the beans. Thus, the high levels of trifluralin could not be attributed to the landfarming practice itself, and therefore, the process should not cause the occurrence of violative residues.

At the 1X rates of application, surface transport of herbicides occurred nearly equally (except for atrazine) in the eroded and runoff phases, but no differences were seen between landfarmed and sprayed treatments. At higher rates of application, surface transport of herbicide residues from landfarmed plots was significantly higher than from sprayed plots. Furthermore, the eroded phase was highly enriched with herbicide residues compared to the runoff phase. Normally, herbicides would be carried largely in the water phase.

Detections of herbicides in lysimeter collected soil-water were infrequent, concentrations were very low and did not correspond to mode of application. Thus, both sprayed and landfarmed herbicides remained largely in the plow layer.

Herbicide concentrations in runoff water were probably not high enough to cause significant toxicity in the algal photosynthetic inhibition bioassay. The Microtox assay also failed to show significant toxicity from herbicide residues in runoff water.

To determine whether degradation of the herbicides in the landfarmed plots could be significantly enhanced, corn and sewage sludge were added to small plots receiving either herbicide sprays or landfarmed contaminated soil. For most treatments, corn meal significantly enhanced degradation of the herbicide residues, but the enhancement was most pronounced at the 5X and 10X rates of application. The results suggested that at the 1X rates of application, degradation is sufficiently fast to mask any pronounced biostimulatory effects. However, at the higher rates of application, where comparatively more mass of herbicide would be present in the water phase and therefore available to microorganisms, nutrient amendments seemed very beneficial in shortening herbicide persistence. The enhanced rate of degradation of the herbicides was echoed by measurements of standing biomass, which showed increased biomass in the 1X plots treated with corn meal and sewage sludge.

Recommendations

The following recommendations emanate directly from observations made about the persistence of landfarmed pesticide residues and potential environmental hazards. The recommendations are offered with the assumption that land used for treatment will have to be returned to production in a timely manner and be safe for future cultivation of potentially sensitive crops.

- (1) Extensive sampling of contaminated soil should be conducted to determine the mean and variance of herbicide residues and to more accurately establish the load of soil needed to meet targeted rates of application. The land designated for receiving the contaminated soil should also be sampled in a representative manner to establish background concentrations of herbicides.
- (2) Manure spreaders or other devices for application of contaminated soil should be calibrated using some of the contaminated soil.
- (3) Waste loading rates should not exceed the equivalent of 1X rates of application based on consideration of the most prevalent pesticide contaminant and/or the most toxic contaminant. If enough land is available, waste-loading rates less than 1X should be used.
- (4) Land chosen for landfarming should have little slope to avoid enhanced surface transport, the land should not drain directly into higher order creeks or streams.
- (5) To avoid excessive hot spots, the soil spreading device should be operated in a manner that gives the best possible homogeneity of application. A preliminary test strip may be necessary to adjust the spreader.
- (6) Because hot spots with greater than 1X equivalent herbicide concentrations may be unavoidable, organic amendments like corn meal should be considered for enhancing degradation rate, other methods of biostimulation may also be considered.
- (7) At least two growing seasons should be allowed for completion of the landfarming process.

- (8) After the specified landfarming period, measurements of pesticide residue concentrations should be taken based on a representative sampling scheme.
- (9) After the specified landfarming period, standard phytotoxicity assays should be conducted on several aliquots of soil to ensure lack of toxicity to subsequently planted crops

Chapter 1. Overview of Landfarming as a Bioremediation Practice

Since the passage of the Resource Conservation and Recovery Act (1976), public attention has been focused on problems of waste disposal. The Superfund program has directed attention to chemical contaminants listed as hazardous pollutants, but many other chemicals not listed as hazardous pollutants may be regulated by the states as special waste. For example, pesticide waste generated at the thousands of agrochemical retail facilities has been particularly problematic. These facilities provide farmers with a variety of services including the custom application of fertilizers and pesticides. Chemicals are often mixed and loaded at one location where occasional spillage may result in the accumulation of high concentrations. Rinsing of equipment and of empty containers also produces contaminated discharges that can move off-site as runoff if not handled properly. Similar conditions of spillage and rinse out may occur on individual farms, especially when the same site is used repeatedly for loading and cleanup. Another waste-generating problem common to commercial operations and individual farms is the storage of fuels in leaky tanks either above or below ground. Fuel may also be spilled during loading or discharged during maintenance of equipment.

When present in the soil at unusually high concentrations, biodegradable chemicals can be extremely persistent, which increases the risk of surface and ground water contamination (Wolfe et al. 1973, Staiff et al. 1975, Davidson et al. 1980, Schoen and Winterlin 1987, Felsot and Dzantor 1990). In a survey of 56 agrochemical retail facilities, the Illinois Department of Public Health has documented that 61% operate water wells that are contaminated by one or more pesticides at levels 1-2 orders of magnitude above U.S. EPA Health Advisories (Long 1989). The Illinois Environmental Protection Agency (IEPA) has investigated 16 agrochemical retail facilities where pesticides have contaminated well water (Taylor 1989). In addition to pesticides, well water at commercial facilities has been contaminated with formulation solvents, fuels, and oils (Long 1989). Problems with waste at commercial facilities has adversely affected soil and groundwater in nearby residential neighborhoods (Long 1989).

Agricultural chemical retail facilities may be investigated by State and Federal Environmental Protection Agencies and subjected to specific enforcement of regulatory programs like the Federal Superfund List. Although new containment regulations mandated by states like Illinois and proposed by the U.S. EPA should prevent widespread contamination in the future, many sites have been contaminated for years as a result of standard operating procedures. The regulatory programs will require the facilities to undertake remedial action to remove and dispose of contaminated soil. An average cleanup at one site could involve several thousand cubic yards of soil. The contaminants may include insecticides, herbicides, and fungicides mixed in the same soil. Even after cleanup and the installation of containment facilities, however, contamination can still occur and may require further remediation (Habecker 1989). Two of the most common contaminants found at agrochemical retail facilities are the herbicides alachlor and atrazine.

In addition to remediation of pesticide waste, new federal and state regulations will require agrochemical facilities (as well as other commercial interests) to upgrade or remove underground fuel tanks. In Illinois alone, the program will require the upgrading of approximately 60,000 fuel tanks over the next 10 years. As many of the tanks are removed, soil contaminated with fuel will require removal and disposal in special waste landfills. The constituents of regulatory concern are benzene, ethylbenzene, toluene, and xylene (BTEX).

When a business has a major chemical spill, state or federal regulatory agencies can order a cleanup, but such action is more difficult for private farms and residences. The nature of the cleanup is more problematic. Contaminated soil is excavated and removed to a "secure" landfill. The end result is perhaps a cleaner site, but the waste has not been detoxified. The most reliable technologies that have been proposed for on-site and/or off-site detoxification of pesticide waste

have focused on liquids (Seiber 1987). Remediation of wastes in soil is more difficult and expensive, especially for small businesses and individual homeowners

The ubiquity of pesticide and fuel waste, the need for cost-control, and the lack of adequate landfill space has stimulated a prolific research interest in decontamination of soils by microbial systems. Several strategies, which are currently used or are being studied include (1) spreading of waste on agricultural or noncropped land to stimulate degradation, transformation, and/or immobilization of contaminants (variously known as landfarming, land treatment, land application, or land spreading), (2) pretreatment of contaminants with various reagents to produce degradates more amenable to microbial mineralization; (3) treatment of soil with microbial enzymes,(4) amendment of soils and groundwater with nutrients and/or alteration of physical conditions to stimulate indigenous microbial metabolism (biostimulation), (5) inoculation of wastes with contaminant-adapted microorganisms (bioaugmentation) The latter four strategies, which have been reviewed from the perspective of pesticide detoxification (Felsot and Dzantor 1990), are largely experimental or under development Landfarming, on the other hand, has been used for several decades to dispose of municipal sludge and oily wastes (Torrey 1979, Crites 1984, Marshall and Devinny 1986)

The objectives of this chapter are two-fold The literature is briefly assessed to determine the state-of-the-art regarding landfarming of waste fuels, petroleum sludges, and pesticide-contaminated soils The potential of biostimulation to be used in conjunction with landfarming of pesticides is also reviewed The second objective is to examine some results from a recently reported experiment that assessed the feasibility and safety of landfarming soil contaminated with the herbicide alachlor

1.1 Disposal of Chemical Wastes by Landfarming

The appellation "landfarming" was probably introduced into the scientific literature in an article describing disposal by biodegradation of oily sludges in soil (Dibble and Bartha 1979) From an engineering perspective, landfarming is a "managed treatment and ultimate disposal process that involves the controlled application of a waste to a soil or soil-vegetation system" (Loehr et al 1985b). For landfarming soils contaminated by agricultural chemicals, the objective is placement of contaminated soil within the plow layer of uncontaminated soil where dilution lowers the pesticide concentration sufficiently to facilitate both chemical and aerobic microbial degradation To have long-term utility, landfarming must not irreversibly affect any potential future uses of a site nor contaminate surface and ground water Of the various strategies for bioremediation, landfarming has been studied the longest and therefore is more amenable to quick implementation

In successful landfarming systems, wastes are degraded, transformed, or immobilized, virtually any type of waste can be treated (Loehr et al. 1985b) In practice, however, most studies and currently operational systems have dealt with municipal wastewater and sludge. The constituents of concern in these wastes are excessive concentrations of nutrients, such as nitrate, and heavy metals. After many years of study, treatment guidelines were developed (e g , Torrey 1979), wastewater and sludge can now be considered recyclable for use in irrigation and as soil fertilizer, respectively

Although few investigations have focused specifically on landfarming of fuels and pesticides, insights from studies of trace synthetic organics in municipal wastewater and sludge are useful for focusing research needs. With the advent of highly sensitive chromatographic and spectrometric instruments in the 1970's, new concerns like groundwater contamination developed about the behavior of trace organics during permitted land treatment operations The importance of sorption and biodegradation processes to the fate of trace organics during land application of

municipal wastewater has been reviewed by Hutchins et al (1985) Reviewed compounds included a detergent, polynuclear aromatics (PNAs), halogenated benzenes and aliphatics, and substituted benzenes

1.2 Fuel Components: Fate in Simulated Landfarming Studies and Remediation

Specific studies indicated that aromatic fuel components like toluene and ethylbenzene were volatilized from soils held in rapid infiltration microcosms (Piwon et al 1986) Volatilization was also an important route of benzene loss from two soils (Rogers et al 1980) Organic carbon normalized sorption coefficients for benzene in soil were less than 150 (Garbarini and Lion 1986; Uchrin and Mangels 1987) According to the U S EPA guidelines on soil leaching potential (Cohen 1984), these sorption data indicate that aromatic fuel components have a comparatively high potential for leaching in addition to volatilizing, therefore, landfarming of gasoline contaminated soils must be undertaken with appropriate regard for off-site movement.

Other studies with fuel components in soils show significant biodegradative potential More toluene degraded when applied to sandy soil columns at a higher application rate than at a lower rate, and less was detected in the column effluent (Wilson et al 1981) In river water to groundwater infiltration systems, dimethyl benzenes are degraded by denitrifying bacteria under anaerobic conditions and can be utilized as sole carbon and energy sources (Kuhn et al 1985) In such systems, aromatic hydrocarbons were more readily degradable than chlorinated aromatics (Schwarzenbach et al 1983) In microcosms containing methanogenic aquifer materials collected near municipal landfills, benzene, ethylbenzene, toluene, and xylene (BTEX) were extensively degraded presumably by biological transformations following a long lag period (Wilson et al 1986) Gasoline components are also known to be degraded in aerobic subsurface environments (Barker et al 1987)

PNAs were very stable under field conditions in small plots to which excessively high rates (200 dry tons/acre) of municipal sludge was applied, lower rates (25 dry tons/acre) of application resulted in significant dissipation (Demirjian et al 1987) One study has indicated that persistent organics like PCBs may be significantly accumulated by grazing animals when sludge is surface-applied (Crites 1984). Sewage sludges and receiving soils have been found to contain the persistent organochlorine insecticides DDT and dieldrin, therefore use of sludge to biostimulate degradation must consider the possibility of introducing additional contaminants

Bioremediation of fuel components seems to be proceeding along two fronts, in situ biodegradation and landfarming. An aquifer contaminated with alkylbenzenes from leaky underground storage tanks has been experimentally remediated in situ using injection of mineral nutrients and oxygen or hydrogen peroxide (Wilson et al. 1989) In another study, groundwater was pumped into sawdust/sand pits that were amended with acetate and nitrate to stimulate benzene biodegradation (Harrison and Barker 1987).

Biodegradation and leaching of landfarmed fuel hydrocarbons (nC12-nC21) were studied in a small plot (250 m²) and in a lysimeter (Oudot et al 1989) After 3 5 yr, 94% and 83% of the hydrocarbons were removed from the field plot and lysimeters, respectively Fuel components were found at 60-80 cm, leachate contained no unmodified hydrocarbons but did contain suspected oxidative metabolites Jet fuel, heating oil, and diesel oil were remediated in landfarming lysimeters by treatment with liming, fertilization, and weekly tilling (Wang and Bartha 1990) Both hydrocarbons and polyaromatic hydrocarbons (Wang et al 1990) dissipated within 20 weeks after bioremediation

Recently, the Iowa Department of Natural Resources (IDNR) issued guidelines for landfarming soils contaminated by leakage from underground storage tanks (IDNR Underground

Storage Tank Program--Notification for Land Farming Petroleum Contaminated Soil) Parameters for landfarming of fuel and oil wastes have been developed in the Netherlands (Soczo and Staps 1988).

1.3 Landfarming of Petroleum Sludges

Petroleum wastes in the form of oily sludges have routinely been landfarmed at oil refineries and petrochemical plants. Until recently, however, little attention had been given to the fate of priority pollutants like aromatic hydrocarbons and 4-5 membered-ring PNAs. During land treatment of an oily waste from refinery lagoons on experimental plots, naphthalenes, alkanes, and certain aromatics were rapidly lost from soil, especially during warmer months ($T_{1/2} < 30$ d; Loehr et al 1985a). Earthworms did not bioaccumulate any of the measured components during the study. Mutagenic activity and microbial assays like Microtox have been used to monitor degradation of land-applied oily waste constituents (Sims et al 1987) and contamination in runoff and leachate (Brown and Donnelly 1984). In small plots receiving oil sludges, greater amounts of mutagenic activity were detected in runoff water than in leachate. The activity, however, decreased with time due to degradation and infiltration (Brown and Donnelly 1984). In an earlier study, oil was not detected in runoff water and leachate, but the concentration of residual oils or oxidation products in treated plots were large enough after nine months to cause significant inhibition of plant growth (Raymond et al 1976).

Several laboratory studies have delineated the environmental and operational factors (e.g. soil moisture, pH, mineral nutrients, micronutrients, organic supplements, loading rate, treatment frequency, and temperature) that affect the biodegradation of oil sludge during landfarming (Dibble and Bartha 1979, Bossert et al 1984). Micronutrients and organic amendments did not stimulate biodegradation of refinery sludge, and sewage sludge interfered with biodegradation. Biodegradation was most rapid when C:N ratios in soil were 60:1 (Dibble and Bartha 1979). In other studies, biodegradation of refinery sludge was optimal at a C:N ratio of 9:1, but petrochemical sludge degraded fastest at a C:N ratio of 124:1 (Brown et al 1983). Several studies agreed that repeated applications of small amounts of sludge resulted in faster biodegradation rates than single large applications (Dibble and Bartha 1979, Brown et al 1983). The fastest degradation rates of aromatics in refinery sludge were associated with higher rather than lower application rates (Dibble and Bartha 1979). Pertinently, xylene at the highest rate of application from a simulated spill degraded more quickly than at the lowest rate of application (Aurelius and Brown 1987).

1.4 Remediation of Pesticides by Landfarming and Potential Role of Biostimulation

Compared to studies of organics in municipal wastewater and petroleum sludges, land application of pesticide-contaminated soils has been given little attention. Most research efforts have focused on bioremediation of chlorophenolic wastes in soil that arise from wood preserving operations (e.g., Crawford and Mohn 1985, McGinnis et al 1989). Soils previously exposed to pentachlorophenol exhibited enhanced rates of biodegradation when retreated, suggesting microbial adaptation and utilization of the pesticide as an energy source. A combination of bioaugmentation and biostimulation has been used in combination with composting in windrows to treat chlorophenol-contaminated soils in Finland (Valo and Salkinoja-Salonen 1986). The effects of tilling and fertilization on biodegradation of PCP were studied in "landfarming chambers" (Mueller et al 1991), degradation rates of PCP were too slow to meet acceptable treatment standards after 90 days of incubation.

Liquid pesticide wastes have been successfully detoxified by pretreatment prior to soil disposal. Chlorinated hydrocarbon pesticides biodegraded during sewage treatment, and diazinon,

parathion, and dieldrin degraded rapidly when composted with cannery wastes (Wilson et al 1983) Liquid wastes of alachlor and atrazine have been exposed to UV light and ozonation prior to disposal in soil (Kearney et al 1988, Somich et al 1988) These pesticides are cometabolically degraded, and the pretreatment degrades the compounds into mineralizable products Land application of composted cotton gin wastes containing pesticides resulted in very low to undetected residues after incorporation of the waste into the soil (Winterlin et al 1986) Solid-state fermentation bioreactors have been tested to detoxify liquid wastes (Berry et al 1993); the resulting spent lignocellulosic matrix upon which the pesticides are initially sorbed was found to be safe for subsequent land application

The feasibility of remediating pesticide-contaminated soils by combining landfarming with biostimulation has been suggested by the results of several studies. Pesticide waste taken from a highly contaminated soil evaporation pit in California was partially detoxified by amendment with a variety of inorganic and organic nutrients and by incubating under aerobic or anaerobic conditions (Winterlin et al 1989) Corn plant residue, corn meal, and municipal sewage sludge effectively stimulated degradation of high concentrations of alachlor in soil (Dzantor and Felsot 1992) A ten-fold dilution of alachlor and metolachlor-contaminated soil with uncontaminated soil to simulate landfarming and an altered physical environment also stimulated pesticide degradation (Felsot 1991) Corn meal has been used in solid state fermentation bioreactors as a source of C to increase microbial activity for pesticide degradation (Berry et al 1993) Peat increased the degradation of several pesticides that had been applied to soil at high concentrations (Schoen and Winterlin 1987) Toxaphene degradation was enhanced in contaminated soil kept under anaerobic conditions and amended with cotton gin waste (Mirsatari et al 1987)

Soil contaminated with the herbicides alachlor, metolachlor, atrazine, and trifluralin were excavated and land applied to small field plots of corn and soybean fields (Felsot et al 1988) These herbicides are cometabolized and microbial adaptations for enhanced biodegradation do not occur (Felsot and Dzantor 1990) Alachlor and metolachlor were more persistent when applied in the contaminated soil than when applied as fresh herbicide sprays (Felsot et al 1990). Minor phytotoxicity to soybeans treated with the highest rates of waste soil occurred in the field and in greenhouse assays The mixture of corn and soybean herbicides was seen as potentially limiting factor in attempting to landfarm the pesticide wastes. Unresolved questions included the translocation of the pesticides and the mechanism of prolonged persistence in the contaminated soils

Trifluralin-contaminated soil excavated from the site of a pesticide warehouse fire was applied to farmland in late summer using a manure spreader (Bicki and Felsot 1994) Initially, contaminated soil was left on the soil surface, but 20 days later, small plots were delineated to test the effects of rototilling and dissipation of trifluralin. Concentration of trifluralin residues recovered from rototilled plots (upper 5 cm) were not significantly different than residues from untilled plots beyond the day of tillage Residues were still high enough, however, to prevent oat growth the following spring These results indicated that landfarming may require at least two growing seasons to remediate residues to levels nontoxic to sensitive crops.

