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Measurement and Model Prediction of Pesticide Partitioning in Field-Scale Turfgrass Plots

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PURPOSE AND OBJECTIVES

The purpose of this research project is to conduct a mass balance assessment of turfgrass pesticides in field plots and use the data obtained in the assessment to test and modify a pesticide transport model. The specific objectives of the project are to:

- a) determine the partitioning of commonly-used turfgrass pesticides among the components of a turfgrass system including the atmosphere, soil, soil-water, leachate, thatch, verdure, and clippings;
- b) assess the ability of mathematical models, such as CHAIN_2D and PRZM2, to accurately predict pesticide movement in a field-plot-scale turfgrass system;
- c) modify the mathematical model and/or change the data collection protocol as necessary to improve the accuracy of model predictions;
- d) test the model using independently-derived data to assess further its predictive capabilities; and
- e) conduct a sensitivity analysis of the mathematical model to determine which input parameters have the greatest effect on the model predictions and therefore should be known to the highest degree of accuracy.

METHODS

Experiment 1

Pesticide Application

The pesticides used in the first experiment were chlorothalonil (Daconil 2787®) and metalaxyl (Subdue®). The environmental fate properties of these pesticides are given in Table 1. The chlorothalonil was applied at a rate of 8 oz/1000 ft² (500 g active ingredient per liter). The total mass of chlorothalonil applied to the lysimeter area of each plot (approximately 1.22 m²) was

1.55 g. The metalaxyl was applied at a rate of 2 oz per 1000 ft² (2 lb active ingredient per gallon). The total mass of metalaxyl applied to the lysimeter area of each plot was 0.186 g. The pesticides were applied by a certified pesticide applicator on September 27, 1995 at approximately 8:00a.m.. Four of the plots (plots 1, 3, 7, and 10) were designated experimental plots; all data were collected from these plots.

Table 1. Properties of chlorothalonil and metalaxyl

| Property | Chlorothalonil | Metalaxyl |
|---|-----------------------|-----------------------|
| degradation half-life (days) | 14 | 28 |
| Henry's constant | 3.44×10^{-5} | 7.71×10^{-8} |
| adsorption coefficient (cm ³ /g) | 60 | 1.264 |
| water solubility (mg/l) | 0.6 | 7100 |

Sample Collection and Analysis

Leachate. Samples of drainage water were collected from each of the test plots on a daily basis. Drain volumes were measured and recorded daily, allowing a calculation of the mass of pesticides leaching from the plots. The volume of water applied by irrigation was also recorded for each plot on a daily basis. Drainage samples were taken for 211 days.

Turfgrass clippings. Samples of the turfgrass clippings were taken from each of the experimental plots one day prior to pesticide application to determine any background concentrations. Clippings samples were also taken on days 1, 3, 5, 7, 9, 12, 22 and 29.

Air. Samples were obtained from the chambers beginning 10 minutes after pesticide application and continuing for a period of 8 days. After nine days, pesticide concentrations in the air samples were below the detection limit, so no further samples were collected.

Soil. Soil samples were obtained from the entire soil profile (47 cm) using a handheld coring device. The diameter of the core obtained was approximately 1.5 in. The soil was divided into five increments (0-2, 2-10, 10-20, 20-32, and 32-47 cm) prior to analysis to permit a determination of the depth distribution of the pesticides in the profile. Soil samples were taken prior to the pesticide application, and on days 0, 2, 7, 15, 30, 60, 90, 120, and 150 after pesticide application.

Experiment 2

Pesticide Application

The pesticides used in the second experiment were chlorpyrifos (Dursban 2E®) and trichlorfon (Dylox®). The environmental fate properties of these pesticides are given in Table 2. The chlorpyrifos was applied at a rate of 2 oz/1000 ft² (2 lb active ingredient per gallon). The trichlorfon was applied at a rate of 3 oz per 1000 ft² (80% active ingredient). The pesticides were applied by a certified pesticide applicator on June 4, 1996 at approximately 8:00 a.m.. Four of the

plots (plots 5, 9, 11, and 12) were designated experimental plots; all data were collected from these plots.

