EXECUTIVE SUMMARY

GROUNDWATER CONTAMINATION POTENTIAL OF PESTICIDES AND FERTILIZERS USED ON THE GOLF COURSE

DR. BRUCE E. BRANHAM

This research project is designed to monitor the movement of pesticides and fertilizers through soil and their potential to subsequently contaminate groundwater. Specifically, the movement of pesticides and nitrates through large, intact monolith lysimeters has been monitored for over 2 years. The movement of phosphorus through specialized greens soil mixes is also being studied. Monitoring the movement of nitrates through soil is only part of a larger project which has examined the environmental fate of fertilizer nitrogen. The goal of this research was to develop a mass balance for the distribution of a single urea application among the various components of the Kentucky bluegrass turfgrass system: clippings, verdure, thatch, soil, leaching, and gaseous losses. Two timings of application, a traditional early spring and a late fall application were made at a rate of 40 kg N/ha (0.8 lb N/M). A stable isotope of nitrogen was used as a tracer in these studies thus permitting the monitoring of each application over the entire three years of this research project.

Results to date have provided a positive view of the turfgrass ecosystem as an environmentally favorable system. The mass balance approach to the fate of nitrogen has again demonstrated the importance of thatch on the fate of applied agrichemicals. Most important is the data related to leaching of nitrogen. Turf management is often criticized for leaching of pesticides and fertilizers into groundwater. This criticism is strictly a perception on the part of the public that a turf system is no different than an agricultural cropping system and in fact is worse because higher rates of fertilizers and pesticides are used on turf. Our research has shown that leaching of nitrogen into groundwater, on a sandy loam soil, is basically nil. After continuously monitoring the leachate of the lysimeters for over two years, recovery of labeled nitrogen in the lysimeter effluent has amounted to 0.01% from the spring applied N and 0.005% from the fall applied N. Mean nitrate nitrogen concentrations over the course of the study have averaged less than 1 PPM with the highest recorded concentration at only 4.5 PPM. These are well below the EPA drinking water standard of 10 PPM. When examining the mass balance of N among the various components of the turfgrass ecosystem, it is interesting to note that less than 20% of the original N application ever reached the soil surface. The thatch layer, an organic matter layer between the green vegetation and the soil surface, is the principal sink for applied N. Whether the N was spring or fall applied, the thatch stored approximately 30% of the application. Another 30% was harvested in the clippings and gaseous losses (ammonia volatilization or denitrification) accounted for 25% of the spring application. These data together suggest that reasonable N application rates (i.e. 4 lbs N/M/YR) leads to no appreciable leaching losses of nitrogen.

A total of eight different pesticides were applied to 2 of the 4 lysimeters during 1991 and 1992. The eight pesticides are the herbicides 2,4-D and dicamba; the insecticide isazophos; and the fungicides fenarimol, chlorothalonil, triadimefon, propiconazole, and metalaxyl. Analyses are not yet completed,
however, leachate samples through January of 1993 have been tested for 7 of the
8 pesticides in the study. Five of the eight pesticides have not yet been detected
in any of the leachate samples. Dicamba, which is known to be mobile, was
detected fairly frequently in the winter following application. 2,4-D has shown at
least one detection but these samples are being reanalyzed. Of the fungicides
evaluated, only triadimefon has been detected at this time. Concentrations have
been very low, with one detection at a level of 32 PPB and the other five
detections at levels of 10 PPB or less. With the exception of dicamba, a herbicide
with a strong leaching tendency, little movement of pesticides through the soil has
been observed.

Our results with phosphorus have also demonstrated the impact of thatch
on nutrient mobility. In most soils, phosphorus will not show mobility unless very
high concentrations of phosphorus are found. The concern with sand based
systems is that they may not sorb high levels of P and leaching could occur in
these sands. Our results again show that even where high levels of P are applied,
most of the P stays in the thatch layer.
1993 PROGRESS REPORT

GROUNDWATER CONTAMINATION POTENTIAL OF PESTICIDES AND FERTILIZERS USED ON THE GOLF COURSE

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INTRODUCTION

This is the third year of a three year study to determine the potential for groundwater contamination from commonly used pesticides and fertilizer elements when applied to turf. The study has three principle components: the fate of nitrogen fertilizers applied to turf, the movement of phosphorus in sand soils, and the movement of pesticides applied to turf.

