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J. B. Belden  
_Iowa State University_

B. W. Clark  
_Iowa State University_

T. A. Phillips  
_Iowa State University_

K. L. Henderson  
_Iowa State University_

E. L. Arthur  
_Iowa State University_

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Abstract
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Disciplines
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Comments
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Authors

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Chapter 12

Detoxification of Pesticide Residues in Soil Using Phytoremediation


Department of Entomology, Iowa State University, Ames, IA 50011

During the past few years, we have conducted a series of experiments to investigate the potential of using plants as tools for the remediation of pesticide-contaminated soil. We have demonstrated that a blend of prairie grasses increases dissipation rates of several pesticides including metolachlor, trifluralin, and pendimethalin. However, in other studies, mulberry trees were not shown to influence pesticide dissipation. Additional studies have demonstrated that metolachlor movement in the soil column may be reduced by the presence of prairie grasses, bioavailability of dinitroaniline herbicides may be reduced during phytoremediation, and soil and leachate from remediated soil may have less toxicity than expected. Current studies within our laboratory are being conducted to determine the role of prairie grass blends in the phytoremediation procedure as compared to individual species and the role of plant uptake of pesticides in the phytoremediation process.
Introduction

Phytoremediation – the use of plants as a remediation agent for contaminated water or soil – has recently become widely investigated as a possible solution for many pollution problems. For example, plants have been used to remove heavy metals from soil, grasses have been used to remediate petroleum hydrocarbons, industrial solvents, and explosives from contaminated soil, and trees have been used to remove atrazine and industrial solvents from groundwater plumes (1). Phytoremediation is able to remediate such diverse contaminants due to the variety of mechanisms plants may use to either remove or detoxify contaminants. Heavy metals and some organic compounds may be removed by plant uptake such as the case for removal of heavy metals from soil and removal of volatile-organic compounds from groundwater. Organic compounds may be further degraded in the plant, while heavy metal uptake requires removal of the plant from the site. Plants are also capable of increasing degradation of organic compounds in the rhizosphere (root zone of the plant). This is often due to the plant releasing exudates from their roots, resulting in increased microbial activity (1); however, a few investigators have reported direct release of degrading enzymes, capable of biotransformation of organic compounds (2).

Our current research has focused on potential for using phytoremediation for cleanup of point-source pesticide contamination. During the manufacturing of pesticides, distribution to agrochemical dealerships, mixing of formulations, and loading of pesticides into tanks for application, there is a great potential for the occurrence of pesticide spillage. In fact, one study estimated that 90% of agrochemical dealerships in Iowa have pesticide contaminated soil and 50% of these sites will need remediation (3). High concentrations of pesticide contamination in soil can impact the environment in several ways, including leaching into groundwater, running off into nearby surface water, or directly impacting local soil organisms.

We have mostly concentrated on a set of pesticides – atrazine, metolachlor, pendimethalin, and trifluralin – that have been among the most heavily used pesticides in the corn-belt region of the United States for many years (4). Atrazine and metolachlor are moderately persistent in the environment and are relatively soluble in water. Studies have shown that they are two of the most common contaminants of ground and surface water (5). Pendimethalin and trifluralin are not very mobile in soil (6); however, they are persistent and tend to bioaccumulate (7).

In a series of studies, we have investigated the potential use of individual prairie grasses, a prairie grass mixture, and mulberry trees for the phytoremediation of these pesticides. Our initial experiments have been conducted to demonstrate that plants can survive in soil moderately
contaminated with pesticides, and their presence increases the degradation rate of pesticides. Further experiments have been designed to evaluate the remediation system by examining pesticide movement in the soil column during remediation and evaluating bioavailability of the remaining residues. The latest experiments have been focused on the mechanisms involved with our phytoremediation strategy, including the impact of mixed grass species as compared to individual species and the amount of pesticide that is taken up by the plant versus degraded in the soil. The purpose of this chapter is to review our recent and current phytoremediation investigations. Full detail of the experiments is being published elsewhere.

Evaluation of Plants for Phytoremediation Potential

The prairie grasses we are investigating – yellow indiangrass, switchgrass, and big bluestem – are deep-rooted perennial plants with long growing seasons, they are tolerant to moderate levels of pesticides, and are commonly available as seed. Prairie grasses have also been shown to have phytoremediation potential for other organics such as petroleum hydrocarbons (8). We have chosen to use a mixture of the three grasses in most of our studies, because mixtures are used for prairie restoration and may have a wider range of degradative capacities in their rhizosphere.