Table 2. Properties of chlorpyrifos and trichlorfon

| Property | Chlorpyrifos | Trichlorfon |
|---|------------------------|-----------------------|
| degradation half-life (days) | 6 - 139 | 3 - 27 |
| Henry's constant | 36.52×10^{-5} | 1.50×10^{-9} |
| adsorption coefficient (cm^3/g) | 2500 - 14800 | 2 - 6 |
| water solubility (mg/l) | 0.4 - 4.8 | 12,000 - 154,000 |

Sample Collection and Analysis

Leachate. Samples of drainage water were collected from each of the test plots on a daily basis. Drain volumes were measured and recorded daily, allowing a calculation of the mass of pesticides leaching from the plots. The volume of water applied by irrigation was also recorded for each plot on a daily basis. Drainage samples were taken for 72 days.

Turfgrass clippings. Samples of the turfgrass clippings were taken from each of the experimental plots one day prior to pesticide application to determine any background concentrations. Clippings samples were also taken on days 1, 3, 4, 6, 8, 10, 11, 13, 15, 17, 20, 22, 24, 27, 31, 34, 38, 43, and 45.

Air. Samples were obtained from the chambers beginning 10 minutes after pesticide application and continuing for a period of 29 days. After that time, pesticide concentrations in the air samples were below the detection limit, so no further samples were collected.

Soil. Soil samples were obtained from the entire soil profile (47 cm) using a handheld coring device. The diameter of the core obtained was approximately 1.5 in. The soil was divided into five increments (0-2, 2-10, 10-20, 20-32, and 32-47 cm) prior to analysis to permit a determination of the depth distribution of the pesticides in the profile. Soil samples were taken prior to the pesticide application, and on days 0, 2, 7, 15, 30, 60, and 90 after pesticide application.

MODELING

The mathematical contaminant transport model used to simulate the environmental fate of chlorothalonil and metalaxyl was CHAIN_2D (Simunek and vanGenuchten, 1995). This model simulates the movement of water, heat, and contaminants in unsaturated, partially saturated, or fully saturated media. The program includes provisions for partitioning between soil and liquid components and between liquid and gaseous components. It also includes water uptake by plant roots, changes due to atmospheric conditions, and first-order degradation processes.

Prior to pesticide application in the first experiment, CHAIN_2D was used to predict the behavior of the two compounds in the putting green lysimeters. The model predictions of the partitioning of the pesticides into the various environmental compartments (soil, water, air, and tissue) are shown in Tables 3 and 4.

Table 3. Predicted Fate of Metalaxyl using CHAIN_2D

| Day | % Leached | % Volatilized | % Degraded | % Remaining |
|-----|-----------|---------------|------------|-------------|
| 0.1 | 0 | 0 | 0 | 100 |
| 7 | 0 | 0 | 18.5 | 81.5 |
| 15 | 0 | 0 | 33.8 | 66.2 |
| 30 | 0 | 0 | 54.5 | 45.5 |
| 90 | 0.0027 | 0 | 88.4 | 11.6 |

Table 4. Predicted Fate of Chlorothalonil using CHAIN_2D

| Day | % Leached | % Volatilized | % Degraded | % Remaining |
|-----|-----------|---------------|------------|-------------|
| 0.1 | 0 | 0 | 0 | 100 |
| 7 | 0 | 0.6 | 35 | 64.4 |
| 15 | 0 | 0.6 | 62 | 37.4 |
| 30 | 0 | 0.6 | 88.1 | 11.3 |
| 90 | 0 | 0.6 | 99.4 | 0 |

Modeling for the second experiment is still underway.

RESULTS

Experiment 1

Metalaxyl

The cumulative volatilization of metalaxyl was 0.08% of the applied mass (Figure 1). This was higher than predicted by the model (0%), however, a negligible amount. The concentrations of metalaxyl in the soil at various depths for 120 days after application are shown in Figure 2. It can be seen that the concentration of the pesticide decreased substantially in the upper 2 cm during that time period. The concentration of metalaxyl in the leachate during the first 150 days of the experiment is shown in Figure 3. It can be seen that the concentration in the leachate was negligible for the first 50 day, then rose to a peak at approximately day 75. This is in good agreement with the model predictions, which estimated that 0% of the applied mass would leach during the first 30 days. The mass of metalaxyl that leached during the experiment was 0.072% of the applied. Approximately 0.139% of the applied mass was removed in the tissue when the turf was mowed (Figure 4). These results, along with the results for the other 3 chemicals, are summarized in Table 5.