1.5 Design and Remedial Action Considerations for Landfarming

Cleanup of a contaminated site is actually a multistage process, and landfarming is only one step that deals with the contaminated soil itself Successful remediation of a site will first depend on a thorough assessment of the areal extent and depth of contamination The decision of how much soil to remove for the landfarming phase will depend on the cleanup targets as dictated by the appropriate regulatory agency Consideration of the extent of excavation will influence the decision about land requirements for landfarming A guiding principle for efficacious and safe landfarming can best be described by the simple maxim "do no harm" To accomplish this goal and meet the objective of landfarming, remedial action strategies must be developed for

pretreatment of the contaminated soil, choosing and assessing the candidate landfarming site, and preparation and management of the site during landfarming. Considerations in developing the plan of action have been discussed by Bicki and Felsot (1994) and are outlined below.

I. Pretreatment of Contaminated Soil

- A Excavation strategy and estimation of soil volume
- B Provisions for storage of soil
- C Grinding, blending, mixing of soil
- D Determination of identity of contaminants and average concentration
- E Decontamination of pretreatment site

II Assessment of Landfarming Site

- A Distance of site from source site
- B Property ownership
- C Contractual relationships with owner
- D Vulnerability of ground and surface water resources
- E Potential for off-target movement
- F Identification and characterization of wells
- G Proposed travel route for transporting contaminated soil
- H Demarcation of site boundaries
- I Installation of monitoring wells if required
- J Landscape position
- K Soil properties
- L Background contaminant levels
- M Tillage and cropping history

III Preparation and Management of Landfarming Site

- A Marking of application area
- B Seeding and establishment of vegetative borders
- C Soil fertility and pH adjustments
- D Tillage treatments
- E Field leveling
- F Plant residue management
- G Timing of application
- H Potential phytotoxicity due to the mix of pesticide contaminants
- I Pesticide registration label restrictions applicable to subsequent crops
- J Calculation of application rate
- K Calibration of application equipment
- L Depth of incorporation
- M Periodic monitoring of pesticide residue levels
- N Closure plan

Chapter 2. Rationale, Objectives, and Hypotheses

Some states have passed legislation enabling certain agencies to permit landfarming, the motivation for these actions are the urgent need to clean up sites and the comparative low cost and ease of landfarming. The technique would seem particularly suitable for pesticide-contaminated soils because the practice involves a technology that has been used for many years to dispose of municipal wastewater and sludges (Soil Science Society of America 1986) Furthermore, at many sites, the pesticides in contaminated soils are usually registered by the U S EPA for application to soil

In the Corn Belt, candidate land to receive contaminated soils will likely be fields that cannot be taken out of production Unresolved questions from previous landfarming experiments included the translocation of pesticides from the receiving land, prolonged persistence of pesticides in contaminated soils, and potential for crop phytotoxicity (Felsot et al 1988, 1990) Because landfarming is a leading candidate for treatment of pesticide-contaminated soils, these questions must be accurately assessed to help define appropriate guidelines and regulations

Chapter 5, Paragraph 819.9 of the Illinois Legislative Act PA86-1172 gave the Illinois Department of Agriculture (IDOA) authority to permit landfarming of pesticide-contaminated soils at agronomic rates. The authorization allowed IDOA to prescribe operational control practices to protect the site of application This project was designed to provide IDOA with reliable information upon which technical criteria can be developed to refine the permitting process The project also addresses the possibilities for enhancing degradation of pesticides during the landfarming process The objectives are

- (1) Determine the effects of soil loading rate, especially beyond the maximum permissible agronomic rate, on degradation of landfarmed pesticides,
- (2) Determine if organic nutrient amendments can stimulate the degradation of landfarmed pesticides;
- (3) Determine the safety of landfarming with respect to off-site movement of pesticides, toxicity of residues, and contamination of on-site crops

2.1 Hypotheses

Appropriate experimental design depends on a well defined hypothesis In this case, the hypothesis is stated as criteria of feasibility that after completion of the experiments should enable a judgment about the effectiveness and safety of landfarming Thus, successful remediation of pesticide-contaminated soil is determined by the satisfaction of four criteria:

- (1) Pesticide residues in control (untreated plots) and contaminated soil-treated plots (hereafter referred to as landfarmed plots) after two growing seasons do not differ significantly In the current design, pesticide behavior in landfarmed plots are compared to pesticide behavior in freshly sprayed plots, which serve as positive controls,
- (2) Contaminant concentrations and toxicity in leachates and runoff water are at levels not significantly different from or are even lower than concentrations and toxicity in the controls,
- (3) Crop phytotoxicity is not greater than expected from conventional sprays,
- (4) Residues of pesticides in crops should not violate established U S. EPA tolerances

Chapter 3. Methods

3.1 Experimental Design

The experiment consisted of three main effects treatments arranged in a completely randomized design. The treatments were herbicide-contaminated waste soil (landfarmed plots), herbicide sprays (freshly sprayed plots), and no pesticide application (checks). Contaminated soil and herbicide sprays were applied at three rates of application based on the most prevalent pesticide in the waste soil. Each combination of pesticide treatment and rate was replicated four times. The checks were replicated six times, three of the checks were hand-weeded, and three were left unweeded.

Our previous studies (Felsot et al 1988, 1990) indicated that landfarming required at least two years to remediate soil containing elevated concentrations of alachlor and metolachlor, concentrations of these contaminants from a theoretical 1X application rate were not significantly different after two years than concentrations of herbicides in untreated soil. Thus, the present landfarming experiment was designed to last a minimum of two years.

Plot Design. Replicates of the pesticide and no-pesticide treatments were randomly assigned to one of 30 experimental plots at the University of Illinois (UI) Cruse Farm. The field encompassed about 0.6 ha on a 3-5% sloped gradient. The soil was classified as a Catlin silt loam (Fine-silty, mixed, mesic Typic Argiudoll). Each plot comprised an area 10 m long x 3 m wide with the length of the plot oriented up-and-down the slope (Figure 1).

The down-gradient end of each of two plots was fitted with metal troughs that directed surface runoff into a 208-L polyethylene barrel housed in a 2.4 m x 2.4 m x 1.2 m pit. A second 208-L barrel sat at a slightly lower elevation to the primary collection barrel and received runoff overflow through a 1:9 flow splitter. The system was designed to receive all the runoff from a 15-year frequency storm. Surface runoff from individual plots was contained by delineating each plot with soil berms along the length and by a metal barrier along the up-gradient end.

Two porous-cup soil-water samplers were placed along the midline of each plot at a distance of 3.7 m from each end. The samplers were installed at a 45° angle to the horizontal so that the ceramic sampling cup was at a perpendicular distance of 60 cm from the surface. Pressure-vacuum sampling tubing issuing from the samplers was buried 40 cm below the soil surface and extended beyond the soil berm.

3.2 Herbicide-Contaminated Soil

During April 1990, water used to fight a fire at a pesticide warehouse in Lexington, IL, flooded the soil surrounding the building and deposited high concentrations of trifluralin and lesser concentrations of atrazine, alachlor, and metolachlor. The soil was excavated and stored until August 1990 at a farm where it was eventually disposed of by landfarming (Felsot 1991, Bicki and Felsot 1994). Analysis of 18 individual cores (5 cm diam. x 10 cm deep) just prior to landfarming showed that trifluralin was the primary constituent, the average concentration was 158 ± 247 ppm (range 3-1003 ppm) (Bicki and Felsot 1994). Approximately 49 Mg of this waste soil was transported to the UI Cruse Farm during August. The soil was covered with a black plastic sheet and stored through the winter. During March 1991, six cores (5 cm diam. x 10 cm deep) were collected randomly from the pile. The following concentrations were found: 118 \pm 58 ppm trifluralin, 18 \pm 14 ppm metolachlor, 1 \pm 1 ppm atrazine, and 1 \pm 1 ppm alachlor.

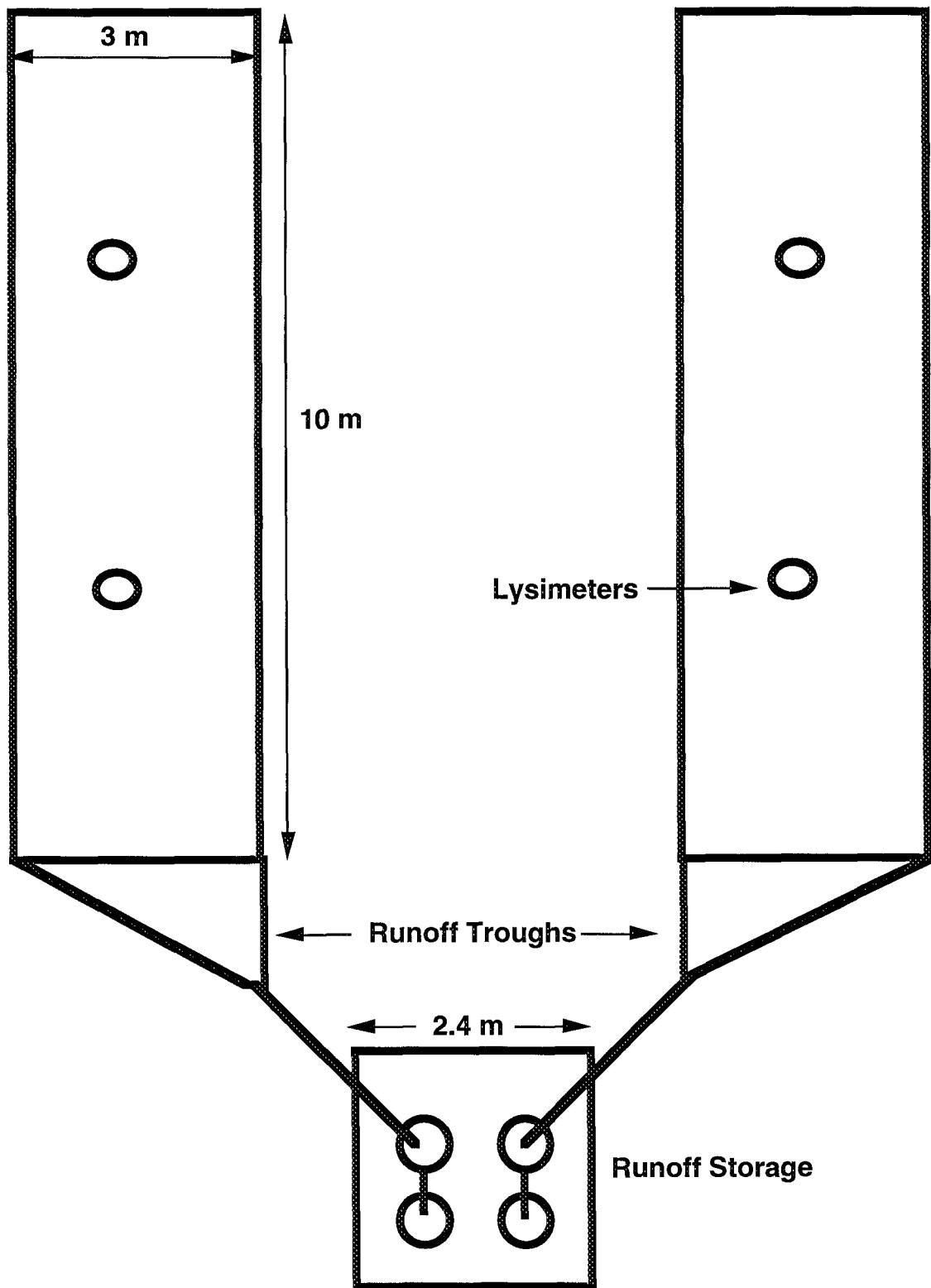


Figure 1. Basic plot design for landfarming experiments at the University of Illinois. Thirty plots were constructed and received either pesticide-contaminated soil or fresh herbicide sprays at different rates of application

Table 1 Theoretical application rates (kg ai/ha) of herbicide contaminants

Proportional Rate	Alachlor	Trifluralin	Metolachlor	Atrazine
1X	4.5	2.6	0.5	0.4
5X	22.4	12.8	2.4	1.8
10X	44.8	25.7	4.8	3.6

Because we were interested in landfarming high concentrations of a greater diversity of herbicides, a simulated spill of alachlor was created on 7 April 1991 by pouring 9.5-L of Lasso 4E (480 g alachlor/L) in 30-cm deep trenches that were dug into the surface of the pile, the trenches were then filled with soil. On 25 April 1991, 1.4 L of Aatrex 4F (480 g atrazine/L) were spilled on the surface of the pile, and the soil was overturned with a spade. On 26 April 1991, a front loader mixed the pile of contaminated soil by completely overturning it in one direction and then overturning it a second time in a direction perpendicular to the first. The soil was then piled about 0.6-0.9 m high within a 7.6 m x 3.0 m area. On 31 May, 10 cores (5 cm diam x 15 cm deep) were collected along a diagonal transect laid across the surface of the pile, and 10 cores were also collected from a depth of 30-45 cm. Herbicide concentrations (oven-dry weight basis) determined in individual cores averaged 172 ± 99 ppm alachlor, 99 ± 53 ppm trifluralin, 18 ± 9 ppm metolachlor, and 14 ± 11 ppm atrazine.

3.3 Rates of Application

Target rates of application were based on the concentration of alachlor in the contaminated soil pile. The maximum legal application rate of alachlor is 4.48 kg ai/ha, this rate represented the 1X level. Five and 10 times the maximum rate were also determined. The theoretical rates of application of trifluralin, metolachlor, and atrazine were based on their soil concentrations in proportion to the concentration of alachlor at the 1X, 5X, and 10X levels (Table I).

3.4 Application of Contaminated Soil and Sprays

The weight of soil needed per plot to give an equivalent alachlor application rate of 4.5, 22.4, and 44.8 kg ai/ha was based on the average concentration (172 ppm) determined in May. Thus, on an oven-dry weight equivalent basis, 78, 391, and 782 kg of contaminated soil were needed to produce proportional application rates of 1X, 5X, and 10X. On 6 June 1991 the appropriate amount of soil was loaded into a 1.3-m wide manure spreader from a front-end loader that had been calibrated by weighing empty and full. The comparatively small plot size necessitated delivery of the soil from the manure spreader without the use of the beater blades, the soil dropped off the back of the spreader as the drive chains moved. The soil was applied in one pass and then raked evenly across the entire 3-m width of the plot.

For the freshly sprayed treatments, enough alachlor (Lasso 4E, 480 g/L), trifluralin (Treflan EC, 480 g/L), metolachlor (Dual 4E, 960 g/L), and atrazine (Aatrex 4L, 480 g/L) were mixed together with tap water to give theoretical application rates equivalent to the proportional rates calculated for the landfarmed plots (Table I). On 5 June 1991 the spray was delivered from a tractor-mounted boom calibrated to deliver 336 L of spray per ha.

3.5 Plot Preparation and Planting

After application of contaminated soil and herbicide sprays, all plots were disked to a depth of 10 cm in an up-and-down slope direction, the soil surface was smoothed with a rolling bar cultivator. On 7 June 1991 four rows of soybeans (*Glycine max* L.) were planted in each plot.

For the second year of the study, all metal barriers and runoff troughs were removed and the plots were disked during May 1992. Soybeans were planted during the first week of June. Barriers and troughs were replaced in the plots, no further field work or fertilization occurred during the second growing season.

3.6 Sampling of Applied Soil and Sprays

During application of contaminated soil and herbicide sprays, three aluminum pans (29.2 x 19.3 cm) were placed along the vertical midline of each plot to intercept the applied material. The pans were packaged in individual polyethylene bags and returned to the laboratory for analysis. Contaminated soil intercepted on the landfarmed plots was weighed, sieved through an 8-mesh screen (3-mm openings), and stored at -20°C before analysis. A subsample was oven-dried to determine the percentage moisture content. Bags containing the pans with intercepted spray material were frozen immediately.

Immediately after application, six cores (5 cm diam. x 10 cm deep) were randomly collected from each plot (landfarmed and sprayed). The cores were placed in individual polyethylene bags and returned to the laboratory for analysis. Each core was sieved and stored at -20°C.

3.7 Water Sampling

Prior to sampling, the depth of water to the bottom of the barrel was measured within 24-48 hours after a runoff event to determine the volume of runoff. The water and sediment were stirred with a paddle, and water was collected for pesticide analysis by submersing two 500-mL glass bottles into a barrel. An additional two samples of mixed sediment and water were collected by submersing a Nalgene bottle into the barrel, this sample was used to determine sediment concentrations necessary to calculate the weight of eroded soil. Samples for pesticide analysis were returned to the laboratory shortly after collection and stored at 4°C for 48-72 hours before analysis. Prior to extraction, water was separated from sediment by filtration through a glass microfiber filter (Whatman no. 934 AH), sediment was weighed wet and after air-drying overnight (Felsot et al 1990). Samples were then frozen at -20°C.

Soil water was collected within 3-4 days of a significant rainfall event or at least once a month. Soil-samplers were kept under a negative pressure of 60 psi. During sampling, the pressure was released and water was pumped under positive pressure into a glass bottle. Water from the two samplers in each plot were composited and stored at 4°C for about 2-3 days before analysis.

3.8 Toxicity Assays

Phytotoxicity of herbicide residues in soil was determined by counting total emerged soybean plants and weeds in each plot during July 1991 and 1992. In September 1991 and August 1992, all plants from two 1 m² areas within a plot were cut at the soil surface and air-dried in a greenhouse for about one week. Air-dry weights were recorded and expressed as standing biomass (grams) per square meter. During September '91-92, soybean plants from the two middle rows of the plots were hand-harvested and placed through a machine thresher to recover the beans for determination of weight.

Toxicity of herbicide residues in selected samples of runoff water were determined by the algal photosynthetic inhibition bioassay (Ross et al 1988). Cultures of the green alga *Selenastrum capricornutum* were exposed to runoff water collected in July 1991. Sodium hydroxide (0.1 N) and ¹⁴C-labelled sodium bicarbonate were added to 20 hour-growth cultures that were then

incubated another 24 hours. Cultures were acidified with concentrated HCl, bubbled to remove unreacted CO₂, and then mixed with scintillation cocktail and counted in a Packard TriCarb scintillation analyzer. Reduction in radioactivity of treated cultures was interpreted as herbicide-induced inhibition of photosynthesis.