Prairie Grasses - Microplot Study

In a four-year study, we investigated the effect of prairie grasses on the rate of pesticide dissipation in soil obtained from a contaminated agrochemical dealership site. The soil (loamy sand, 1.6% organic matter), originally containing 110 mg/kg pendimethalin and 10 mg/kg metolachlor, was treated with 25 mg/kg atrazine, trifluralin, and metolachlor. Microplots were constructed in plastic tubs (24 x 30-cm base and 18 cm-depth), which were kept in outdoor plots in Ames, IA during the summer and in the greenhouse during winter months. After an initial aging period of 30 days, individual microplots were either planted with a mixture of the three prairie grasses, or left unvegetated (n=4). Each microplot was sampled by taking three soil cores at various points in time up to 1,026 days. After 1,026 days, soil from each plot was allowed to dry and then mixed thoroughly. Soil samples were extracted with ethyl acetate and the concentration of pesticides was determined by gas chromatography with thermionic specific detection (9).

Initial measurements taken over the first 200 days of this study indicated a trend of increased atrazine and metolachlor dissipation in the prairie grass plots.
However, by the end of the study, less than 2% of the atrazine and less than 15% of initial metolachlor was recoverable. At this point, there was no significant difference between unvegetated and vegetated treatment of soil for either compound. The dinitroaniline herbicides, pendimethalin and trifluralin, were much more persistent. As shown in Figure 1, greater than 40%, and up to 70%, of the residues remained after 1,000 days. Lower amounts of dinitroaniline herbicides (pendimethalin and trifluralin) were recoverable from soil vegetated with prairie grasses (p=0.004). Individually statistical analysis did not show vegetation differences for pendimethalin, however the percentage of trifluralin residue remaining was significantly lower in vegetated columns (t-test, p<0.05).

![Figure 1. Vegetation with prairie grasses significantly decreased the percentage of pendimethalin and trifluralin remaining in soil after 1,000 days of remediation (F = 12.6, p = 0.004).](image)

**Prairie Grasses - Column Study**

Further investigation of the prairie grass mixture for phytoremediation of pesticides was conducted using artificial soil columns. Eight soil columns were constructed in PVC (polyvinylchloride) pipe (10-cm diameter and 21-cm depth) with the bottom of the column secured with glass wool and aluminum screen. The base of the column was packed with 7 cm unfortified soil from an agronomic site that has not received pesticide application for over 15 years (sandy loam, 2.4% organic matter). An additional 14 cm of the same soil
fortified with atrazine, alachlor, metolachlor, and pendimethalin at 25 mg/kg was added to the top of the column. The bulk density of the soil in the columns was 1.2 g/cm$^3$. After aging the columns for 60 days, half of the columns were planted with plugs of the prairie grass mixture previously described, while the remaining columns were left unvegetated.

The columns were placed in a greenhouse for 240 days and watered as needed to keep the columns moist, but not to cause water to come out of the bottom of the column. At the end of the study, a “storm event” was performed which entailed adding 608 ml water to each column (corresponding to 7.5 cm of rain). This amount of water resulted in leaching through the column. The leachate was extracted by solid-phase extraction. After 10 days without water, the columns were divided into three soil profile regions, and the soil was extracted by shaking with ethyl acetate. Extracts were analyzed by gas chromatography with thermionic specific detection. Full methods for the analysis techniques have been previously reported (9, 10).

Alachlor and atrazine degraded rapidly in the columns; less than 2% of the applied amount was recovered from the system and no differences were found between vegetated and unvegetated treatments. As shown in Figure 2, vegetation with prairie grasses did significantly reduce the total amount of metolachlor (p<0.01) and pendimethalin (p<0.01) recoverable from the soil column and leachate.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** After 250 days of remediation, artificial soil columns planted with prairie grasses had significantly less extractable metolachlor and pendimethalin as compared with unvegetated soil columns.
Mulberry Trees

Mulberry trees (*Morus rubra*) have been suggested as potential phytoremediation tools due to root structure and composition of root exudates (11). This rapid-growth species of tree thrives in the Midwestern U.S.; therefore, we designed a study to investigate their use as a phytoremediation tool for pesticides. Soil fortified with 100 mg/kg atrazine, and 25 mg/kg trifluralin and metolachlor, was packed inside PVC pipe 15 cm in diameter and 30 cm long. Columns were allowed to age for 60 days to better reflect the type of pesticide residues found at agrochemical dealerships. Subsequently, ten artificial soil columns were planted with mulberry trees, and ten were left unvegetated. After 170 days, soil from 5 vegetated and 5 unvegetated columns was measured for pesticide concentration. Measurements were taken from the remaining columns at 330 days. Soil concentrations were determined using solvent extraction of the soil followed by analysis by gas chromatography and thermionic specific detection as previously described (9).