Chlorothalonil

The mass of chlorothalonil that volatilized during the experiment was 0.017% (Figure 5). The model predicted that 0.6% of the applied mass would volatilize within 7 days of application. Figure 6 shows the concentration of chlorothalonil in the soil for 120 days of the experiment. Detectable concentrations were seen throughout the entire soil profile by day 2 of the experiment, and measurable concentrations were detected at all depths at day 15. The model predicted that none of the chlorothalonil would be detected in the leachate. As can be seen in Figure 7, detectable concentrations of the compound were found for at least 150 days. However, the concentrations were very low (less than 0.25 ppb). Only 0.0012% of the applied mass of chlorothalonil leached through the rootzone. Figure 8 shows that the total amount of chlorothalonil removed in the clippings was 0.137% of the total applied.

Experiment 2

Chlorpyrifos

The cumulative volatilization of chlorpyrifos was 15.7% of the applied mass (Figure 9). The concentrations of chlorpyrifos in the soil at various depths for 90 days after application are shown in Figure 10. It can be seen that the concentration of the pesticide decreased substantially in the upper 2 cm during that time period. Essentially no chlorpyrifos was detectable in the soil below a depth of 20 cm. The concentration of chlorpyrifos in the leachate during the first 72 days of the experiment is shown in Figure 11. No discernible peak was seen in the leachate; the concentrations measured were very low, and near the analytical detection limit for the compound.

A very small fraction (0.00037%) of the compound leached through the soil (Figure 12). Approximately 0.237% of the applied mass was removed in the tissue when the turf was mowed (Figure 13).

Trichlorfon

The mass of trichlorfon that volatilized during the experiment was 0.094% (Figure 14). Figure 15 shows the concentration of trichlorfon in the soil for 90 days of the experiment. Detectable concentrations were seen throughout the entire soil profile by day 2 of the experiment, and measurable concentrations were detected at all depths at day 90. As can be seen in Figure 16, detectable concentrations of the compound in the leachate were found for 72 days. The concentration peaked at about day 20, and moved through the system in a pulse for another few weeks. Only 0.00303% of the applied mass of trichlorfon leached through the rootzone (Figure 17). Figure 18 shows that the total amount of trichlorfon removed in the clippings was 0.05% of the total applied.

Table 5. Summary of Partitioning of Pesticides into Environmental Compartments

| % of Applied | Metalaxyl | Chlorothalonil | Chlorpyrifos | Trichlorfon |
|------------------------|-----------|----------------|--------------|-------------|
| volatilized | 0.08 | 0.017 | 15.7 | 0.094 |
| leached | 0.072 | 0.0012 | 0.00037 | 0.00303 |
| removed (clippings) | 0.139 | 0.137 | 0.237 | 0.05 |

PLANS FOR NEXT SIX MONTHS

A manuscript describing the results of experiment 1 is being written and will be submitted for publication. Modeling of the second experiment will be conducted, and further assessment of model predictions will be made. Refinements to the model or to model input values will be made, based on the results of model predictions.