The fate of nitrogen study follows the overall fate of a single $^{15}$N application made either in the late fall or early spring to a Kentucky bluegrass turf. This is the most in depth part of our study using $^{15}$N to develop a mass balance for the fate of a single N application, to follow the movement of fertilizer N through the soil, and to examine cycling of N between inorganic and organic forms. The pesticide leaching study was designed to monitor the lysimeter effluent for eight different pesticides that were applied either singly or, in the case of chlorothalonil and metalaxyl, applied several times throughout the 1992 growing season. The phosphorus portion of our study looks at the mobility of P through sand soils. In addition, phosphorus isotherms for a number of sands used for green construction are being determined.

Results

We continue to collect considerable data from the nitrogen fate portion of this project. In our last report we noted that the spring applied nitrogen treatment had a initial recovery of 55% of the total nitrogen applied. This number is a sum of all the recovered $^{15}$N in the soil divided by the total amount applied. Gaseous losses are determined by subtraction and represent the only assumption in the study, i.e. that recovery from soil is quantitative and gaseous losses are the only other avenue for losing N from the system. Hence, we concluded that 45% of the applied N was lost to ammonia volatilization. This was disappointing and we concluded that ammonia volatilization was a more significant loss mechanism than previously thought since the urea had been watered in immediately after application. We then begun a secondary study to determine if our recoveries were quantitative and to determine how rapidly ammonia was being volatilized from the turf. This study was initiated in June and the results are still being determined. However, we discovered a software error in the mass spectrometer used to determine total N and $^{15}$N content. This error occurred because an operator of the instrument tried to correct for a bad standard by changing the basic software. This change was not corrected when the bad standard was replaced and occurred just prior to our using the mass spectrometer. Therefore, all of our previously reported data on $^{15}$N recovery underestimated actual recovery by approximately 50%. Thus, our initial recovery of the spring applied urea application was a more reassuring 76% indicating a 24% loss to ammonia volatilization. In addition the initial recovery from the fall treatment was reported as 68% whereas the correct value is 110%(almost too good!). Therefore, the data presented here supersedes all previous data and provides additional evidence that data such as this should not be published or discussed too carefully until the project is completed.

The data on distribution of N in the various components on the turfgrass system yields some very interesting points regarding the fate of nitrogen in turf. The spring applied N treatment was initiated on April 26, 1991 when 40 kg
N/ha (0.8 lb N/M) of urea enriched with 25% $^{15}$N was applied. We have followed the fate of that single N application by continuously monitoring the effluent from the large lysimeters since that time and by removing cores of soil 20 cm in diameter by 60 cm deep. For both spring and fall applied N, 4 core samples were removed the first season after application, 2 sets of cores during the 2nd year following application and one core sample during the 3rd year following application. We have analyzed the first six core samples for the spring applied N leaving the year three sample yet to be analyzed. Five of the fall applied N cores have been analyzed to date with two sets of samples for the fall applied N treatment still in the ground. At this point, the data for both application timings provide valuable information on the fate of N applied to turfgrass systems.

Figures 1 and 2 show the distribution of the recovered $^{15}$N in clippings, verdure, thatch, and soil. Some $^{15}$N has been detected in the leachate however, the amount is so low as to be essentially zero. For example, in the spring applied treatment at 584 days after treatment (DAT), we have recovered the equivalent of 4 gms/HA in the leachate which is 0.01% of the total $^{15}$N originally applied. Therefore, in the mass balance data leachate is not even included because it is insignificant. This data, by itself, shows that turf is a unique system that does not behave as do other agricultural systems.