Toxicity of residues in water were also determined by the Microtox® assay (Microbics Corp, Carlsbad, CA) (Bulich et al 1981). The test measured the light output of the luminescent bacterium, *Photobacterium phosphoreum* after exposure to selected runoff water samples. Because light production by the bacterium depends on generation and use of ATP, any reduction in normal respiratory metabolism could inhibit or reduce light production. The reagents, bacterium culture, photometer, and test instructions were supplied by Microbics Corp. To determine the threshold of toxicity in the test, runoff water was spiked up to a level of 2 µg/mL with a mixture of alachlor, trifluralin, atrazine, and metolachlor.

3.9 Effects of Organic Nutrient Amendments on Dissipation of Landfarmed and Sprayed Herbicide Residues

In separate plots (1 m²) adjacent to the runoff plots, contaminated soil and sprays were applied at 1X, 5X, and 10X equivalent alachlor rates, which were similar to rates applied in the larger landfarming plots. These plots were designated "biostimulation plots." Sewage sludge (25 g kg⁻¹ soil based on a 7.5 cm depth) and corn meal (50 g kg⁻¹ soil) were incorporated into the top 5 cm of selected plots to stimulate the degradation of herbicide residues. Unamended, pesticide-treated plots were used as positive controls, and amended, no-pesticide plots were used as controls for determination of analytical background and microbial activity. During June 1991, the plots were planted with 10 corn seeds; plots were not cultivated further during the first growing season of the experiment. During June 1992, plots were raked to loosen the soil, but no further cultivation occurred. Three soil cores (7.5 cm deep x 5 cm diam) were collected from each plot through 428 days after application of soil and sprays. Individual cores were sieved and extracted as described below. Microbial activity (soil dehydrogenase activity) was determined on triplicate subsamples of bulked cores from each plot (Dzantor and Felsot 1991). During August 1992, all plants within a plot were cut at the soil surface, returned to a greenhouse for air drying, and weighted to determine standing biomass.

3.10 Analytical Methods

Pans containing intercepted spray residues were extracted by rinsing with acetone. Plastic bags were rinsed twice with hexane and then cut into small pieces and stirred with 150 mL of hexane for 30 min. Extracts were diluted to a final volume of 250 mL before analysis.

Thirty-grams of soil were slurried with 12 mL of glass-distilled water and extracted three times by stirring with 60 mL glass-distilled ethyl acetate. The solvent was decanted into a standard taper flask and rotary evaporated to dryness under vacuum at 35°C. The zero-day extracts were reconstituted in 10 mL of ethyl acetate, but extracts from other days were placed in a final volume of 2 mL.

Water (usually 500 mL) was extracted twice in a separatory funnel with 50 mL of glass-distilled methylene chloride. The methylene chloride extract was passed through oven-dried (110°C) sodium sulfate and then rotary evaporated like the soil extracts. The extract was reconstituted in 2 mL of ethyl acetate.

Eroded sediments along with the filter paper were extracted twice by stirring with 60 mL of 2:1 hexane/acetone. The solvent was decanted through glass wool after each extraction. The extract was rotary-evaporated and placed in a final volume of 2 mL of ethyl acetate.

Following harvesting, mature soybeans were stored at -20°C until extracted. The method described by Felsot et al (1988) was modified as follows. Beans were ground to flour and then extracted twice in 75 mL acetonitrile on a Sorvall Omni-Mixer. The mixture was decanted through glass microfiber filter paper and then transferred to a separatory funnel. The acetonitrile was back-extracted twice with 50 mL of hexane. The hexane was discarded and the acetonitrile was evaporated under vacuum (35°C) to dryness. Ten mL of hexane was added to dried extract, which was then transferred to an activated 10-g Florisil column. The column was washed with 40 mL hexane and the herbicides were eluted with 100 mL 15% acetone in hexane. The eluant was rotary evaporated to dryness and reconstituted in 1 mL of ethyl acetate.

Herbicide residues in soil and water were determined on a Packard model 438 gas-liquid chromatograph with a nitrogen-phosphorous detector and autosampler. The column (90 cm 5% Apiezon + 0.1% DEGS) and operating conditions have been described previously (26). Herbicide residues in soybeans were quantitated on a DB5, 0.32 mm i.d. x 25-m long capillary using a Hewlett Packard 5890 gas chromatograph. The initial column temperature was held for 1 minute at 160°C and then increased to 225°C at 20°C/min with a hold of 6 min. The identity of the residues was qualified by comparison to the retention time of external standards that were injected after every 7 extract samples. Residues were quantified by multilevel calibration with external standards.

Limits of reliable quantification were 70 ppb in soil and 1 ppb in water, although lower levels could be detected (30 ppb soil and 0.5 ppb water). Extraction efficiencies from soil and water were determined by use of fortified blanks, which consisted of soil and runoff water collected from untreated plots. Recovery of all herbicides from soil were greater than 80% (21). From water fortified at 1 ppb, recoveries were 64% for trifluralin and >85% for atrazine, alachlor, and metolachlor. The lower recoveries of trifluralin were caused by volatilization during evaporative concentration. Data were not corrected for extraction efficiencies.

Residues in crops were quantitated on the Packard model 438 GC described above, residue identity was tentatively confirmed on a Hewlett-Packard 8990 GC using a 30 m x 0.25 mm DB-5 capillary column and nitrogen phosphorus detection. A herbicide peak had to appear on chromatograms from both instruments before considering it as a positive detection. Limits of reliable quantification for residues in soybeans were 10 ppb, although 2 ppb of atrazine could be detected. Recoveries of alachlor, atrazine, and metolachlor were greater than 85% when beans were fortified to a level of 400 ppb, recoveries of trifluralin were 70%. No corrections were made for extraction efficiency.

Chapter 4. Initial Recovery and Variability of Herbicide Residues

4.1 Initial Herbicide Residues

Because a major criterion of feasibility of landfarming was to be determined by comparing herbicide residue behavior in landfarmed and sprayed plots, an accurate assessment of actual material applied and initial concentrations in soil was imperative. The actual rates of herbicides applied were determined by analysis of spray and soil intercepted by pans placed in three locations in the plots and compared to the target rates of application (Table 2). In each case, residues intercepted by pans in sprayed plots were approximately 2-3 times lower than the theoretical application rate. Average residues recovered from soil cores yielded rates of application similar to those calculated from interceptor pans and confirmed the lower than expected application rate of the sprays. An analysis of the actual spray solution indicated that the amount of pesticides added to the tanks were near theoretical amounts, thus, it was concluded that the application of finished spray at a targeted rate of 336 L/ha was not achieved. Indeed, an excessive volume of spray solution remaining after application supported this hypothesis and suggested that either the sprayer was improperly calibrated and/or the tractor speed was excessive.

Table 2 Targeted and calculated rates of application of herbicides based on initial recovery of residues

Targeted Rate	Rate of Application (kg/ha) Calculated from Recovered Residues			
	Herbicide Spray		Landfarmed Soil	
	Interceptor Pans	Soil Cores	Interceptor Pans	Soil Cores
Alachlor				
4.5	2.3	1.9	4.8	6.4
22.4	13.9	11.9	32.8	32.5
44.8	20.2	17.3	48.4	54.7
Trifluralin				
2.6	0.9	0.8	3.0	4.1
12.8	7.1	6.1	20.8	19.0
25.7	10.8	9.3	30.7	30.3
Metolachlor				
0.5	0.2	0.2	0.5	0.7
2.4	1.1	1.0	3.3	3.6
4.8	1.6	1.3	4.9	6.4
Atrazine				
0.4	0.2	0.1	0.4	0.5
1.8	1.0	0.8	2.7	3.6
3.6	1.7	1.5	4.0	6.2

After application of contaminated soil, soil collected in the interceptor pans was weighed and scaled up to a plot area basis (Table 3). For the 1X and 10X treatment the actual weight of soil applied per plot was within 8% of the target rate, the weight of soil applied in the 5X plot was 26% greater than the target weight. In contrast to residues

Table 3 Dry weight (kg) of contaminated soil applied per plot

Proportional Rate	Targeted Weight	Actual Weight
1X	78	72
5X	391	493
10X	782	729

recovered after spraying, residues recovered after application of contaminated soil tended to be higher than the expected amounts (Table II). The largest discrepancies (approximately 150-160% of target rates) were observed in the 5X plots as expected from the weights of soil actually applied.

4.2 Intra- and Inter-plot Variability of Herbicide Residues

In a previous landfarming study, comparisons between sprayed and landfarmed treatments were complicated by large coefficients of variation, especially with samples collected immediately after application (Felsot et al. 1988). Resolution of differences between treatments by analysis of variance was only observed after a full year of sampling. In an attempt to lessen sampling variance, the number of cores taken per plot in the current experiment was increased to six, furthermore, each core was analyzed individually. Concentrations in the six cores were averaged before an analysis of variance was conducted on the four true experimental units or replicates. An analysis of the alachlor and trifluralin concentrations in the 1X and 10X treatments showed that the standard deviations for average concentrations calculated from individual soil cores within a plot were always larger than the standard deviations for average concentrations calculated across the four replicate plots (Figure 2,3). As suggested by Figures 2 and 3, the average coefficient of variation for all herbicide concentrations determined in individual soil cores within a plot ($71.7 \pm 23.7\%$) were much higher than the average coefficients of variation determined by averaging concentrations between plots ($27.2 \pm 9.6\%$). Thus, spatial variability in herbicide concentrations for similar treatments across the whole field seemed to have been lowered by averaging out the variability within a plot.

Studies directed specifically at the nature of variability associated with sampling pesticide residues in soil have shown that coefficients of variation can be lowered to about 20% at best (Taylor et al. 1971; Walker and Brown 1983); such reductions are only achieved by increasing the number of samples per replicate experimental unit. Although more expensive, collecting a large number of subsamples per replicate allows better resolution of differences between treatments if such differences exist. When testing waste disposal methodologies, such resolution is desirable to promote confidence in environmental safety of the process or to discern the most efficacious process from among many possible techniques. In the case of waste disposal by landfarming, intensive sampling of waste-contaminated soil would allow a better assessment of initial loading rates. Furthermore, actual field residues following application could vary by as much as two-fold from the mean (Walker and Brown 1983), such variance could have important implications for crop phytotoxicity. Accurate assessment of sampling variance would therefore be important for predicting environmental safety during landfarming.

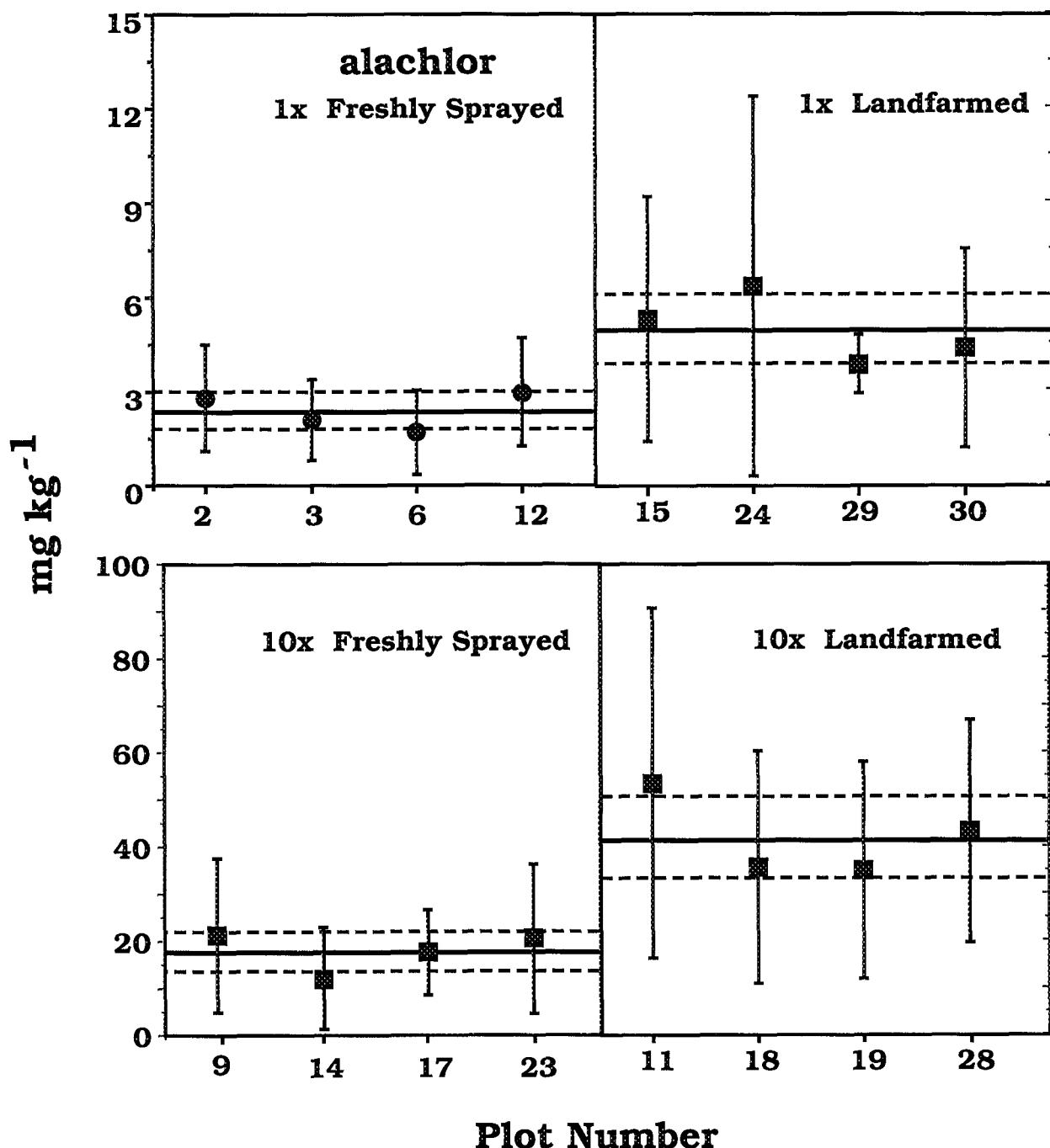


Figure 2. Intra- and inter-plot variability of alachlor residues immediately following application by landfarming or spraying. Plot numbers represent replicate experimental units. Vertical lines represent standard deviations about the mean of six individual soil cores from within one plot. Heavy horizontal line represents the mean of four replicate plots, broken horizontal lines represent the upper and lower limit of the standard

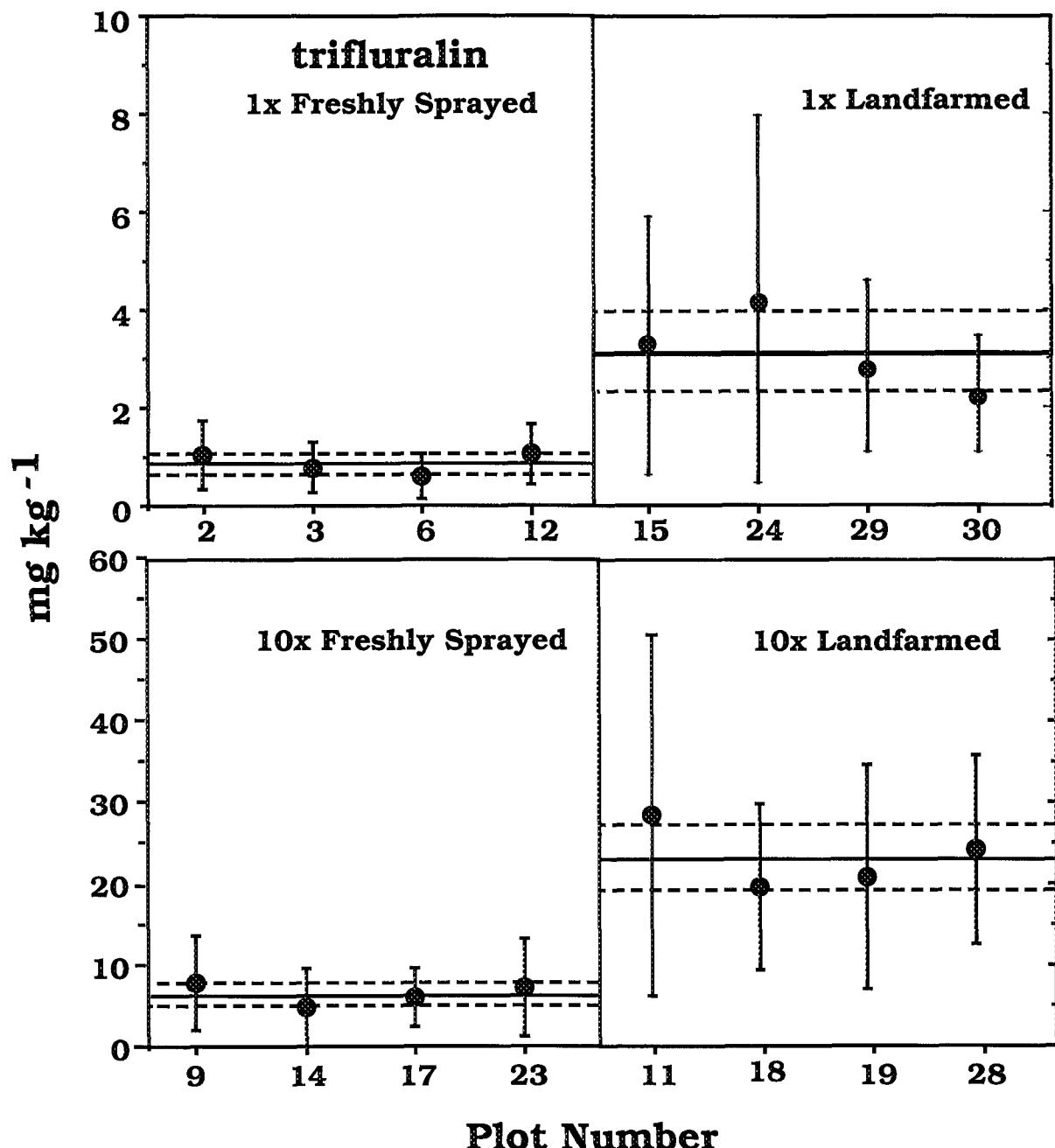


Figure 2. Intra- and inter-plot variability of trifluralin residues immediately following application by landfarming or spraying. Plot numbers represent replicate experimental units. Vertical lines represent standard deviations about the mean of six individual soil cores from within one plot. Heavy horizontal line represents the mean of four replicate plots, broken horizontal lines represent the upper and lower limit of the standard.

Chapter 5. Dissipation of Herbicide Residues in Landfarming Runoff Plots

Because average initial residues of the herbicides in sprayed plots were 2-3 times lower than average initial residues in the landfarmed plots, a direct comparison of degradation was feasible only if the kinetics of degradation were first order, i.e., the rate of degradation was independent of the initial concentration. If so, then residue data could be normalized to a percentage of actual amounts applied, and first-order kinetic constants calculated for sprayed and landfarmed degradation curves could be compared directly. A test of this hypothesis was conducted on the residues data for alachlor obtained over 425 days (Table 4).