Figure 1. Metalaxyl -
Cumulative Volatilization

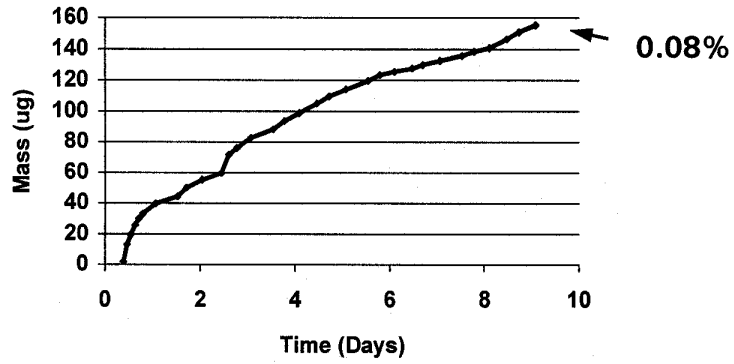


Figure 2. Metalaxyl in Soil

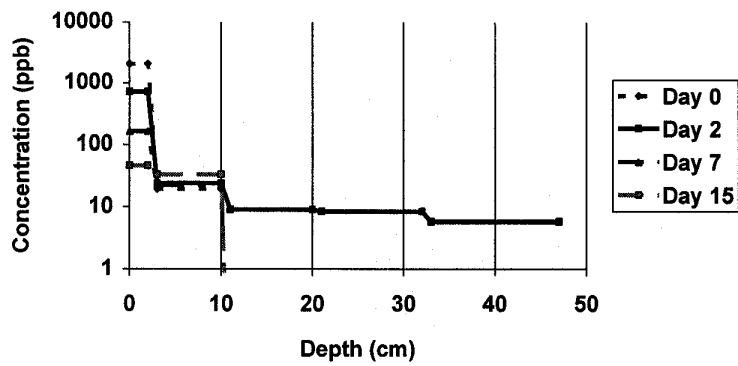


Figure 3. Metalaxyl in Leachate

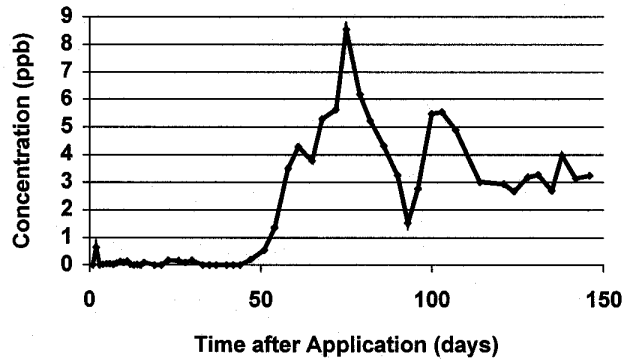


Figure 4. Metalaxyl - Cumulative Removal in Clippings

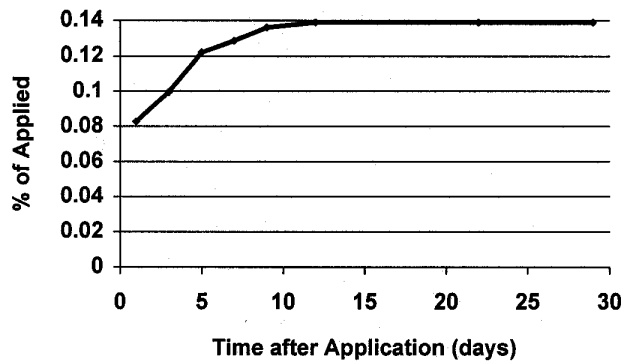


Figure 5. Chlorothalonil -
Cumulative Volatilization

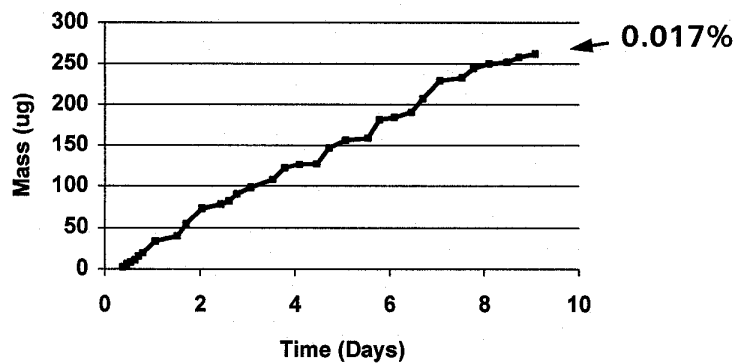


Figure 6. Chlorothalonil in
Soil

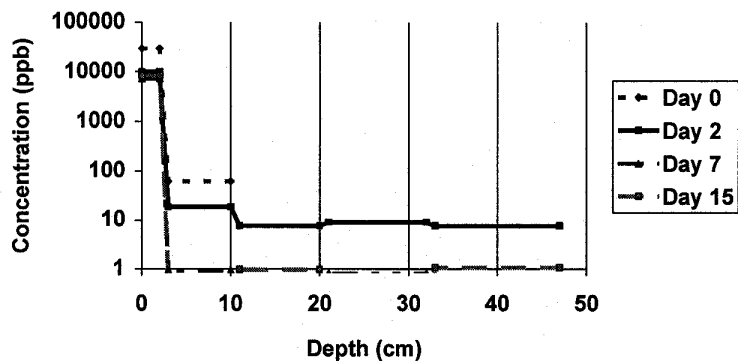