The trees grew at a slower rate than expected. Examination of the roots revealed limited growth in a twisted pattern, leading us to believe inhibition of root growth occurred, likely as a result of trifluralin. As shown in Figure 3, the presence of mulberry trees did not reduce the amount of pesticide present as compared to unvegetated controls. In fact, the mulberry containing soil columns contained significantly higher levels of metolachlor than did unvegetated columns (p<0.01). Several factors may influence the potential of mulberry trees for phytoremediation. First, as with all phytoremediation, damage to the plant by the contaminant may reduce the impact of the plant. Second, mulberry trees have been reported to release exudates in seasonal cycles with a greater release of phenols in the fall during senescing (11). However, because this experiment was conducted in a greenhouse, environmental factors may not have been appropriate to result in high releases of exudates. Third, the release of phenolic compounds in root exudate is likely to cause a shift in microbial populations (11). As a result, this shift may increase or decrease the degradation of contaminants on a contaminant-specific basis. Finally, soil obtained for this study had a previous history of metolachlor treatment. Therefore, if a population of microbes with metolachlor-degrading capabilities was already present, a decrease in this microbial activity in the mulberry columns may account for the results.

Evaluation of Phytoremediation Success Using Alternative Endpoints

Phytoremediation, as with all bioremediation, may take an extended period of time before remediation is successful. During this time, movement of the pesticide or metabolites generated in the process into biota, surface water, or
Figure 3. Percentage of applied atrazine, metolachlor, and pendimethalin recovered from columns as a whole at day 170 and 330. Presence of mulberry trees did not affect the percentage of atrazine and trifluralin remaining; however, mulberry did significantly increase the percentage of remaining metolachlor ($p<0.01$).

ground water may cause undesirable environmental effects. In order to evaluate our phytoremediation method thoroughly, we have evaluated many of our phytoremediation studies using alternative endpoints, in addition to the traditional approach of chemically measuring the concentration of the contaminants of interest.

**Pesticide Movement within the Soil Column During Phytoremediation**

In the study previously described as the “Column Study”, concentrations of pesticide were measured throughout the column and in leachate recovered from the bottom of the column after a “storm” event. Figure 4 illustrates the percentage of total recoverable metolachlor obtained from the leachate. Interestingly, the vegetated columns not only reduced the total amount of metolachlor present as previously noted (see Figure 2), but also decreased downward leaching of metolachlor. After 160 days of remediation, vegetation resulted in a two-fold decrease in the total amount of metolachlor recovered from the system, while a five-fold decrease was noted for the amount of metolachlor that was recovered from leachate. After 250 days, the presence of vegetation resulted in a four-fold decrease recorded for total metolachlor, while a 20-fold decrease was noted for leachate.
Figure 4. Percentage of total metolachlor recovered from the system, that was recovered in leachate. Significantly less metolachlor was recovered in leachate from vegetated columns as compared with unvegetated columns (p<0.01).

Bioavailability of Pesticide Residues

As compounds age in soil, they often have reduced bioavailability, potentially resulting in decreased environmental risk (12); however, the rate of bioremediation may also decrease. During phytoremediation, plant-induced changes in the soil environment may potentially change bioavailability as well; therefore it is important to monitor bioavailability while evaluating phytoremediation techniques. We have used two main assays for determining bioavailability in remediating soil. The first assay, an 8-day earthworm bioavailability test, was conducted as previously described (12). Earthworms (Eisenia fetida) were exposed to the contaminated soil, followed by analysis of the worms and test soil for pendimethalin and metolachlor. The ratio of the concentration in the worm compared to the concentration in the soil was determined (biological accumulation factor; BAF). The bioassay was conducted on soil immediately after fortification of pendimethalin and with soil obtained during the phytoremediation experiment previously described as the Column Study. The ratio of the BAF determined for the remediated soil was divided by the BAF determined for fresh residues to obtain percent bioavailability for earthworms.
The second bioassay used to evaluate bioavailability was lettuce seedling growth. Percentage inhibition was determined seven days after adding seeds to soil. Multiple concentrations of pendimethalin and metolachlor were evaluated as fresh residues to obtain dose-response relationships. Seedling growth was then measured in soil obtained from the previously described Column Study. Comparison of pesticide concentrations in the Column Study soil to the dose-response data obtained for each pesticide suggested that pendimethalin was the major toxicant in the system to lettuce. Therefore, the seedling inhibition rates determined for Column Study soil were used to calculated effective soil concentrations using the dose-response curve for pendimethalin. The effective concentration was then divided by the measured soil concentration of pendimethalin to obtain the percent bioavailability for lettuce.