Table 4 First-order kinetic analysis for alachlor degradation in sprayed and landfarmed runoff plots

Proportional Application Rate	k (day ⁻¹)	T _{1/2} (days)	R ²
Sprayed Plots			
1X	-0.0047	147	0.78 *
5X	-0.0051	136	0.72 *
10X	-0.0051	135	0.92 *
Landfarmed Plots			
1X	-0.0019	367	0.58 **
5X	-0.0024	287	0.76 *
10X	-0.0023	296	0.92 *

* p ≤ 0.05

** p ≤ 0.10

Correlation coefficients obtained by regression of log concentration over time indicated significant deviation from zero slope and conformation of the data to first-order kinetics (Table 4). Examination of the dissipation curves, however, showed that after 100 days, loss of alachlor significantly slowed; indeed, with the exception of the 10X sprayed and landfarmed plots, the correlation coefficients could account for only 60 to 80% of the variability in concentration relative to time. Thus, the first-order model was not the best model for analyzing the data.

Because environmental dissipation is a mixture of chemical and microbial degradation and includes volatilization, runoff, and leaching, Hamaker (1972) suggested comparing pesticide loss by visual examination of the dissipation curve (i.e., concentration recovered vs. time) and determining the point of 50% disappearance (DT_{50%}). Figures 4-7 and Table 5 show the dissipation curves transformed to a percentage of initially recovered herbicide and the DT_{50%} and DT_{90%} obtained by visual examination of each curve.

5.1 Alachlor Dissipation

All curves exhibited a fast degradation phase within the first 96 days after application, followed by a much slower degradation over the next year (Figure 4). At the 1X rate of application, alachlor had an estimated DT-50% of 25 days in landfarmed and sprayed plots (Table 5), however, by the end of the experiment (425 days after application), recovery of alachlor residues in landfarmed plots were greater than in sprayed plots (0.47 ppm vs. 0.06 ppm). Alachlor also seemed to persist longer in landfarmed plots than in sprayed plots at the 5X and 10X application levels, furthermore, initial rates of degradation in both landfarmed and sprayed plots

were much slower at the higher loading rates than at the 1X rate. Based on the degradation curves for alachlor, 1X rates of application seemed safe for landfarming because compared to sprayed residues, there was little difference in proportion of residues remaining following two growing seasons. Absolute concentrations recovered were 0.47 ± 0.30 ppm in landfarmed plots compared to 0.02 ± 0.01 ppm in sprayed plots. Because alachlor is registered for both beans and corn, such levels would not likely present a phytotoxicity problem.

Table 5 Estimated times in days to 50% (DT50%) and 90% (DT90%) disappearance of alachlor in landfarmed and sprayed field plots

Rate of Application	Sprayed		Landfarmed	
	DT50%	DT90%	DT50%	DT90%
Alachlor				
1X	26	85	25	390
5X	51	88	30	180
10X	50	125	70	400
Trifluralin				
1X	111	>425	21	>425
5X	80	>425	30	>425
10X	140	>425	255	>425
Atrazine				
1X	50	187	62	>425
5X	42	142	43	375
10X	50	150	88	360
Metolachlor				
1X	28	175	145	>425
5X	100	425	95	>425
10X	160	425	328	>425

At higher rates of application, however, initial rates of degradation in landfarmed plots were slower. The concentration of alachlor recovered in 10X landfarmed plots 3.715 ± 1.28 ppm was 50-fold greater than in sprayed plots (0.07 ± 0.02 ppm) and nearly two fold higher than a 1x application over a 15-cm profile of soil (Felsot et al 1988). It is pertinent that plots at the higher rates of application had little vegetative cover, even after the second growing season, which suggested that herbicide residues resulting from landfarming at the higher loading rates were still phytotoxic after two growing seasons, although the combination of alachlor with the other herbicides was most likely responsible for the high phytotoxicity. In contrast, 1X plots had an abundant weed population, and the rhizosphere may have stimulated degradation of alachlor.

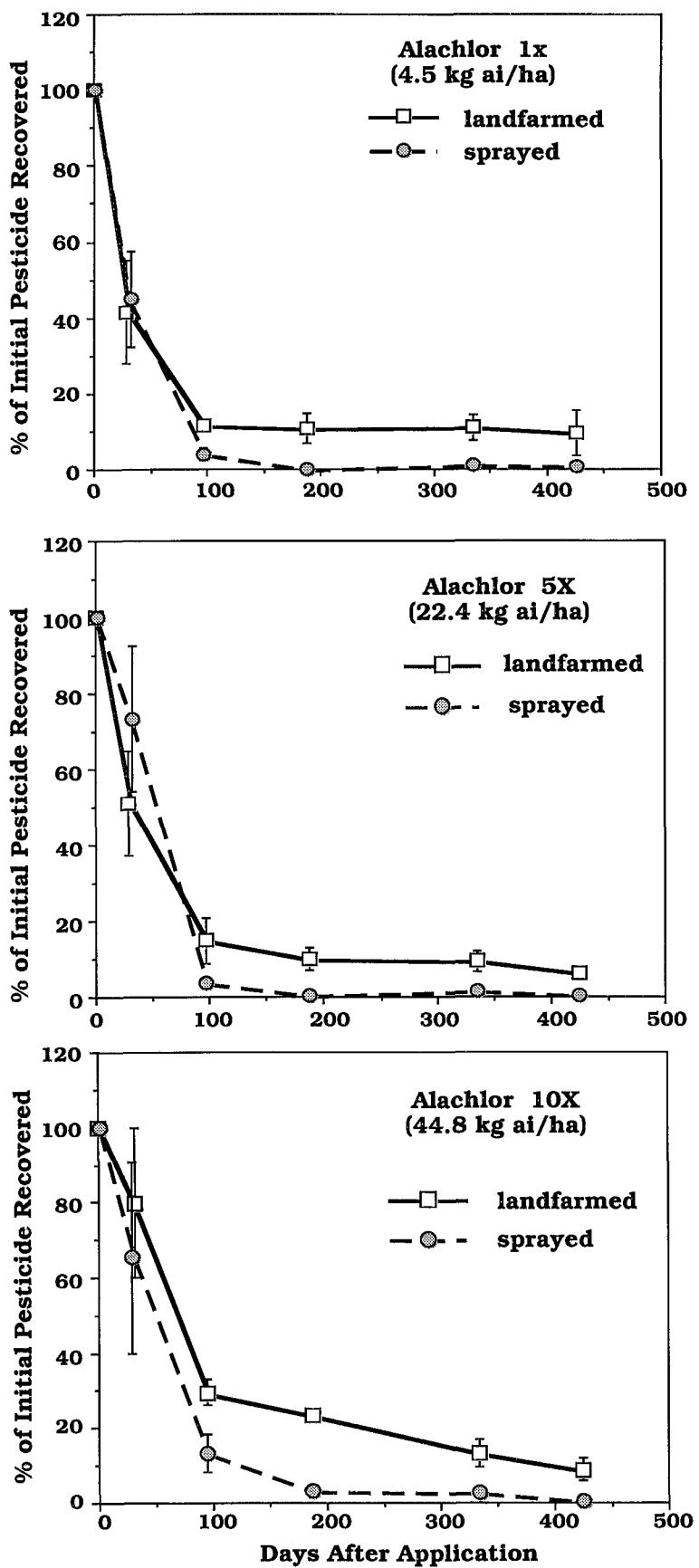


Figure 4 Dissipation of alachlor following application of three loading rates by landfarming or spraying

5.2 Trifluralin Dissipation

In 1X and 5X plots, trifluralin seemed to dissipate more quickly in landfarmed plots (DT50% 21-30 d) than in sprayed plots (DT50% 80-111 d), but after 300 days, percentage recoveries of residues were similar (DT90% > 425 d) (Figure 5, Table 1)). Although DT50% derived from 10X landfarmed plots was substantially greater in than in sprayed plots (255 vs 140 d), this discrepancy was due to an unusually high recovery of trifluralin on day 187 post application. Through 100 d, dissipation rate at the 10X level was similar between sprayed and landfarmed plots, but the percentage recovery at 425 d post application was significantly higher from landfarmed plots ($25.7 \pm 7.3\%$ vs $16.2 \pm 2.7\%$). Percentage recoveries at 1X rates of application were not significantly different on 425 d post application ($22.2 \pm 13.1\%$ vs. $17.8 \pm 4.2\%$), but the absolute concentration recovered in the 1X plot was 0.70 ± 0.41 ppm, which could still be phytotoxic to a sensitive crop like corn.

5.3 Atrazine Dissipation

Rates of atrazine dissipation as evidenced by the DT50% values were similar between landfarmed and sprayed plots, especially at the 1X and 5X levels of application (Figure 6, Table 5) DT90% for all loads of landfarmed atrazine were over twice as large as sprayed atrazine. Because initial concentrations of landfarmed atrazine were low (0.34 ± 0.07 ppm), the final concentration on day 425 was only 0.05 ± 0.03 ppm, which should not be phytotoxic to a sensitive crop like soybeans.

5.4 Metolachlor Dissipation

Initial metolachlor concentrations were less than 0.5 ppm, recoverey from sprayed plots over time was highly variable and made direct comparision with recoveries from landfarmed plots untenable. However, at the higher 5X and 10X loadings, metolachlor dissipation seemed slower in landfarmed plots than in sprayed plots with significantly higher percentages recovered from landfarmed plots (Figure 7). Although metolachlor is an acetanilide herbicide analogous is structure to alachlor, it has been shown more persistent in soil. A comparison of the DT50% and DT90% between alachlor and metolachlor agrees with past observations (Table 5).

In general, dissipation of landfarmed and sprayed herbicide residues did not differ significantly when applied at the 1X rate of application if only the first 100 days was considered. Beyond 100 days, the landfarmed residues seemed to degrade more slowly, which is consistent with previous reported observations for alachlor and metolachlor (Felsot et al 1990). Herbicide residues in the untreated Check plots ranged up to 15 ppb by 425 days after the start of the experiments (data not shown). Residues in the 1X sprayed plots were just at or above these levels, however, 1X landfarmed residues of alachlor, trifluralin, and metolachlor were more than an order of magnitude above these levels. Residues levels were not measured beyond 425 days; thus, further dissipation of residues may have taken place prior to the start of a theoretical third growing season.

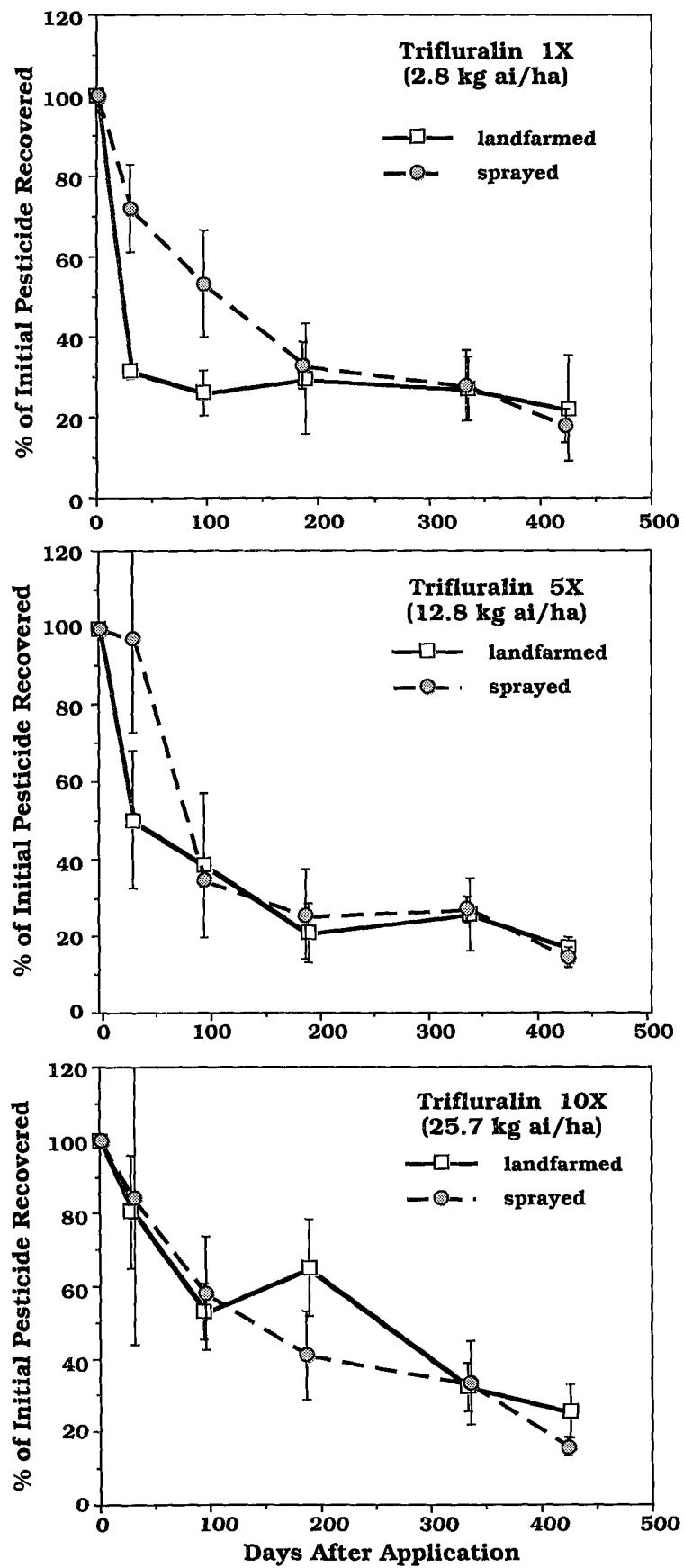


Figure 5 Dissipation of trifluralin following application of three loading rates by landfarming or spraying

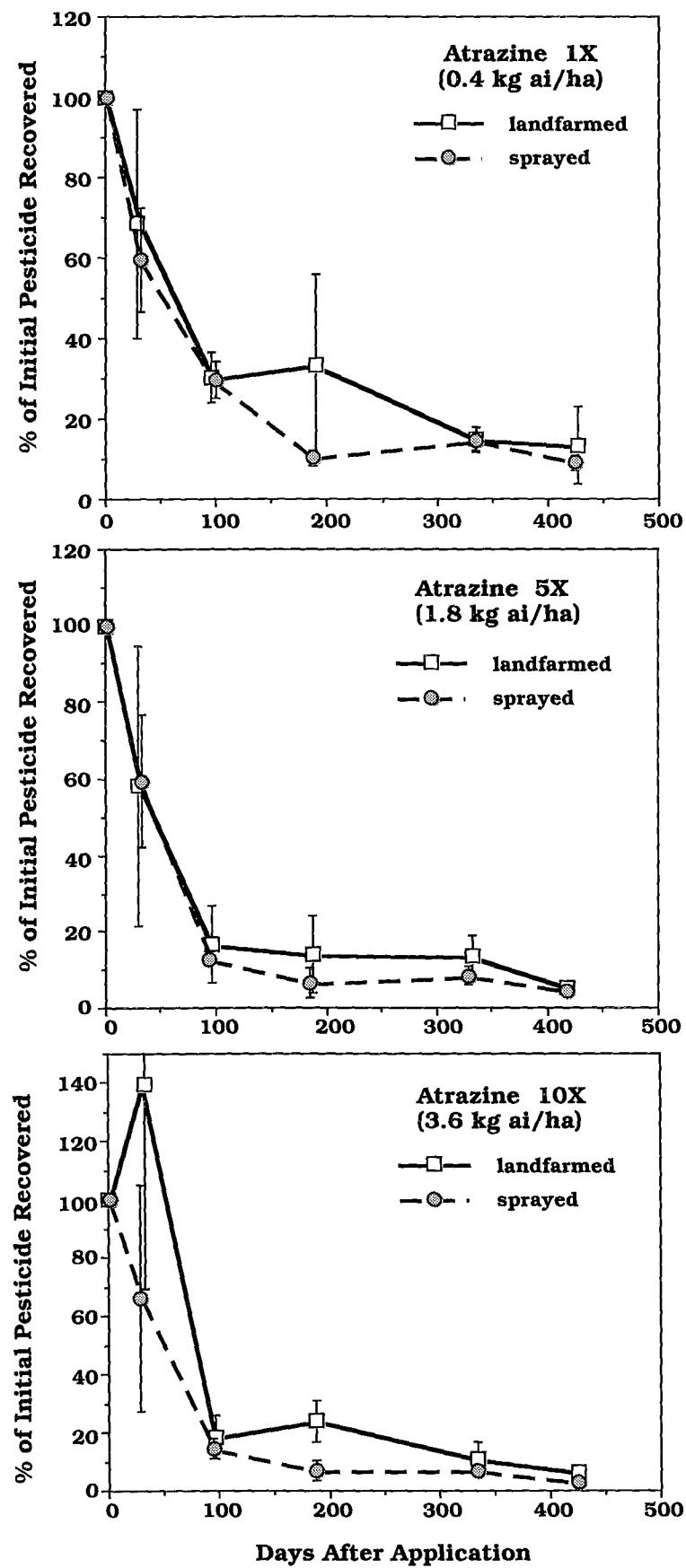


Figure 6 Dissipation of atrazine following application of three loading rates by landfarming or spraying

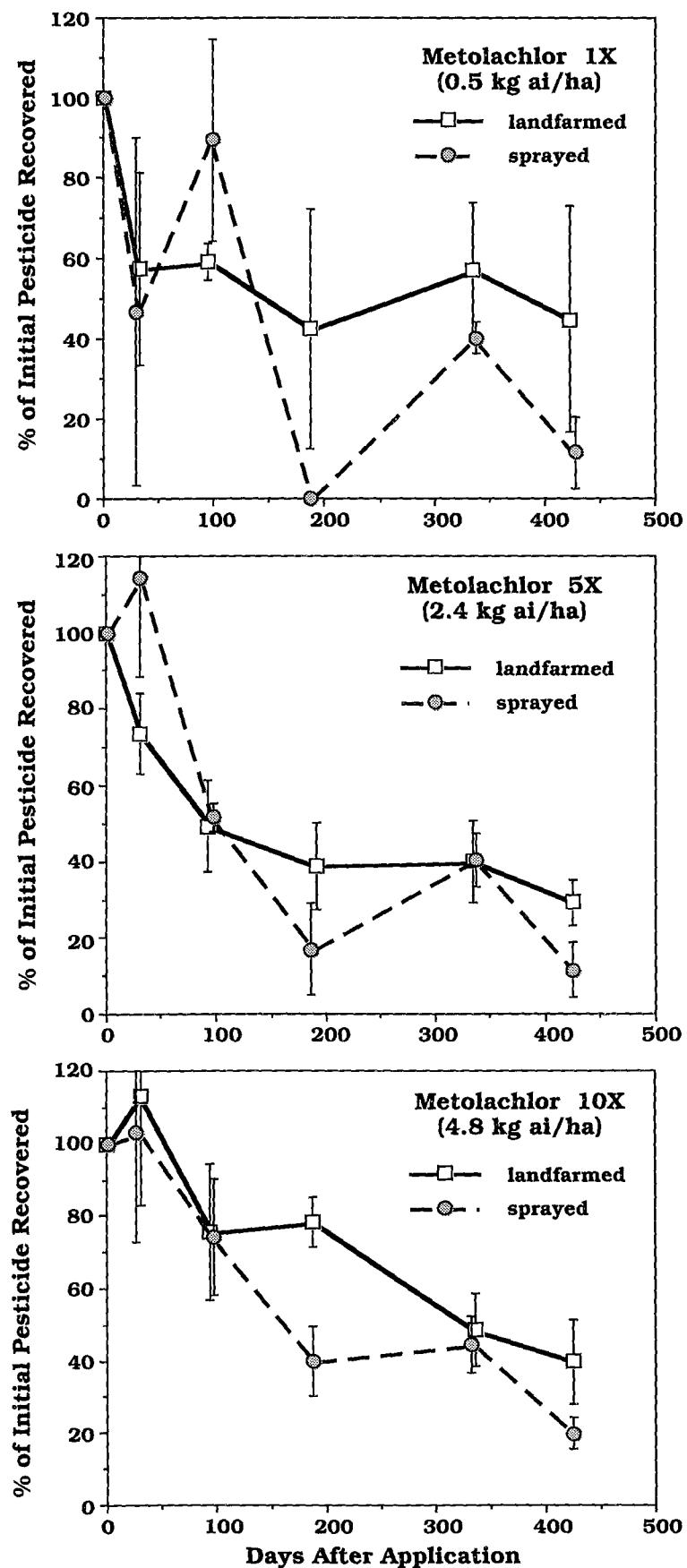


Figure 7 Dissipation of metolachlor following application of three loading rates by landfarming or spraying

Chapter 6. Phytotoxicity Assays

6.1 Soybean and Weed Emergence

During the 1991 crop year, the total number of soybean plants in 1X landfarmed plots was significantly less ($p<0.05$) than the number of plants in check plots (Table V). The number of soybean plants in 1X sprayed plots was also lower but not significantly. Phytotoxicity was attributed to the presence of atrazine which is not registered for use on soybeans. The greater inhibition of soybean growth in the 1X landfarmed plots than in the sprayed plots probably resulted from the greater initial concentrations of atrazine (0.39 vs. 0.17 $\mu\text{g/g}$ soil). Inhibition of soybean germination was greatest for 5X and 10X sprayed plots, which did not differ from one another. Activity against weeds was evidenced by the significantly lower plant numbers in all treatments (except 1X landfarmed plots) when compared to the check. By the end of the growing season landfarmed and sprayed 5X and 10X plots had little vegetative growth other than a few soybean plants.