Figure 7. Chlorothalonil in Leachate

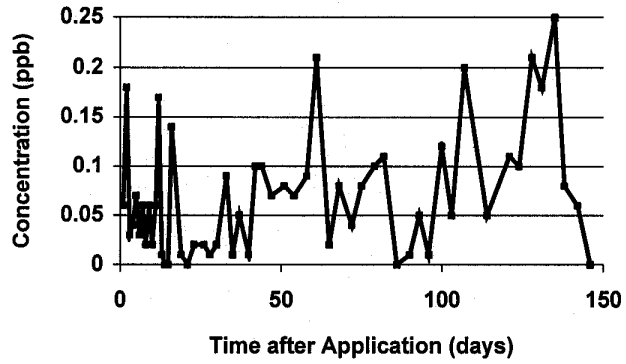


Figure 8. Chlorothalonil - Cumulative Removal in Clippings

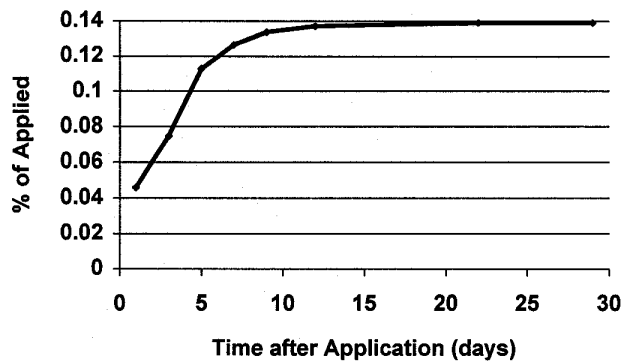


Figure 9. Chlorpyrifos -
Cumulative Volatilization

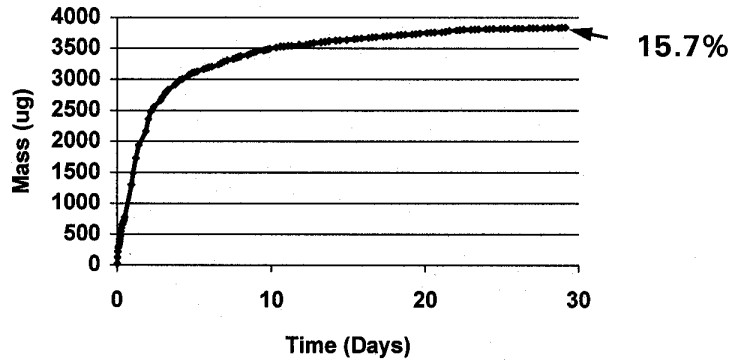


Figure 10. Chlorpyrifos
(Dursban) in Soil

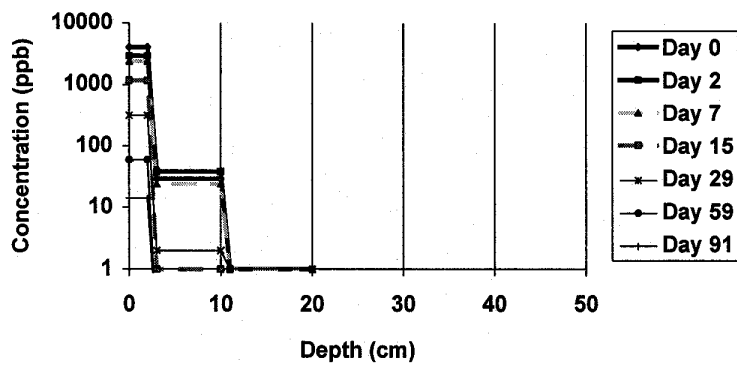


Figure 11. Chlorpyrifos in Leachate

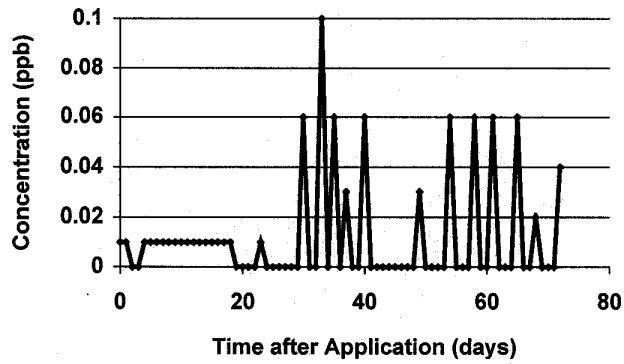


Figure 12. Chlorpyrifos - Cumulative Leaching

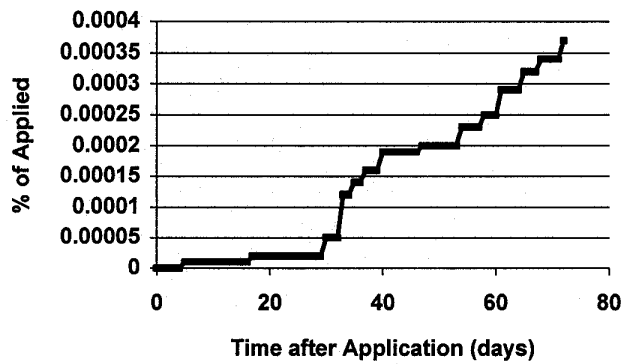