When examining the data on N distribution (Figures 1 and 2), the importance of the thatch layer on the fate of N applied to turf is strikingly clear. In the spring applied N treatment, there is a near constant level of $^{15}$N in the thatch from the application date through 396 DAT. The data point at 173 DAT for thatch does not follow this trend and we suspect that it is simply a bad data point. The concentration of $^{15}$N in the 173 DAT sample was similar to the other sampling times for thatch, however, the weight of the thatch in this sample was low compared to the other sampling times. The thatch layer seems to be the primary sink for applied N. Note that in both treatments (figures 1 and 2) the amount of $^{15}$N in the thatch is above 10 kg N/ha (25% of total) for the first year after application. The consistent level of $^{15}$N in the thatch also implies that the N present is in mostly unavailable, organic forms of N. Our data indicates that a significant portion of the applied N is converted into organic matter that is resistant to breakdown and represents a storage of organic N forms in the system. This data supports the data presented in the review article of Petrovic (1991) that showed long term build-up of N in soils under turf. This is particularly true for the late fall applied N treatment. At 16 DAT, 25 kg/ha of $^{15}$N (or 62.5% of the total applied) is in the thatch layer. Apparently, a significant amount of the $^{15}$N in the thatch is already in the turfgrass roots and shoots within the thatch at 16 DAT but has not moved upward out of the thatch. This occurs fairly rapidly next spring as the amount of $^{15}$N in the clippings jumps quickly in the spring after the late fall N was applied (Figure 2 and 3). Note in figure 3 the rapid rate of $^{15}$N uptake into the clippings in the spring following application. In a one week interval, 4.5 kg $^{15}$N/ha (or 11% of the total applied) was removed in clippings from the late fall fertilized plots. In the first month of growth in the spring following the late fall $^{15}$N application, 9.0 kg $^{15}$N/ha (22.5% of total) were removed with the clippings. The rate of uptake from the spring applied N is not quite as rapid as observed in the late fall N treatment, indicating better N use efficiency from late fall nitrogen in
the same uptake window as for spring applied N. This analysis is somewhat
confounded because the spring applied N was applied in 1991 and uptake was
measured in 1991 while the late fall N was applied in November of 1991 and the
uptake was measured in the spring of 1992. Therefore, some of the differences
observed could be due to between season variability.

Equally interesting are the low levels of $^{15}$N reaching the soil. This is
perhaps not surprising in light of the low leaching numbers obtained from the large
lysimeters. The soil values listed in Figures 1 and 2 are for the total amount of
$^{15}$N throughout the entire 60 cm profile of the sample although as would be
expected, most of the $^{15}$N found in the soil is in the top 5 cm layer. In the spring
application, the maximum $^{15}$N reaching the soil is 7.9 kg/ha or 20% of the total
application rate. This maxima was reached at 396 DAT and began to decline by
the next sampling date, 584 DAT. For the late fall applied N, the maximum
amount of $^{15}$N reaching the soil occurred at the last sampling date for which we
have data and amounted to 6.2 kg/ha or 15.5% of the total $^{15}$N applied. Once
the N reaches the soil, its mobility is low indicating that the N is not in the NO3
form. Data in table 1 which gives the same data seen in figures 1 and 2 except
that the thatch and soil $^{15}$N totals are partitioned further into thatch soil and
thatch organic matter values and inorganic, organic, and total soil N values. As
can be observed in table 1, the $^{15}$N present in the soil is mostly present in organic
forms of N (a range of 78-96% organic N over all sampling dates).

A significant amount of effort has been expended exhaustively analyzing the
soil by depth intervals for total soil N and $^{15}$N, biomass N and $^{15}$N, non-living
organic N and $^{15}$N, and inorganic N and $^{15}$N. This in-depth analysis is probably
related to the number of soil scientists working on this project, or more likely,
decided based upon data obtained from the application of $^{15}$N to field crops.
However as our data shows, very little is going on in the soil because very little N
actually reaches the soil.

The data compiled so far paints a very positive picture of the fate of
nitrogen applied to Kentucky bluegrass. More importantly, the impact of a thatch
layer on the fate of nitrogen has been demonstrated to be significant and positive
from an environmental standpoint. Other turfs which contain a significant thatch
layer should be expected to respond in a similar manner. Turfs which do not
possess a significant thatch layer, e.g. tall fescue or perennial ryegrass, may
behave differently with regards to the fate of nitrogen.
TABLE 1. RECOVERY OF $^{15}$N IN VARIOUS COMPONENTS OF THE TURFGRASS ECOSYSTEM. FOR EACH TREATMENT, 39.2 KG N/HA WAS APPLIED.