Table 6. Phytotoxicity of Sprayed Herbicides and Landfarmed Soil

Application Rate	No. of Soybean Plants Per Plot		No. of Weeds Per Plot	
	Sprayed	Landfarmed	Sprayed	Landfarmed
Check	459	--	210	--
1X	389	267	90	130
5X	107	140	14	16
10X	92	84	16	18
LSD ^{1/}	114	--	86	--

^{1/} Fishers' Least Significant Difference Test at $p=0.05$, applicable to comparisons between plot types (sprayed vs. landfarmed) and rates of application

The following growing season (June 1992), soybean plant stand counts were similar in 1X landfarmed and sprayed plots (Figure 8). Counts in the 5X and 10X sprayed did not differ significantly from the hand weeded and unweeded checks, but counts in the landfarmed plots were much lower. Weed counts (per square meter) indicated that the herbicide residues in all treated plots were still phytotoxic, significantly less weeds were observed in treated plots than in untreated control plots. The soil surfaces of the 5X and 10X plots remained nearly bare except for scattered soybean plants throughout the second year of the study.

6.2 Standing Biomass

Plant stand counts were not taken again after July, but standing biomass was measured during August (1992) or September (1991). In 1991, biomass was significantly lower ($p<0.05$) in all herbicide treated plots than in the unweeded check, showing that the herbicide residues in landfarmed plots were bioactive. Biomass was not significantly ($p<0.10$) different between landfarmed and sprayed treatments at any loading rate. Differences among loading rates in the landfarmed treatment were not significant because of very high variability among treatment means, but among sprayed treatments, biomass from the 1X plots was significantly greater than from the 5X and 10X plots.

During 1992, biomass in August did not differ significantly ($p=0.10$) from the unweeded CHECK nor did biomass differ significantly between the various loading rates.

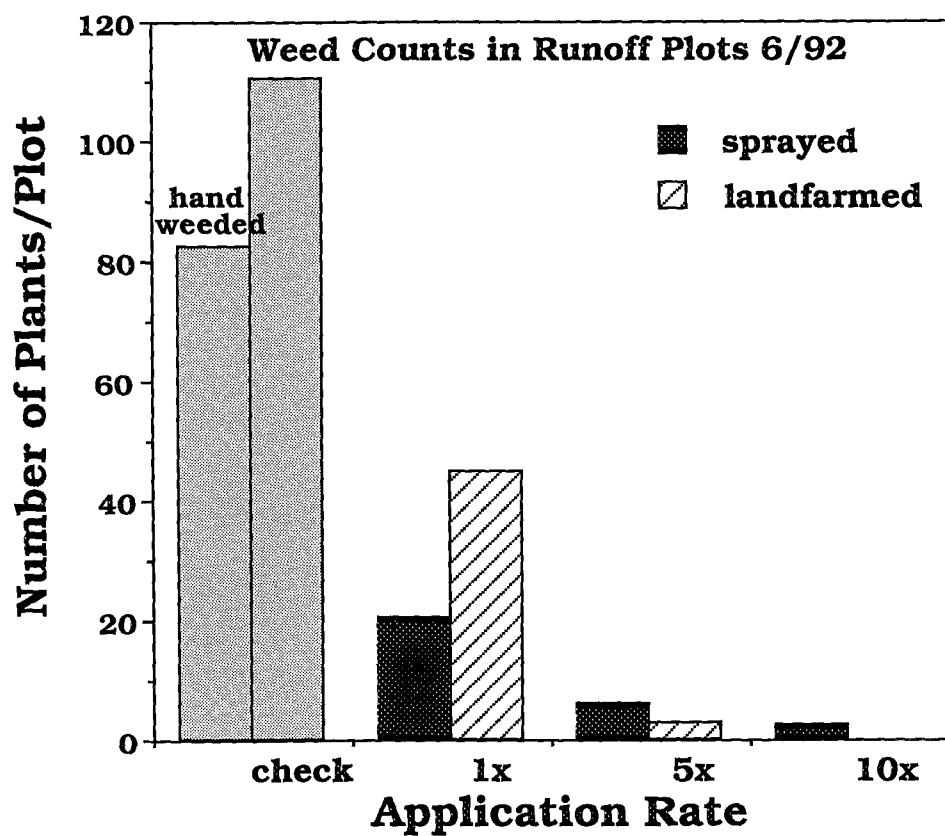
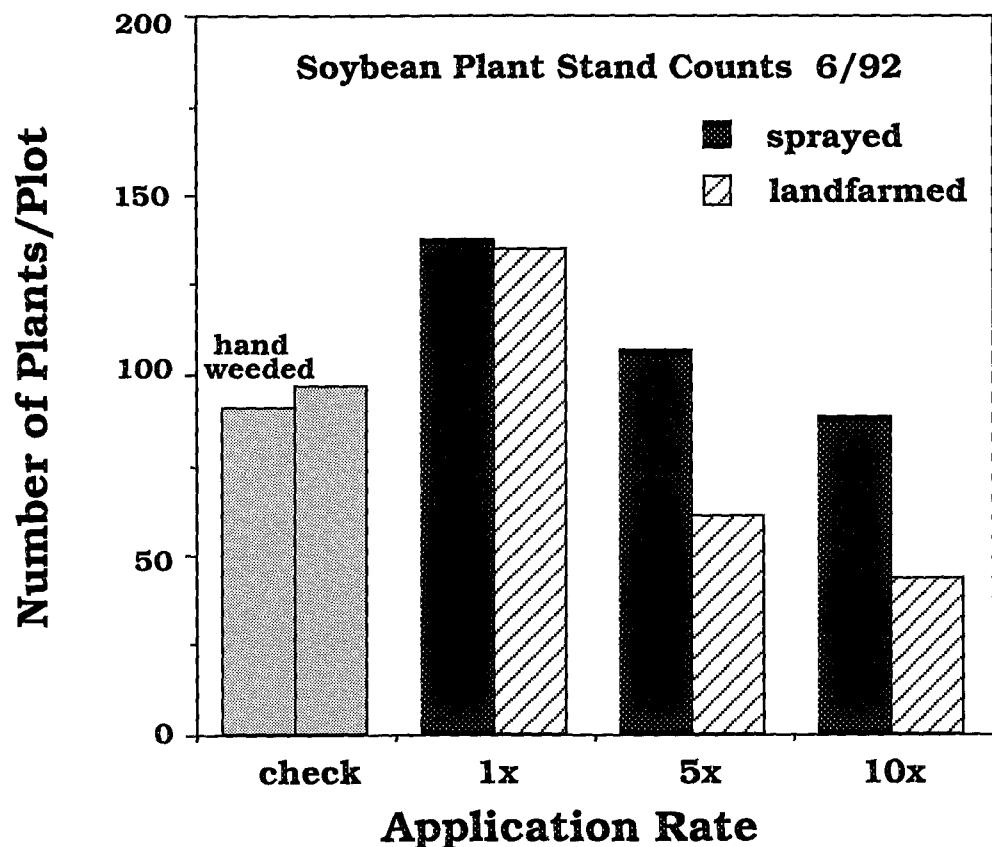


Figure 8. Plant stand and weed counts in runoff plots during the second season following application of contaminated soil and herbicide spray mixtures.

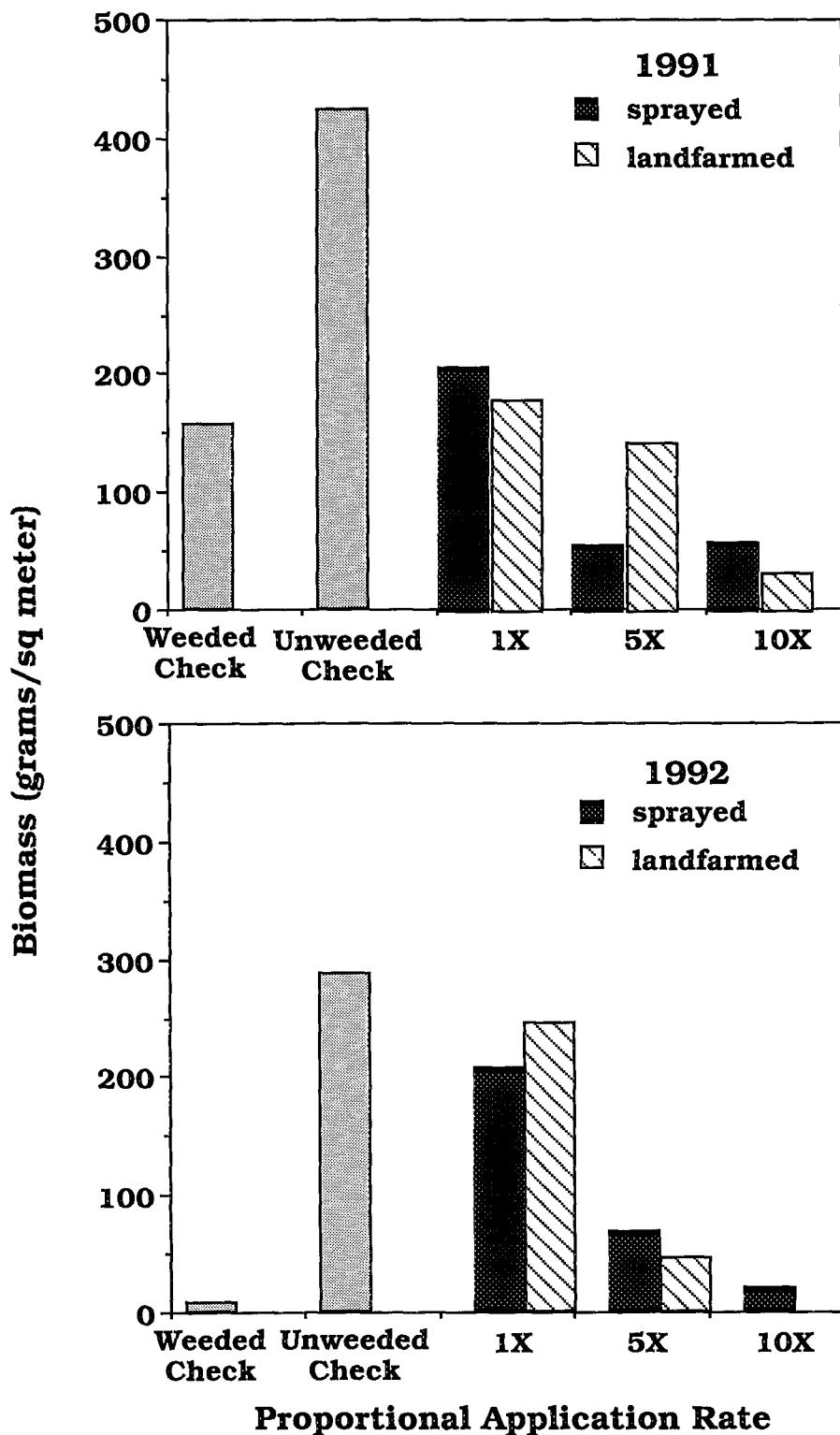


Figure 9. Standing biomass (grams/m²) recovered from sprayed and landfarmed plots during September 1991 and August 1992.

on sprayed and landfarmed plots. Sprayed and landfarmed plots treated at 1X rate did differ significantly from the 5X and 10X treatments. Thus, after two years, herbicide residues in 5X and 10X plots retained substantial bioactivity.

6.3 Soybean Yield

In a paired comparison, bean yields during 1991 and 1992 were significantly higher ($p < 0.10$) in 1X sprayed plots than in 1X landfarmed plots (Table 7), however, sprayed and landfarmed plots did not differ significantly from one another at the higher application rates nor were differences observed when comparison was made to the unweeded CHECK plots. The unweeded 10X and CHECK plots treatments had the lowest yields, which would be consistent with high levels of phytotoxicity or severe competition between soybeans and other plants.

Table 7 Yield of soybeans during 1991 and 1992 (grams/plot)

Proportional Rate of Application	Sprayed	Landfarmed
	<u>1991</u>	
Unweeded Check	128 ± 77	--
Weeded Check	829 ± 492	--
1X	978 ± 581	184 ± 122
5X	227 ± 134	127 ± 180
10X	85 ± 91	72 ± 84
	<u>1992</u>	
Unweeded Check	72 ± 58	
Weeded Check	518 ± 402	
1X	879 ± 329	399 ± 253
5X	1243 ± 534	418 ± 59
10X	524 ± 237	212 ± 245

6.4 Relationship Between Herbicide Concentration and Toxic Dosage in Soil

After a landfarming project is completed, information about potentially toxic herbicide residues would help subsequent planning for tolerant cropping systems. Ideally, all concentrations after one or two growing seasons would be at levels similar to untreated soil or background. As noted in Chapter 4, however, herbicide residues recovered from 1X landfarmed plots still exceeded residues recovered from the Check plots. Another perspective on future hazards is afforded by examining the residues recovered in relationship to established dosage-response relationships. For weeds, the dosage-relationship can be defined as the effective dosage or concentration in soil that reduces growth of a test species by 50% compared to the same species in an untreated soil (i.e., the ED₅₀). Although not as well characterized as animal toxicity, herbicidal dose-response relationships have been developed for a few soil/herbicide combinations.

Figure 10 plots the relationship between the concentration of alachlor, trifluralin, atrazine, and metolachlor over time relative to the ED₅₀ or ED₈₀ (trifluralin only) as determined in a sandy soil. A sandy soil represent a worst-case scenario for production of phytotoxic effects. The ED₅₀ for alachlor (0.2 ppm) and atrazine (0.3 ppm) was based on the response of oat or millet in a Plainfield sand (Guo et al. 1991). The data for metolachlor (ED₅₀=0.23 ppm) was based on the

control of barnyard grass in field plots of a Norfolk sand (Weber et al 1981) For trifluralin, only ED₈₀ (0.2 ppm) data were available for a Norfolk sand, the concentrations controlling broadleaves would be nearly twice as high (Peter and Weber 1985)

Atrazine and metolachlor residues recovered from 1X landfarmed treatments after 425 days were at or below the reported ED₅₀ of atrazine and metolachlor in a sandy soil (Figure 10) Decline of alachlor and trifluralin residues plateaued with a little change beyond 100 days, consequently residues were above the ED₅₀ for sandy soil. The data suggest that after one full year of degradation, residues from a 1X application rate could still be high enough to affect subsequent sensitive crops. However, the experiment did not encompass the resulting residue levels following a complete second year of degradation, and the benchmark of phytotoxicity was chosen to be very conservative, i.e., herbicides will be most bioactive in sandy soils. Indeed, the ED₈₀ for trifluralin on a Rains silt loam soil was extrapolated as 0.65 ppm (Peter and Weber 1985), which is about the level of the 1X landfarmed treatment after 425 days

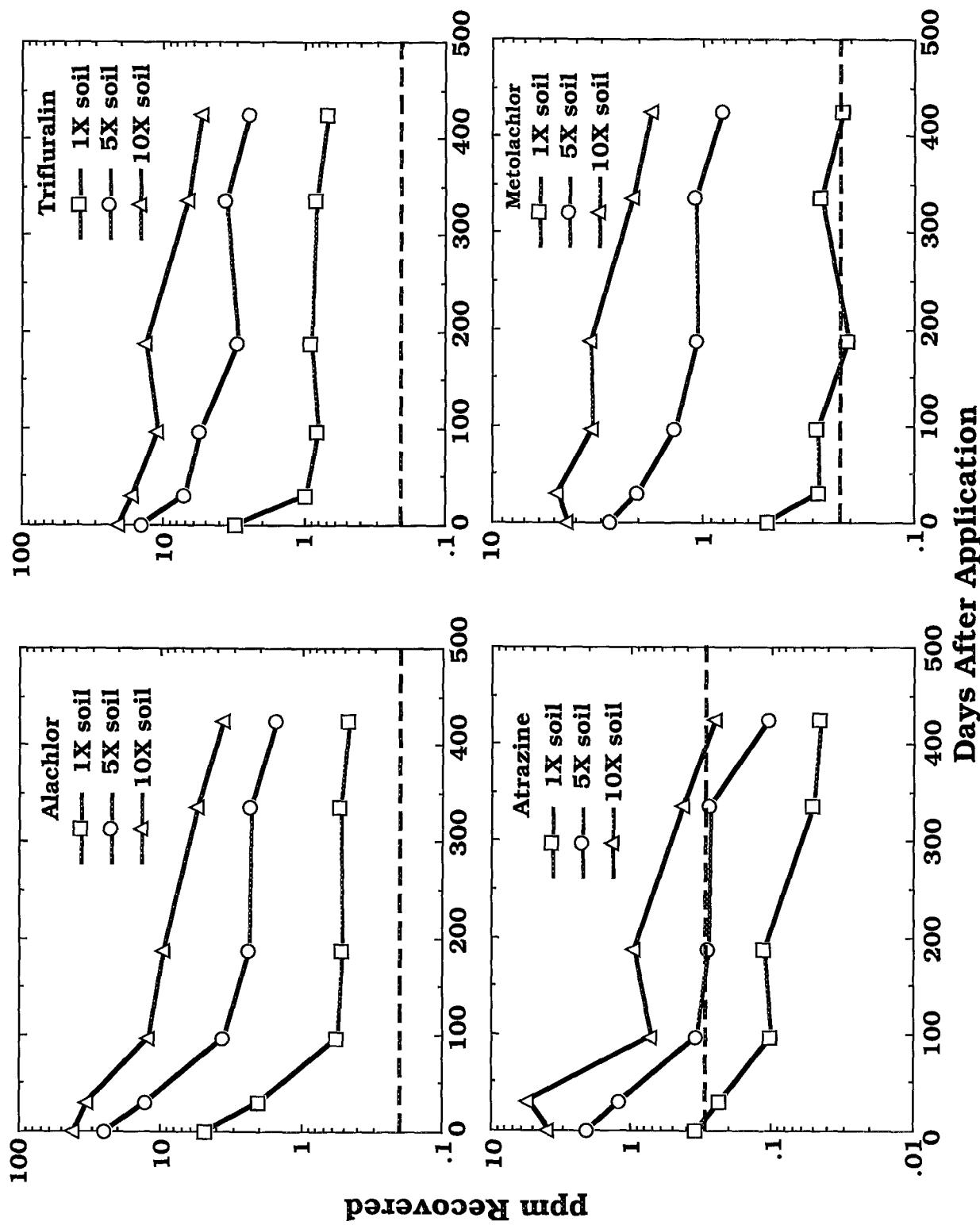


Figure 10 Relationship between concentration of herbicide residues recovered from landfarmed plots and ED50 of alachlor, atrazine, metolachlor, and ED80 of trifluralin in sandy soils. Dashed horizontal line represents the effective dosage or concentration causing phytotoxicity in 50% or 80% of the test population.