Figure 13. Chlorpyrifos -
Cumulative Removal in Clippings

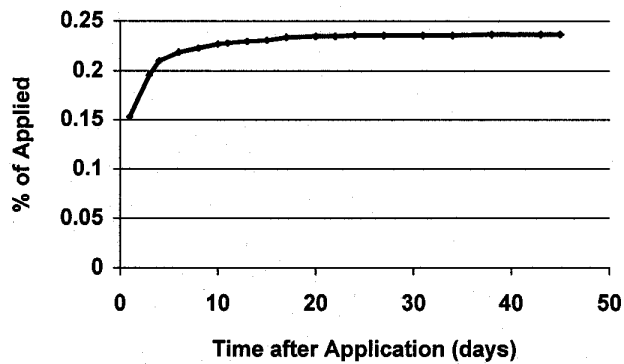


Figure 14. Trichlorfon -
Cumulative Volatilization

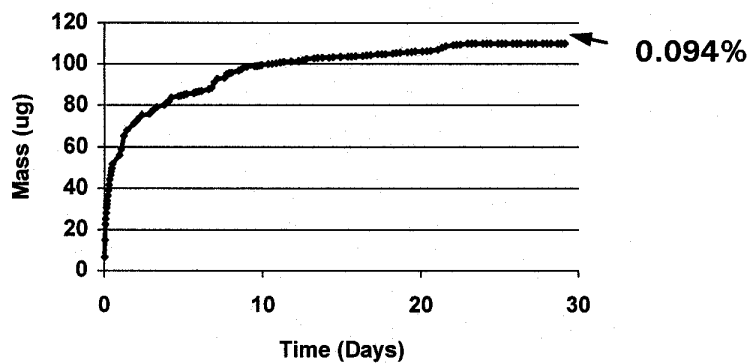


Figure 15. Trichlorfon
(Dylox) in Soil

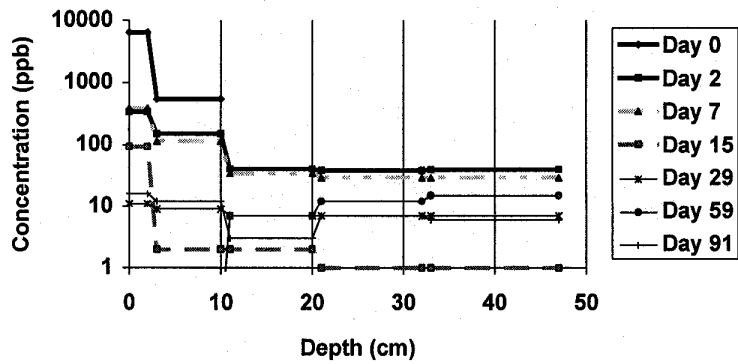


Figure 16. Trichlorfon in
Leachate

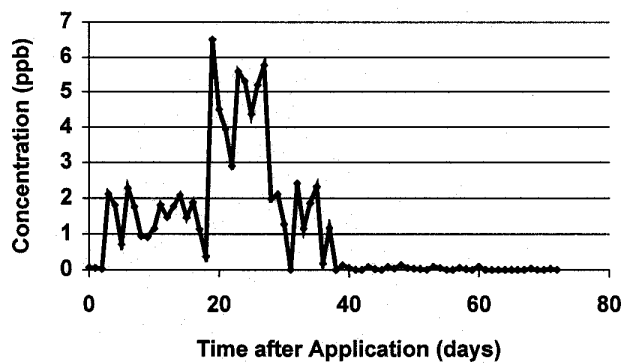


Figure 17. Trichlorfon - Cumulative Leaching

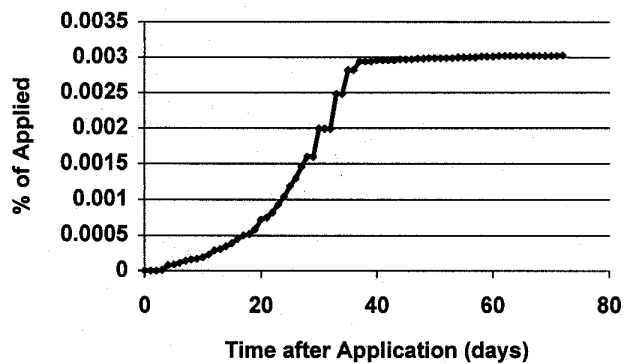


Figure 18. Trichlorfon - Cumulative Removal in Clippings