As shown in Figure 5, the bioavailability of pendimethalin, as measured by the earthworm assay and the lettuce assay, was reduced by the presence of vegetation and by section after 160 days. The section effect is likely due to the addition of organic matter (in the form of potting soil) into the top section during the addition of plants (and potting soils plugs into controls). Vegetation also adds organic matter to soil and may increase microbial activity and the turnover rate of organic matter. These processes could be responsible for the vegetation related decrease in bioavailability.

The decrease in bioavailability was of greater magnitude for lettuce as compared to earthworm uptake. The difference is likely due to the uptake mechanism differences between the species (plant and animal). Lettuce uptake is primarily through partitioning of the toxicant from soil, into soil water, and then into the plant root. Since earthworms ingest soil, enzymes and other gut factors may aid in the uptake of the pesticide. Chemical differences between lettuce and earthworm cuticles may also be very important. When calculating bioavailability, it is important to acknowledge that large differences may exist between types of biota, and between biological and chemical endpoints.

**Current Research in Understanding and Improving Phytoremediation Techniques**

In order to improve and fully utilize phytoremediation for cleaning up pesticide-contaminated soil, we need more basic knowledge about the process. We are actively conducting research in two areas that should improve our understanding of the role of plants within the system. In the first area, we are evaluating the fate of radiolabeled pesticides within prairie grass-soil systems. Plants may increase dissipation rate through uptake of the pesticide or through increased degradation in the rhizosphere. Understanding the role of plants is
Figure 5. Bioavailability of pendimethalin as measured by earthworm uptake and lettuce seedling growth was reduced by the presence of vegetation ($p<0.05$, $p<0.01$, respectively) in the top and middle sections of soil columns.

crucial in efforts to improve phytoremediation technologies. Currently, separate studies investigating the fate of atrazine, metolachlor, and pendimethalin are being conducted.

The second area of study involves evaluating the role of species type and species mixture on phytoremediation capability. In one experiment, we investigated the effect of prairie grasses, individually and as a mixture, on the dissipation rate of pendimethalin in a sandy loam soil (2.7% organic matter) collected from a corn field near Ames, IA that has a history of no pesticide treatment. The soil was fortified with 25 mg/kg pendimethalin and aged for 30 days. After aging, 500 g of treated soil was added to each of 20 cones (6.5-cm diameter and 25.4-cm depth), and plugs were added: potting soil only (control), big bluestem, yellow indiangrass, switchgrass, or a mixture of all three prairie grasses (4 reps/treatment). After 180 days of remediation, soil from each cone was mixed thoroughly, extracted with ethyl acetate, and analyzed by gas chromatography (9).

After 180 days, significantly lower amounts of pendimethalin were recovered in soil vegetated with switchgrass, big bluestem, and a mixture of all three prairie grasses compared to unvegetated soil ($p<0.05$; Figure 6). These results indicate that switchgrass and big bluestem are more effective at increasing dissipation rates of pendimethalin as compared to yellow indiangrass. The mixture of prairie grasses had a similar effect on dissipation of pendimethalin as big bluestem and switchgrass. Switchgrass had the least
Figure 6. Big bluestem, switchgrass, and mixed prairie grasses all significantly reduced the amount of recovered pendimethalin after 180 days of remediation (*p*<0.05). Treatments with the same letter are not significantly different.

Biomass at the end of the study, indicating that the results are not strictly tied to growth and productivity of the grasses.

**Conclusions**

We have found substantial evidence that the presence of vegetation can increase dissipation rates of pesticide residues in soil. Further evidence implies that vegetation may stabilize the pesticide residues, decreasing the potential for leaching and uptake into biota; thus, phytoremediation may prove to be a valuable tool in clean up of moderately contaminated sites. However, several considerations should be made regarding this technology:

1]. Plant selection is crucial. In the studies presented here, some grass species increased dissipation, one grass species had little observable effect, and mulberry trees may have inhibited metolachlor dissipation. Additionally, as seen in the mulberry experiment, pesticide damage to the plant may reduce plant growth and therefore, the impact of the plant on the environment.
2. The process is slow. Our results have demonstrated that plants may help stabilize the system, however, if severe environmental impact is imminent, other remediation may be necessary.

3. Changes in bioavailability may hinder the complete clean-up of the site. Potential exists for aged residues, which are not available to degrading organisms to remain on the site. If strict concentration-based action limits exist for the site, the remediation technique may not be successful. However, if the compounds are not available for degradation, it is likely that the compound has limited availability to sensitive organisms or potential to leach into groundwater.

Further research studying the mechanisms and factors influencing phytoremediation may help us to improve the technology by increasing the rate of pesticide degradation and increasing our are capabilities in stabilizing remaining residues.

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