Chapter 7. Runoff, Erosion, and Leaching of Herbicide Residues

7.1 Cumulative Runoff and Erosion

Runoff and erosion from landfarmed and sprayed plots were measured from July 1991 to August 1992. A total of 82.9 cm of precipitation was recorded, the greatest proportion of rain and consequently runoff was recorded during the 1992 growing season. Average slopes of plots ranged from 2.8 - 3.4%. Plant residue cover was significantly influenced by proportional rate of alachlor application (Table 8), which suggested that excessive herbicide residues inhibited development of standing biomass. The inhibition of biomass was most pronounced in the 10X sprayed and landfarmed plots with residue cover ranging from 0-10%, measurements of standing biomass were $>200 \text{ g m}^{-2}$ in 1X plots but only $<25 \text{ g m}^{-2}$ in 10X plots (Figure 9). Coincident with the lower levels of plant residue, runoff and erosion tended to be greater in 5X and 10X plots than in 1X plots (with the exception of the contrast between the 1X and 5X sprayed treatment).

Table 8 Cumulative runoff and erosion from landfarmed and sprayed plots (July 1991 - August 1992)

	Proportional Rate of Application		
	1X	5X	10X
Slope (%)			
Landfarmed	2.8	3.2	3.1
Sprayed	3.4	3.0	3.1
Residue Cover (%) [†]			
Landfarmed	42 - 92	26 - 13	0 - 0
Sprayed	54 - 86	14 - 44	4 - 9
Runoff (L)			
Landfarmed	4249	7963	9030
Sprayed	7696	8460	9409
Sediment (kg)			
Landfarmed	25	236	339
Sprayed	153	104	294

[†] Highest % residue cover during the growing season (May-September) of 1991 and 1992

To compare the effect of spraying and landfarming on herbicide runoff, herbicide loads in individual runoff events were calculated from the product of total runoff volume and herbicide concentration in a 0.5 L water sample. Similarly, herbicide loads in eroded sediment were calculated as the product of total eroded sediment and herbicide concentration in a sediment sample that had been obtained by filtering the runoff sample. The total runoff and eroded herbicide loads were cumulated over all runoff events and expressed as a percentage of the initially applied amounts recovered in the aluminum interceptor pans.

Cumulative percent-of-applied runoff and erosion of alachlor residues were similar in 1X landfarmed and sprayed treatments (Figure 11). In sprayed treatments, alachlor was transported more in water runoff than in the sediment phase, which is consistent with other runoff studies (Felsot et al 1990). In the 1X landfarmed plot, however, the reverse was observed despite the

significantly less erosion in the landfarmed plot than in the sprayed plot (Table 8). This difference may have been caused by the comparatively higher concentrations of alachlor in the soils of the landfarmed plots.

Transport of alachlor from 5X and 10X landfarmed plots was also largely by erosion rather than runoff and was disproportionately much higher than from sprayed plots (Figure 11). Percentage of cumulative alachlor runoff from 5X and 10X sprayed plots was similar to runoff from 1X plots. Runoff volume was actually higher in the sprayed plots than in the landfarmed plots, and with the exception of the 5X treatment, differences in soil erosion were not heavily biased toward landfarming. The significantly lower levels of alachlor runoff in sprayed plots may be explained by a comparatively quicker degradation of alachlor in the sprayed plots resulting in lower residues than in the landfarmed plots.

The extremely high levels of alachlor in sediment compared to water could reflect "residue aging", where nonequilibrium sorption on intraparticle micropores provides protection from microbial degradation and a very slow diffusion back into bulk solution (Steinberg et al. 1987, Pignatello and Huang 1991, Scribner et al. 1992). Thus, alachlor was applied to landfarming plots in soil that had weathered prior to the start of the experiments and continued to age so that the only mechanism of transport was functionally via particle detachment and erosion. In the freshly sprayed plots, alachlor residues would have progressively "aged", especially during the second growing season after application, and consequently be transported largely by erosion.

Like alachlor, greater proportions of trifluralin, atrazine, and metolachlor were translocated during runoff from 5X and 10X landfarmed plots than from sprayed plots. Surface transport of these herbicides from 1X plots did not differ between application treatments. Atrazine exhibited the greatest proportion of movement in runoff from 1X sprayed plots (~1% of the applied amount). These data are consistent with the relative ubiquity of atrazine in many surface water monitoring studies (Frank et al. 1982). At the higher rates of pesticide application, however, herbicide movement was largely by eroded soil. The 5X and 10X plots had very little vegetation, but the differences between landfarmed and sprayed plots in percentage residues cover (Table 8) and biomass (Figure 9) was not as large as the relative difference in percentage herbicide in eroded soil. Among the herbicides, proportion of alachlor in runoff and erosion was lowest, which could be attributed to a comparatively faster dissipation at all loading rates.

7.2 Concentration of Pesticides in Soil-Water

Soil-water was sampled on 12 July 1991 and approximately monthly thereafter through July 1992. As a result of low precipitation during the first month of the experiment, pesticide leaching was negligible. During July, 1991 atrazine and alachlor were occasionally detected in water from the checks (range of 1.3-23.6 µg/L) or 5X landfarmed treatments (range of 4.4-9.1 µg/L), because the field had been treated with a variety of herbicides during previous growing seasons, trace residues in runoff or soil-water from the Check plots were expected. Trifluralin and metolachlor were not detected in any of the leachates during July. In subsequent samplings, a consistent pattern of herbicide detection was not observed, indeed, most samples were below detectable levels. The lack of herbicide residues in soil-water sampled at a depth of 60-cm suggested minimal leaching of residues from both sprayed and landfarmed plots.

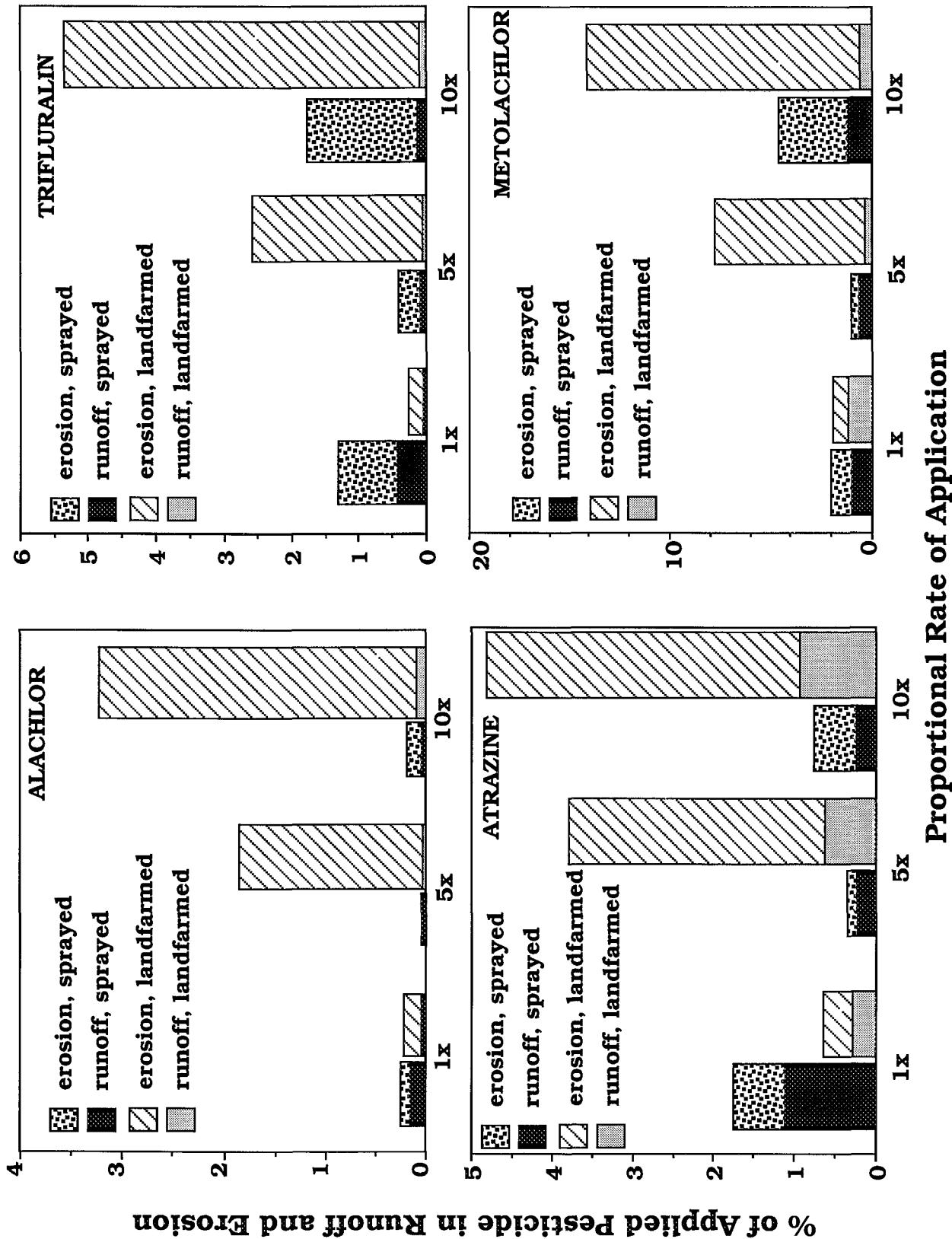


Figure 11. Recovery (as % of applied) of herbicides in runoff and erosion from landfarmed and sprayed plots.

Chapter 8. Toxicity of Runoff Water

8.1 Inhibition of Algal Photosynthesis

Inhibition of algal photosynthesis was tested using runoff water from July 11 and 12. Because there was no significant interaction between date and response, the data from each day were combined and transformed to a percentage of the response in the check. Algal photosynthesis was significantly inhibited ($p < 0.025$) by the 1X landfarming treatment (Figure 12), although not significant, inhibition by water from the 10X landfarmed treatment was also greater than inhibition by water from the sprayed plots. Such results were expected as a result of the higher concentrations of herbicides in the landfarmed plots, however, a normal dose-response relationship was not observed because negligible inhibition of photosynthesis occurred with water from the 5X treatments. Furthermore, the level of inhibition by water from the 10X plots was not significantly different than the level in the 1X plots, although residues in water from the 10X plots were 10-fold greater. In water from the 10X landfarmed plots the highest concentration of atrazine was 36 $\mu\text{g/L}$. In some studies, atrazine, which is known to inhibit photosynthesis, produced adverse chronic effects on phytoplankton populations at concentrations as low as 15 ppb (Mayasich et al 1987), but concentrations this low have not been shown to elicit acute effects as measured in the photosynthetic inhibition bioassay. All of these observations suggested that the photosynthetic response to herbicide contamination was highly variable and not necessarily related to the levels in the water.

8.2 Microtox Assay

Repeated tests using the commercial Microtox system and runoff water collected after several precipitation events failed to show any adverse effects on photoluminescence by the test bacterium. To determine the threshold for a response in the test, runoff water collected during September 1991 and October 1992 was fortified with a mixture of the four herbicides to produce concentrations up to 2 mg/L (Figure 13). Adverse response in the assay was observed when the herbicides were added at levels between 0.25 and 0.50 mg/L. These concentrations are extremely high compared to the ppb levels recovered in runoff water (Figure 13). Thus, runoff water, although containing substantial quantities of herbicide, does not seem to be toxic in the Microtox assay.

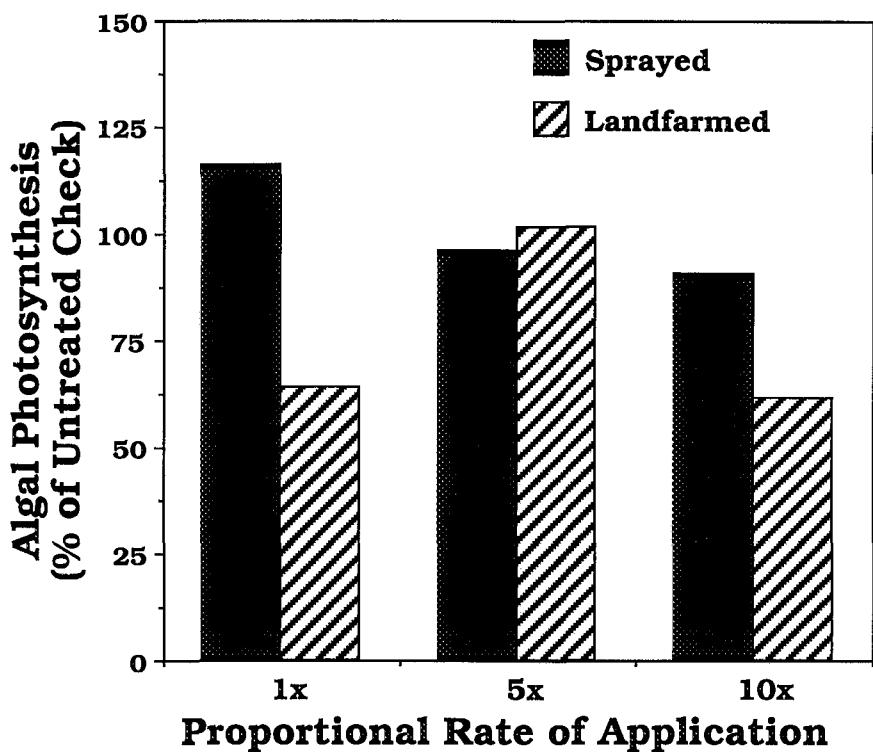


Figure 12. Inhibition of algal photosynthesis in runoff water collected during July 1991.

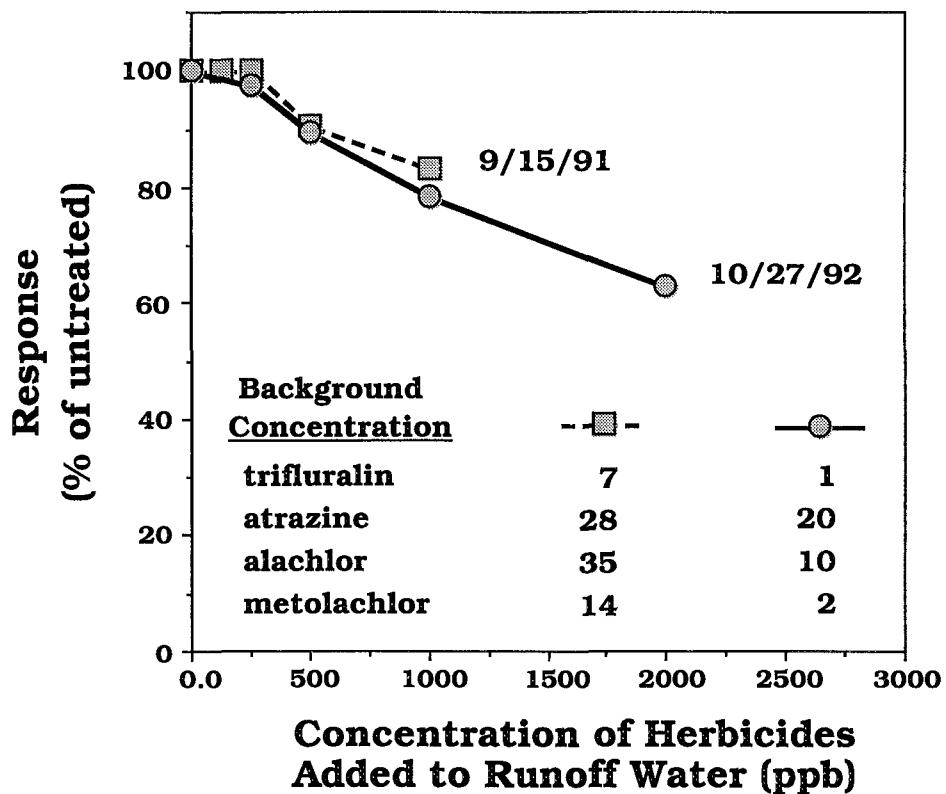


Figure 13 Dose-response relationship for herbicides in the Microtox assay.

Chapter 9. Herbicide Residues in Harvested Soybeans

Because no relationship was found between proportional rate of application and residues recovered, all data for each application treatment were combined. During 1991, every soybean sample including the untreated checks had detectable levels of trifluralin (Table 9). Range of mean trifluralin residues in soybeans from landfarmed plots ranged from 57-77 ppb, which was similar to the range from sprayed plots and did not differ much from residues recovered in the unweeded Check plots. Mean residues of alachlor were <10 ppb, but occasionally residues up to 12 ppb were detected. Residues of atrazine and metolachlor were less than the limits of detection. The higher and more frequent recoveries of trifluralin in soybeans probably results from having a water solubility of 0.3 ppm, which is significantly lower than the other herbicides, thus, the tendency for unmetabolized residues to bioconcentrate in soybean oil could have been associated with the very high residues. Trifluralin residues in beans from the untreated Check plots is consistent with the occasional detections of trifluralin in Check soil at levels <100 ppb.