<table>
<thead>
<tr>
<th>Sample date</th>
<th>treatment</th>
<th>Clippings</th>
<th>Verdure</th>
<th>Thatch soil OM</th>
<th>Thatch total</th>
<th>Thatch inorganic</th>
<th>Soil organic</th>
<th>Soil total</th>
<th>leachate</th>
<th>total recovered</th>
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<tr>
<td>5/14/91</td>
<td>Spring</td>
<td>0.94</td>
<td>14.23</td>
<td>3.35</td>
<td>8.78</td>
<td>12.13</td>
<td>0.44</td>
<td>2.72</td>
<td>3.06</td>
<td>0</td>
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<td>Spring</td>
<td>7.82</td>
<td>8.01</td>
<td>3.55</td>
<td>8.67</td>
<td>12.22</td>
<td>0.13</td>
<td>4.17</td>
<td>4.30</td>
<td>0</td>
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<td>Spring</td>
<td>11.87</td>
<td>3.35</td>
<td>3.40</td>
<td>4.03</td>
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<td>0.22</td>
<td>5.93</td>
<td>6.15</td>
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<td>Spring</td>
<td>12.07</td>
<td>3.02</td>
<td>5.74</td>
<td>6.78</td>
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<td>0.22</td>
<td>6.5</td>
<td>6.72</td>
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<td>12.70</td>
<td>1.53</td>
<td>6.34</td>
<td>7.36</td>
<td>13.7</td>
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<td>Spring</td>
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<td>0.97</td>
<td>6.94</td>
<td>1.43</td>
<td>8.37</td>
<td></td>
<td>6.56</td>
<td>0.00427</td>
<td>30.3</td>
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<tr>
<td>11/26/91</td>
<td>Fall</td>
<td>0</td>
<td>14.14</td>
<td>3.61</td>
<td>20.89</td>
<td>24.50</td>
<td>0.47</td>
<td>4.34</td>
<td>4.82</td>
<td>0</td>
</tr>
<tr>
<td>5/26/92</td>
<td>Fall</td>
<td>8.56</td>
<td>8.98</td>
<td>4.41</td>
<td>17.72</td>
<td>22.13</td>
<td>0.84</td>
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<td>6/29/92</td>
<td>Fall</td>
<td>10.6</td>
<td>7.66</td>
<td>7.0</td>
<td>7.01</td>
<td>14.01</td>
<td>0.61</td>
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<td>2.79</td>
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<td>11/30/92</td>
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<td>14.31</td>
<td>1.75</td>
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<td>10.02</td>
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<td>6.23</td>
<td>0.00224</td>
<td>32.3</td>
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</table>
PESTICIDE LEACHING

The study of the leaching of pesticides was undertaken to determine "real world" levels of pesticides reaching groundwater from typical applications to turfgrass. Fate of pesticides was not considered by this investigator to be as important since data on the fate of many pesticides in soil and in turf have been previously reported. Furthermore, it is not so much the fate of pesticides that concerns regulatory agencies and the general public but the movement of pesticides away from the site of application. Currently, much attention is focused on leaching to groundwater.

The pesticides examined in this study are shown in table 2. These were picked on the basis of the frequency of use on golf courses as well as their potential to reach groundwater which is estimated by the half-life of the pesticide, water solubility, and strength of sorption to organic matter. Based upon the data presented in table 2, dicamba, 2,4-D and metalaxyl would be expected to reach groundwater. In addition, propiconazole, triadimefon, and isazophos would also be likely candidates for movement into groundwater. Fenarimol would be moderately mobile with only a slight chance of detection under our conditions while chlorothalonil would not be expected to reach groundwater and if found would be indicative of a problem in the experiment.