During 1992, residues of all herbicides were found only occasionally, one Check sample and one 10X landfarmed sample had alachlor residues of 20 ppb, but nearly every trifluralin detection was below 10 ppb. These data are in agreement with the substantially lower herbicide residues in soil during the second year of the study.

The detection limits achieved in the analytical method were significantly below the tolerances for the parent pesticides in soybeans and corn. For examples, the tolerance for trifluralin in beans and corn is 50 ppb. Alachlor, metolachlor, and atrazine hold even higher tolerances ranging from 100-250 ppb. During 1991, residues of the latter three herbicides were well below established tolerances, but trifluralin residues in the 1X landfarmed treatments would have been above the tolerances. However, trifluralin also violated the tolerance in soybeans from the unweeded Check, and therefore the appearance of residues in the beans does not seem related to the type of treatment. Residues recovered during 1992 were below tolerances.

Table 9 Range of mean residues of herbicides in soybeans after harvest in 1991

Herbicide	Mean Parts Per Billion Recovered			
	Sprayed	Landfarmed	Weeded Check	Unweeded Check
alachlor	<10 ^a	<10 ^b	<10 ^c	<10
trifluralin	41 - 77	57 - 77	40	80
atrazine	<2	<2	<2	<2
metolachlor	<10	<10	<10	<10

^a 2 samples with 11-12 ppb

^b 2 samples with 11 ppb

^c 1 sample with 12 ppb

Chapter 10. Effects of Organic Nutrient Amendments on Dissipation of Sprayed and Landfarmed Herbicide Residues

10.1 Degradation of Herbicide Residues

In laboratory experiments, corn meal and sewage sludge have been shown to enhance the biodegradation of high concentrations of alachlor (Dzantor and Felsot 1992). To determine the feasibility of using these organic amendments in the field to augment the degradation of landfarmed herbicide residues, corn meal and sewage sludge were added to small plots containing landfarmed and sprayed herbicide residues. Herbicide residues were expressed as a percentage of residues initially recovered immediately after application of contaminated soil, sprays, and organic amendments (Figure 14-17).

Corn meal and municipal sewage sludge stimulated degradation of alachlor residues derived from contaminated soil (Figure 14, 5X and 10X Landfarmed) or sprays (Figure 2, 5X & 10X Sprayed). Percentages of alachlor recovered from unamended 1X plots after 100 days were not significantly different than the percentages recovered in amended plots, this similarity in recovery suggested that the stimulatory effects of amendments did not significantly affect alachlor degradation beyond two months. Residues recovered from corn meal-amended 10X plots (3.37 ppm landfarmed plots, 0.05 ppm sprayed plots) were still lower at 428 days post application than residues recovered from unamended plots (6.74 ppm landfarmed plots, 0.42 ppm sprayed plots).

In contrast to alachlor, trifluralin degradation was generally stimulated only by corn meal (with the exception of no effect in the 1X sprayed plots). Sewage sludge seemed to slow the degradation of trifluralin compared to the degradation in unamended plots. Trifluralin has a high affinity for organic carbon because of its low water solubility. Guo et al (1992) showed that municipal sewage sludge mixed with sandy soil could increase the sorption coefficient of various herbicides. The results with trifluralin in the presence of sewage sludge suggested that sorption made the pesticide less available for degradation.

In all treatments except the 1X landfarmed plots, atrazine degradation seemed to be enhanced by treatment with corn meal (Figure 16). In contrast to trifluralin, atrazine degradation was not slowed by sewage sludge, and the degradation curves even suggested some stimulation of degradation in 10X landfarmed and 1X and 10X sprayed plots. Laboratory studies using static shake flasks containing soil amended with corn plant residue failed to show any enhancement of atrazine nor trifluralin degradation (Felsot 1991), however, under field conditions such stimulation of degradation may be possible owing to abundant moisture and aeration.

Metolachlor degradation, like its analog alachlor, was significantly enhanced by corn meal in all treatments, however, in the 1X landfarmed treatment metolachlor degradation was enhanced only during the first two months of the study (Figure 17). In contrast to alachlor, however, sewage sludge seemed to have little effect on metolachlor degradation. The lack of enhancement of degradation of metolachlor and alachlor at the lower application levels over the 428 days of the experiment may have resulted from a generally quick innate degradation rate with subsequent residues too low to resolve differences among the treatments.

10.2 Effects on Soil Dehydrogenase Enzyme

In addition to following herbicide concentrations, soil dehydrogenase was measured in soil collected from each plot. Data were not separated by application level.

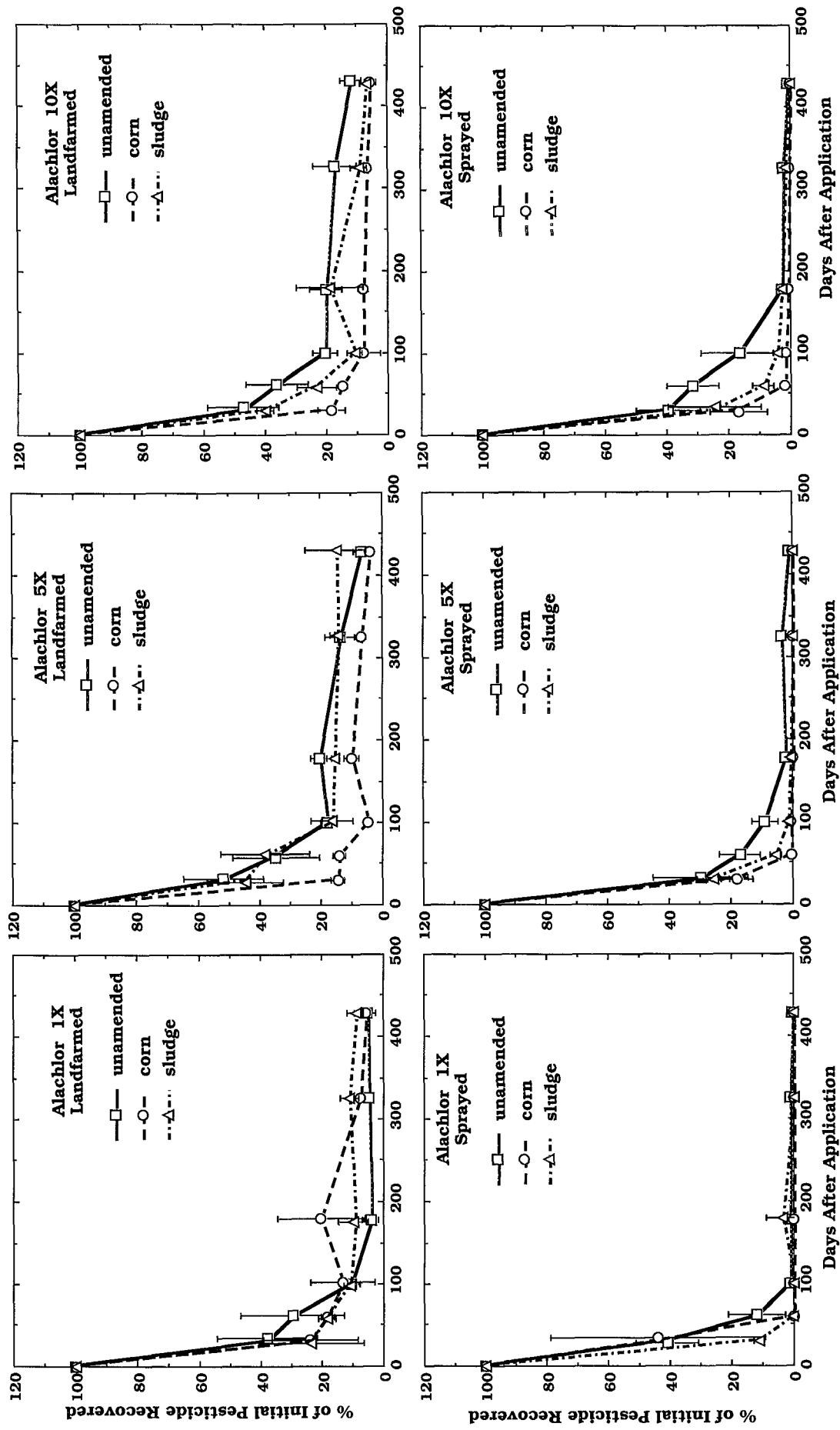


Figure 14. Effect of organic nutrient amendments on recovery of sprayed and landfarmed alachlor residues from small plots.

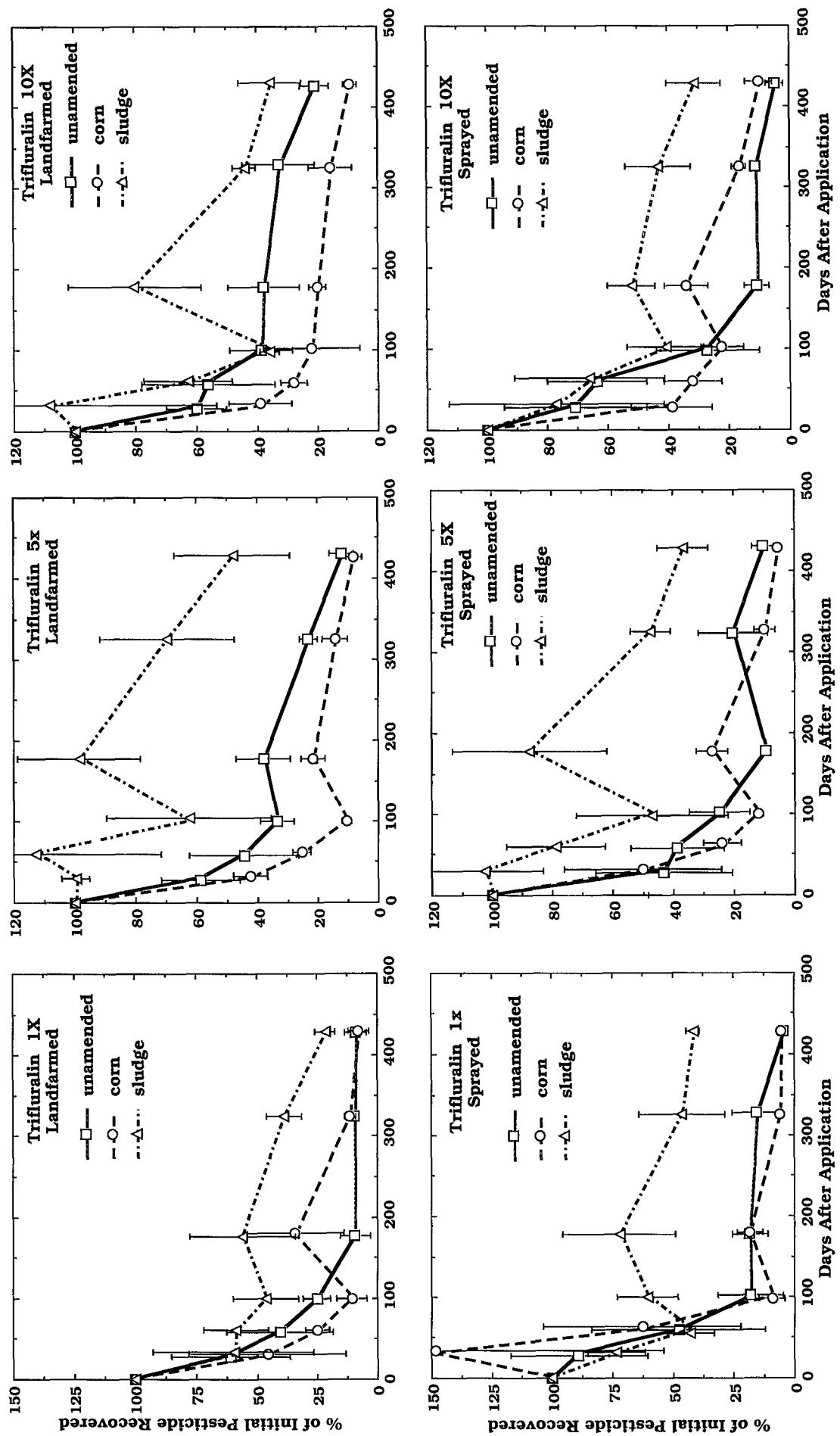


Figure 15. Effect of organic nutrient amendments on recovery of sprayed and landfarmed trifluralin residues from small plots.

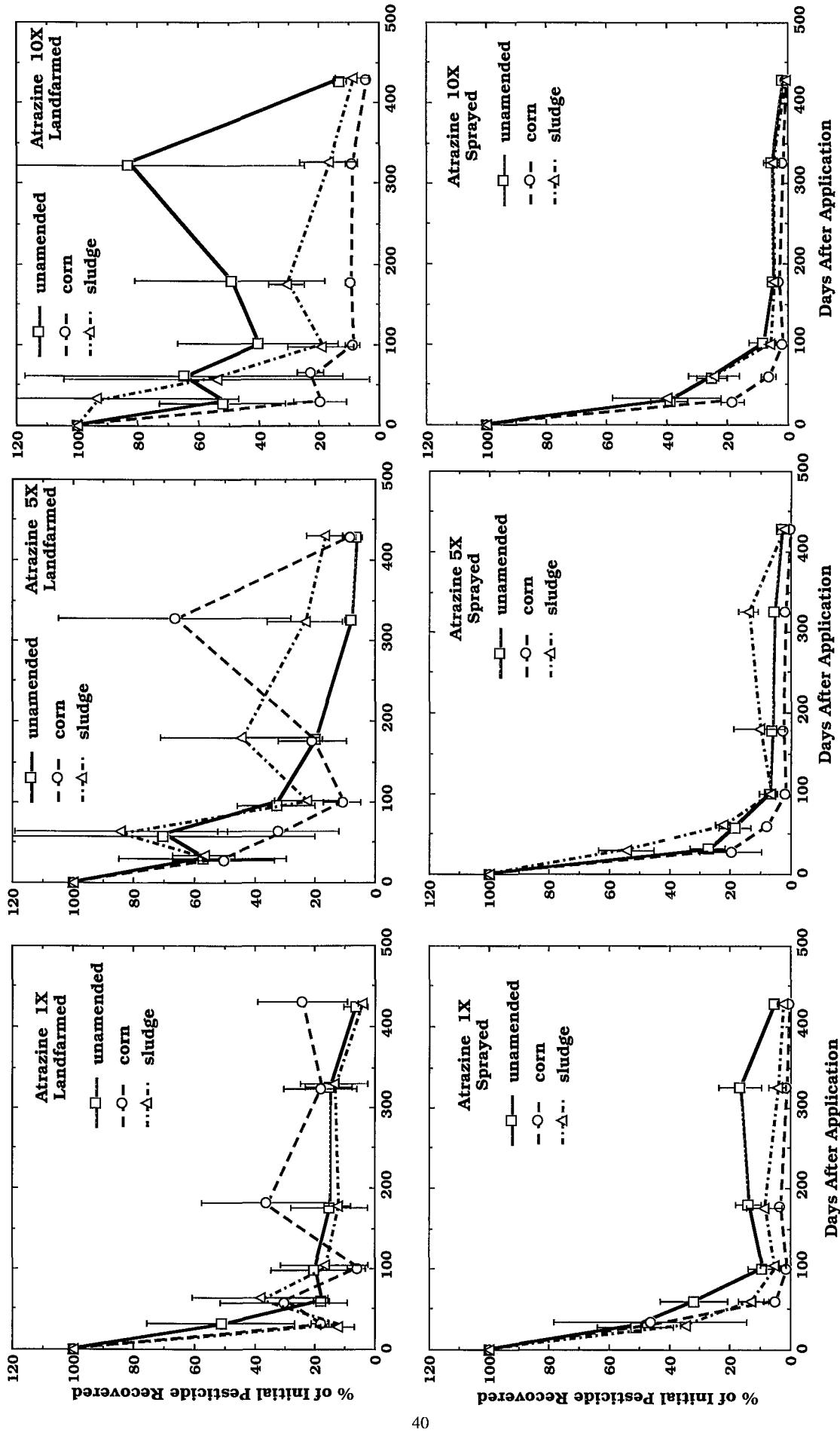


Figure 16. Effect of organic nutrient amendments on recovery of sprayed and landfarmed atrazine residues from small plots.

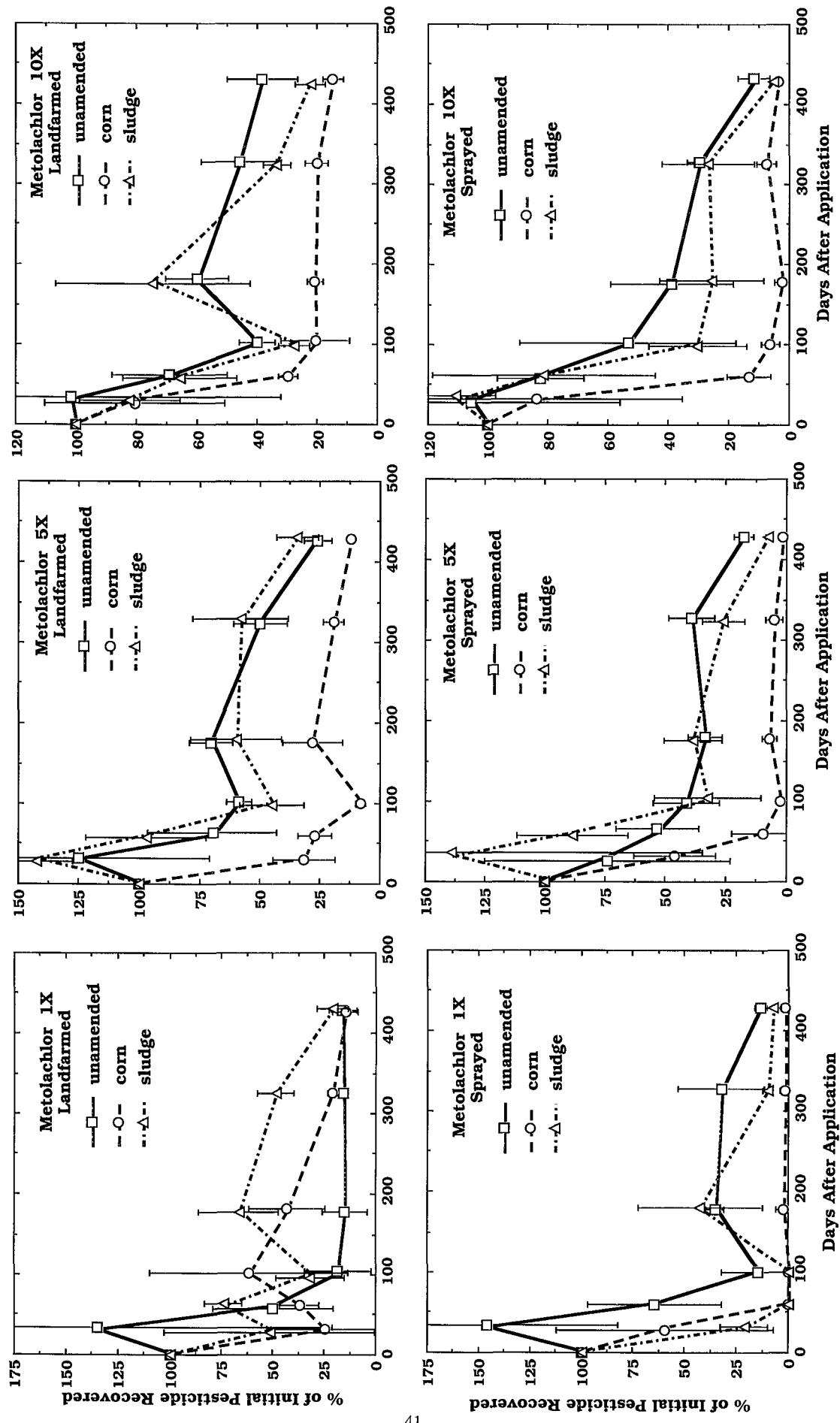


Figure 17. Effect of organic nutrient amendments on recovery of sprayed and landfarmed metolachlor residues from small plots.

Compared to unamended soil, dehydrogenase activity was significantly elevated for at least 177 days following corn meal and sewage sludge amendments (Figure 18). Increased dehydrogenase activity suggested that enhanced degradation of the herbicides at the 5X and 10X rates of application was associated with increases in general microbial activity

Soil dehydrogenase has been traditionally measured as a surrogate for general microbial activity (Tabatabai 1982, Nanipieii et al 1990). Although not always well correlated with microbial numbers, dehydrogenase activity has been correlated with oxygen uptake and has significantly increased after addition of organic amendments (Stenvenson 1959, 1962, Casida 1977). Additions of organic nutrients cause substantial increases in dehydrogenase activity, which has been interpreted as a generalized increase in soil metabolism of readily available nutrients (Nannipieri et al 1990, Martens et al 1992). Because the four herbicides have been shown to be cometabolized (Novick et al 1986) rather than mineralized, any additions of energy-producing substrates could potentially increase their rate of transformation. In an attempt to stimulate degradation, corn meal was chosen because previous studies showed that corn plant residue stimulated degradation of 100 mg/kg alachlor (Dzantoi and Felsot 1991), and in preliminary studies corn meal was even more effective than corn plant residue, furthermore, it had been previously tested for remediating pesticide waste in California (Winterlin et al 1989). Significantly enhanced losses of alachlor in soil amended with corn meal suggested that there are significant numbers of microorganisms that have the ability to at least partially metabolize alachlor in the presence of extraneous nutrient sources. The results suggest that manipulation of soil microbial ecology through addition of organic amendments may be feasible for enhancing the cometabolism of pesticide waste in soil by allowing pesticide-tolerant organisms to thrive.

10.3 Standing Biomass in Biostimulation Plots

Further evidence of the biostimulatory effect of corn meal and sewage sludge was seen in the measurements of standing biomass (Figure 19). Compared to the unamended plots, total biomass in corn and sewage sludge amended plots was significantly higher, indicating substantial reduction in herbicide toxicity after two years. Plots treated at rates of 5X and 10X still had high enough residues to inhibit plant growth compared to the Check and 1X plots, but in the 5X and 10X landfarmed plots, corn amended plots had the highest standing biomass.

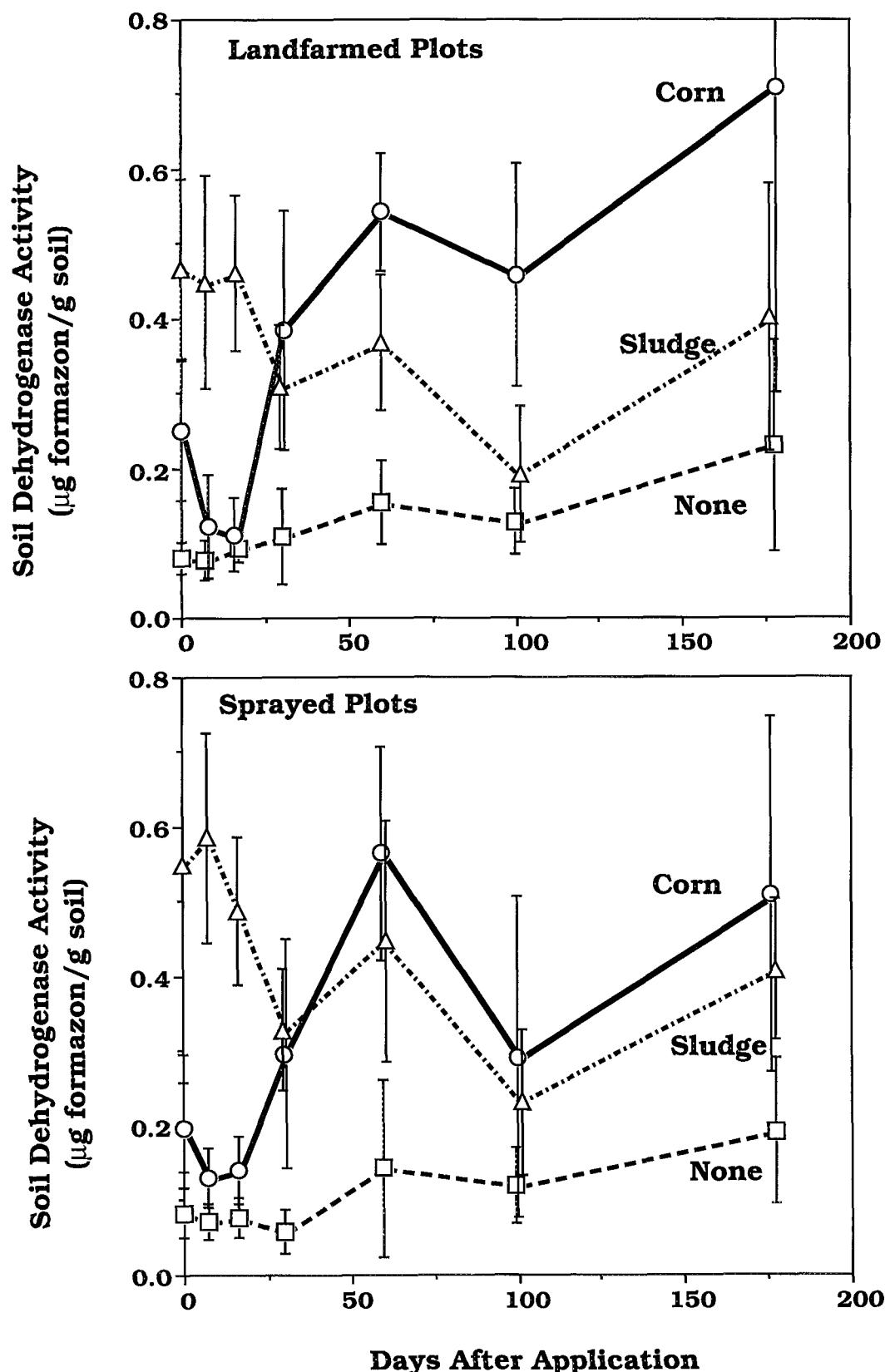


Figure 18. Dehydrogenase activity in soil amended with corn meal or sewage sludge. Data were combined by rate of application.

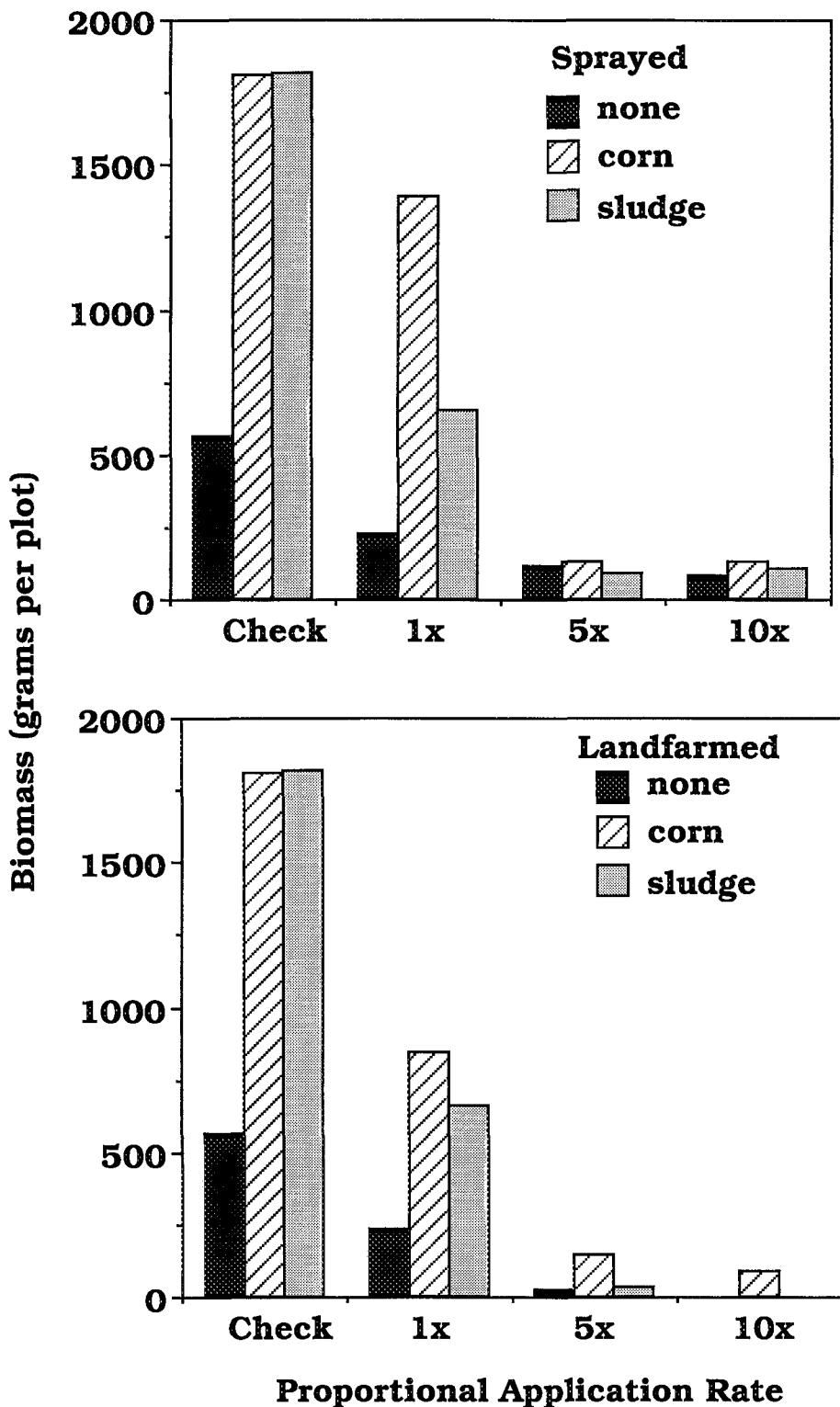


Figure 19. Standing biomass measured in biostimulation plots during August 1992.

Chapter 11. Conclusions

An experimental design for determining the degradation, translocation, and phytotoxicity of herbicide contaminants in landfarmed waste under field conditions was developed and tested at the University of Illinois during the 1991 and 1992 growing seasons. One major objective of the design was to provide adequate experimental units for a statistical comparison of herbicide behavior after spraying with herbicide behavior after landfarming. Results of initially recovered herbicide residues in soil were analyzed to determine the feasibility of the design. By analyzing six individual soil cores per replicate plot, variance of the mean herbicide concentration between replicate plots was lowered to levels that could be reasonably expected for a field study.

Although herbicide residue data from runoff plot soils could be fit to a first-order rate equation, this model was not the most appropriate because slope of the log concentration-time curve varied over time, indicating that rate varied with concentration. Indeed, after the first 100 days, the curves for all herbicides flattened out, showing a significant slowing of degradation.

To determine whether landfarming of herbicide contaminants was efficacious, all data were transformed to percentages of initially recovered residues and then the times to 50% and 90% disappearance (i.e., DT_{50%} and DT_{90%}) were measured. With the exception of metolachlor, which was subject to much variation in recoveries, landfarmed herbicides applied at an equivalent load of 1X (based on alachlor concentrations) dissipated within similar time frames over the first 100 days as the sprayed material. However, the DT_{90%} for alachlor, atrazine, and metolachlor residues was prolonged in the landfarming plots, suggesting a very slow degradation beyond 100 days. Felsot et al. (1990) had also observed recovery of significantly higher residues of alachlor and metolachlor from landfarmed plots in a study conducted during 1986-1988 in Galesville, IL. Thus, while landfarmed herbicide residues quickly degrade during the first 100 days after application, some unknown interaction with soil thereafter causes a slowing of degradation in comparison to sprayed residues.

At rates of application higher than 1X, DT_{90%} was also significantly prolonged in landfarmed plots compared to sprayed plots. The DT_{50%} however showed no consistent pattern in persistence, for example, the DT_{50%} for alachlor at the 5X sprayed treatment was longer than for the landfarmed treatment, but the reverse was true at the 10X application rate. The data, however, do suggest that application rates greater than 1X can result in unpredictably prolonged persistence of herbicide residues.

The phytotoxic hazard of herbicide residues following landfarming was assessed by examination of soybean plant stand counts and yield, weed counts, and biomass. Although dissipation of herbicide residues in the landfarmed plots at the 1X rates of application was prolonged compared to dissipation in the sprayed plots, plant stand counts and biomass during 1992 showed no differences between the two application modes. Thus, higher residues in the landfarmed soils did not automatically translate to higher phytotoxicity. The latter concern would be an important consideration in deciding when a site for landfarming could be brought back into production. The data suggested that a two year period may be necessary to avoid liability problems as a result of unexpected toxicity to subsequent crops.

Residues of herbicides recovered in soybeans were quite low, although during 1991, all samples contained trifluralin residues. In some samples, the residues violated the 0.05 ppm tolerance for soybeans, but this level was also violated in the unweeded Check treatment. Thus, the high levels of trifluralin could not be attributed to the landfarming practice itself, and therefore, the process should not cause the occurrence of violative residues.

Runoff collectors had enough capacity to collect storm runoff of 5.5 cm or less. At the 1X rates of application, surface transport of herbicides occurred nearly equally (except for atrazine).

in the eroded and runoff phases, but no differences were seen between landfarmed and sprayed treatments. At higher rates of application, surface transport of herbicide residues from landfarmed plots was significantly higher than from sprayed plots. Furthermore, the eroded phase was highly enriched with herbicide residues compared to the runoff phase. Normally, herbicides would be carried largely in the water phase, and significant movement in the eroded phase was unexpected. The data suggested a strong binding to the landfarmed soil and an equilibrium that was not shifted to the water phase upon saturation of the soil surface during high intensity storms.

Detections of herbicides in lysimeter-collected soil-water were infrequent, concentrations were very low and did not correspond to mode of application. Thus, both sprayed and landfarmed herbicides remained largely in the plow layer.

Herbicide concentrations in runoff water were probably not high enough to cause significant toxicity in the algal photosynthetic inhibition bioassay. The Microtox assay also failed to show significant toxicity from herbicide residues in runoff water. The Microtox assay was calibrated with known herbicide concentrations, the assay seemed sensitive to concentrations >250 ppb, which would be significantly larger than any concentrations recovered in runoff water in this study.

To determine whether degradation of the herbicides in the landfarmed plots could be significantly enhanced, corn and sewage sludge were added to small plots receiving either herbicide sprays or landfarmed contaminated soil. For most treatments, corn meal significantly enhanced degradation of the herbicide residues, but the enhancement was most pronounced at the 5X and 10X rates of application. The results suggested that at the 1X rates of application, degradation is sufficiently fast to mask any pronounced biostimulatory effects. However, at the higher rates of application, where comparatively more mass of herbicide would be present in the water phase and therefore available to microorganisms, nutrient amendments seemed very beneficial in shortening persistence.

The enhanced rate of degradation of the herbicides was echoed by measurements of standing biomass, which showed increased biomass in the 1X plots treated with corn meal and sewage sludge. Biomass in check plots was similar in corn- and sludge-treated plots and much higher than in the unamended plots, suggesting a stimulatory effect of nutrients on plant growth. However, in the various herbicide-treated plots, biomass was much greater in corn-amended plots than in sludge-amended plots and biomass in unamended plots gave evidence of phytotoxicity. Thus, corn meal was responsible for effectively reducing herbicide residues to lower levels as well as providing nutrients to stimulate plant growth.

In summary, herbicide residues in landfarmed plots degraded at a similar rate to residues in sprayed plots within the first 100 days after application, but degradation slowed appreciably thereafter. No excessive phytotoxicity was noted if landfarmed herbicides were applied at 1X rates. Cumulative runoff and erosion of residues at the 1X rate of application was similar between treatments, but at the 5X and 10X rates, higher loads of herbicides were generated by the landfarming plots than by the sprayed plots. Infrequent, low-level detections of herbicides in soil-water at a 60-cm depth suggested lack of significant leaching potential of both landfarmed and sprayed herbicide residues. The concentrations of herbicides in the runoff water were not high enough to produce adverse toxic effects in two types of aquatic bioassays. With the exception of trifluralin, herbicide residues in soybeans were well below established tolerances. Trifluralin residues did violate the established tolerance in some samples, but the excessive residues were unrelated to plot treatments. Corn meal affords the opportunity to enhance the degradation of herbicide residues during landfarming.

Chapter 12. Recommendations

The following recommendations emanate directly from observations made about the persistence of landfarmed pesticide residues and potential environmental hazards. The recommendations are offered with the assumption that land used for treatment will have to be returned to production in a timely manner and be safe for future cultivation of potentially sensitive crops.

- (1) Extensive sampling of contaminated soil should be conducted to determine the mean and variance of herbicide residues and to more accurately establish the load of soil needed to meet targeted rates of application. The land designated for receiving the contaminated soil should also be sampled in a representative manner to establish background concentrations of herbicides
- (2) Manure spreaders or other devices for application of contaminated soil should be calibrated using some of the contaminated soil
- (3) Waste loading rates should not exceed the equivalent of 1X rates of application based on consideration of the most prevalent pesticide contaminant and/or the most toxic contaminant. If enough land is available, waste-loading rates less than 1X should be used
- (4) Land chosen for landfarming should have little slope to avoid enhanced surface transport, the land should not drain directly into higher order creeks or streams.
- (5) To avoid excessive hot spots, the soil spreading device should be operated in a manner that gives the best possible homogeneity of application. A preliminary test strip may be necessary to adjust the spreader
- (6) Because hot spots with greater than 1X equivalent herbicide concentrations may be unavoidable, organic amendments like corn meal should be considered for enhancing degradation rate; other methods of biostimulation may also be considered.
- (7) At least two growing seasons should be allowed for completion of the landfarming process
- (8) After the specified landfarming period, measurements of pesticide residue concentrations should be taken based on a representative sampling scheme
- (9) After the specified landfarming period, standard phytotoxicity assays should be conducted on several aliquots of soil to ensure lack of toxicity to subsequently planted crops

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