Our results to date indicate that under this turf system, leaching of most pesticides is quite insignificant. Only two pesticides of the eight applied to the monolith lysimeters have been detected in the leachate for samples analyzed through 1/29/93. Dicamba was frequently detected at concentrations up to 3 mg/l (figure 4). Dicamba was applied on 9/17/91 and the first detections were found in the sample collected on 10/26 from lysimeter 2 (i.e. rep2) and on 10/27 from lysimeter #1. Dicamba seemed to elute from the lysimeters in three bands with the major band coming out in December of 1991. The two lysimeters showed slightly different leaching patterns as lysimeter #2 had a large pulse of

Table 2. Application information and environmental data for pesticides applied to lysimeters 1 and 2.

<table>
<thead>
<tr>
<th>PESTICIDE</th>
<th>APP RATE (kg/ha)</th>
<th>APP DATE</th>
<th>SOIL T1/2 (days)</th>
<th>WATER SOL (mg/L)</th>
<th>KOC</th>
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</thead>
<tbody>
<tr>
<td>isazophos</td>
<td>2.24</td>
<td>8/12/91</td>
<td>34</td>
<td>69</td>
<td>100</td>
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<tr>
<td>2,4-D</td>
<td>1.14</td>
<td>9/17/91</td>
<td>10</td>
<td>890</td>
<td>20</td>
</tr>
<tr>
<td>dicamba</td>
<td>0.12</td>
<td>9/17/91</td>
<td>14</td>
<td>400,000</td>
<td>2</td>
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<tr>
<td>chlorothalonil*</td>
<td>9.56</td>
<td>8/21/91</td>
<td>30</td>
<td>0.6</td>
<td>1380</td>
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<tr>
<td>propiconazole</td>
<td>6/18/92</td>
<td>110</td>
<td>110</td>
<td>650</td>
<td></td>
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<tr>
<td>fenarimol</td>
<td>0.76</td>
<td>5/3/92</td>
<td>360</td>
<td>14</td>
<td>600</td>
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<tr>
<td>triadimefon</td>
<td>1.53</td>
<td>7/21/92</td>
<td>26</td>
<td>71.5</td>
<td>300</td>
</tr>
<tr>
<td>metalaxyl*</td>
<td>1.53</td>
<td>8/5/92</td>
<td>70</td>
<td>8400</td>
<td>50</td>
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</table>

* chlorothalonil was also applied to lysimeters 3 and 4 on 7/21, 8/5, 8/20, and 9/4/92.

metalaxyl was applied also applied to lysimeters 3 and 4 on 7/21, 8/13, and 9/4/92.
dicamba in the December 3 sampling date while lysimeter #1 had a bi-modal elution pattern with dicamba eluting in smaller quantities than lysimeter #2 on November 20 and December 18 effectively bracketing the dicamba peak seen from lysimeter #2. The slightly different elution patterns should be expected in light of the sample collection procedure. In order to observe all leaching that occurs, the entire leachate volume is collected, weighed, and subsamples stored for analysis. Effluent is allowed to collect, depending on flow intensity, from 1 day to 2 weeks. With this collection method, any analyte can be expected to appear on multiple collection dates and may be diluted by large leaching events.

Dicamba appeared in the effluent of both lysimeters at two other periods in the winter of 1992. Small leaching events were also observed at the end of February and in April. After April of 1992, no other detections of Dicamba occurred.

The only other pesticide detected with some frequency was the fungicide triadimefon. The recovery of triadimefon in the leachate samples was very low with the highest recorded concentration of 32 PPB on October 15, 1992 sampling date (figure 5). All the other detections were within 5 times the limit of detection. The amount of triadimefon detected was therefore quite small and not unexpected for a pesticide with a water solubility of 71.5 PPM and a soil t1/2 of 26 days. However, what is troubling is the lack of occurrence of metaxyl and propiconazole which, based upon their reported properties would be expected to leach more readily than triadimefon. We are continuing to study this issue although several explanations can be proffered. Most likely is that the above ground plant material and the thatch have effectively sorbed or degraded the other fungicide products, preventing them from moving into the soil. While this is possible, it would still raise the question of why triadimefon behaves differently. The physico-chemical data on these fungicides could be in error leading to erroneous predictions of their fate in turf or soil. Another possible explanation is that the detections of triadimefon are false positives. We have some water remaining for each sampling date and are looking into the possibility of confirming the analysis by another method such as mass spectroscopy. Regardless, we will attempt to confirm the positive detections of triadimefon from stored samples.

Another important observation is that these non-ionic organic pesticides will be partitioned between the soil water and the soil itself which will retard their movement through the soil profile. These fungicides were applied in the summer of 1992 and so have only been in the lysimeter for 15 months. Our analyses our current through 1/29/93 or only about 8 months after application. Analysis of 1993 leaching samples should further clarify this subject. However because of the potentially long residence times within the soil core and in order for this study to be valid, it will be necessary to continue to collect and analyze leachate samples through calendar year 1994.

PHOSPHOROUS MOBILITY IN SAND SOILS

There are two portions to this study on phosphorus mobility in soils used for putting green mixes. The field portion of this study is a 3 year project examining the movement of various rates of phosphorus through a 100% sand green. Various rates and methods of application of phosphorus are applied and the movement through the soil is being followed by repeated sampling and...
determining phosphorus levels through soil tests. A second portion of the study involved collecting typical putting green rootzone mixes from around the United States and estimating their phosphorus adsorption capacity by determining the phosphorus adsorption isotherms for each sand mix. With the help of the USGA green section regional agronomists, we have collected about 30 samples of greens mixes from around the country. We will begin determining P adsorption isotherms in November. This should take 4-6 weeks to complete.

Data on the movement of phosphorus is shown in table 3. This data again demonstrates that on a turf with a well-developed thatch layer, phosphorus is also strongly sorbed by this layer. Little movement of phosphorus to lower depths has occurred although there is some evidence of downward migration with some of the higher application rates.
FIGURE 1. DISTRIBUTION OF 15N FROM SPRING APPLIED N

- 18 DAT
- 56 DAT
- 173 DAT
- 214 DAT
- 396 DAT
- 584 DAT

KG 15N/HA

CLIPPINGS
VERDURE
THATCH
SOIL
FIGURE 2. DISTRIBUTION OF FALL APPLIED 15N

- **Clippings**
- **Verdure**
- **Thatch**
- **Soil**

**KG 15N/HA**

- 16 DAT
- 198 DAT
- 232 DAT
- 386 DAT
FIGURE 3. CUMULATIVE 15N IN CLIPPINGS

- SPRING APPLIED N 1992
- FALL APPLIED N 1992
FIGURE 4. LEACHING OF DICAMBA THROUGH MONOLITH LYSIMETERS

- lysimeter #1
- lysimeter #2
FIGURE 5. LEACHING OF TRIADIMEFON IN MONOLITH LYSIMETERS

Limit of detection = 0.002
### TABLE 3. SOIL TEST P LEVELS

**PRIOR TO TREATMENT**

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Control</th>
<th>24.5</th>
<th>49</th>
<th>98</th>
<th>Bray P1</th>
<th>Olsen Inj</th>
<th>49 Inj</th>
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<tr>
<td>0 - 7.5</td>
<td>6.3</td>
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<td>6.3</td>
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<td>5.3</td>
<td>5.5</td>
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<td>15 - 22.5</td>
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<td>5.3</td>
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**AUGUST 1992**

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<th>Depth (cm)</th>
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<th>49</th>
<th>98</th>
<th>Bray P1</th>
<th>Olsen n</th>
<th>49 Inj</th>
<th>Bray P1 Inj</th>
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<tr>
<td>Thatch</td>
<td>16.5</td>
<td>34.3</td>
<td>51.5</td>
<td>201.5</td>
<td>177.0</td>
<td>434.3</td>
<td>30.3</td>
<td>76.0</td>
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<td>4.0</td>
<td>15.8</td>
<td>0</td>
<td>5.0</td>
</tr>
<tr>
<td>15 - 22.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>19.5</td>
<td>0</td>
<td>2.8</td>
</tr>
</tbody>
</table>

FPLSD (P=0.05) Thatch = 111.1; D1 = NS; D2 = 6.6; D3 = 7.8