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TITLE: Evaluation of the Potential Movement of Pesticides Following Application to Golf Courses

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EVALUATION OF THE POTENTIAL MOVEMENT OF PESTICIDES FOLLOWING APPLICATION TO GOLF COURSES

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EXECUTIVE SUMMARY

This 1992 annual report references methods developed during the first year of this research program. Therefore, the total accumulated file of reports and publications is included with this report to reference specific methods and installation designs. Research completed since the filing of the 1992 semi-annual report includes completion of the first repetition of the greenhouse and field lysimeter experiments with treatments of 2,4-D, dicamba, and MCPP to 'Tifdwarf' bermudagrass and 'Pencross' bentgrass. The effluent water from the lysimeters receiving the 2,4-D and dicamba treatments were analyzed and the data are reported in this report. The MCPP subsamples will be extracted and analyzed in the near future as will the soil and foliage samples from all treatments.

The data from the greenhouse and field lysimeters correlated quite well. Only minimum quantities of herbicide were transported in the elutriated water from both types of lysimeters. In the greenhouse experiments similar amounts of 2,4-D were transported from lysimeters regardless of quantity of organic matter in the rooting media or formulation of 2,4-D (DMA or LV) used in the treatments. In all instances the 2,4-D concentration in the collected samples was very low with maximum concentrations of slightly more than 6 $\mu g\ L^{-1}$. This is an order of magnitude below the MCL of 70 $\mu g\ L^{-1}$ established by the Office of Drinking Water U. S. EPA.

Only dicamba was found in the samples collected from the field lysimeters and it was found to be transported during week 6 from lysimeters containing both turfgrass species. The maximum concentration of dicamba found in the leachates from the field lysimeters was 2.58 $\mu g\ L^{-1}$. The results, included in this report, corroborate the results obtained from the greenhouse research conducted last winter with 2,4-D and reported in the 1992 semi-annual report. All data indicate that the GWCP ratings and the GLEAMS model overestimate the potential for the acid herbicides to be transported through the golf course greens mixture. Differences between the measured and predicted transport can partially be accounted for by the lack of a quantitative understanding of herbicide fate on the vegetative surface and in the turfgrass thatch horizon. These experiments will be repeated for confirmation of results and publication.

INTRODUCTION

The relative potential for selected turfgrass pesticides to leach through soils has been estimated by Weber (1990) and was termed as the Herbicide Leaching Potential Index (HLP). The herbicides that have a high water solubility and a low K_{oc} (<50 ml g^{-1}) result in an extremely low HLP index and a high HLP rating. The leaching potential of a soil depends on many factors but ones that are of greatest importance to herbicide movement are texture, organic matter, and pH. In order to develop a Soil Leaching Potential (SLP), Weber (1990) assigned weighted factors of 3, 10, and 4, respectively. Dissolved chemicals move most readily through sand and silt and least readily through clay and muck thus the rating scheme for various soil textures range from 1 for clay and muck and 10 for sand, loamy sand, sandy loam, loam, silt-loam, or silt. The texture component of the SLP is the product of the rating and the weight factor. Adsorption increases and mobility decreases as soil organic matter content increases, thus the rating scheme for various organic matter levels ranges from 1 for soils with high organic matter content to 10 for soils with low organic matter content. The organic matter component of the SLP is the product of the rating and the weight factor. The rating scheme for various soil pH levels ranges from 1, for soils with pH levels less than 5, to 10, for soils with pH levels greater than 7.0. The pH component of the SLP is the product of the rating and the weight factor. The SLP is the sum of these components. Using a matrix for the SLP and HLP allows one to determine the Ground Water Contamination Potential (GWCP). The GWCP ratings range from "hazardous" when the herbicide has a high HLP and it is to be used on a soil with a high SLP to "safe" when herbicides with low HLPs are considered for use on soils with high, moderate or low SLPs (Weber,1990).

Using the best estimated parameters for 37 soil series common to the southeastern United States, 11 soil series would have a SLP rating of High and 10 soil series would have a rating of Moderate. The GWCP for the acid herbicides (ie. 2,4-D; dalapon; dicamba; ethofumesate; MCPA; mecoprop; and triclopyr) that have an HLP rating of high would be classed as Hazardous for use on the 11 soils with the High SLP rating and Risky for the 10 soils with a Moderate SLP rating. If the pesticide-use controlling agencies were to use classifications such as the GWCP rating system many of these herbicides would become restricted use pesticides for turfgrass and possibly would be restricted from use on many golf course fairways in the southeastern United States.

Many golf course greens are constructed for maximum infiltration and percolation of water through the rooting media. The use of mathematical equations and models indicate that these characteristics of the root zone mixture could result in uninhibited rapid movement of pesticides through the rooting mixture allowing for a potential source of contamination of effluent water from the greens into surface water drainage channels. For purposes of this report the term of Water Contamination Potential (WCP) will replace the terminology GWCP in reference to golf course greens. When using the ground water contamination potential classification proposed by Weber (1990) as a criterion for determining herbicide use on golf course greens the DMA salts of the acid herbicides; 2,4-D, dicamba, and MCPP; would be considered "RISKY" (Table 1). Bensulide and ethofumesate would be classed as risky and dithiopyr, fenarimol, and MSMA are considered as safe according the WCP ratings. The apparent disparity in the GWCP rating of Hazardous for the soil series, of heavier texture, common to the southeastern United States compared to the WCP of Risky for the coarse sand greens is due to the higher organic matter content in the greens mix compared to the native soil series.

The "GLEAMS (Groundwater Loading Effects of Agricultural Management Systems) mathematical model (Leonard et al.,1987) is being used to aid in the identification of significant chemical and soil properties, and plant and meteorological factors influencing the transport of herbicides through golf course greens. Observations of herbicide transport for evaluating the GLEAMS model were derived from the bermudagrass golf course greens simulated in the controlled greenhouse lysimeter system described in manuscripts appended to this report (Int. Turfgrass Conference Publication "Potential leaching of herbicides applied to golf course greens" J. Environ. Qual. "A greenhouse system for determining pesticide movement from golf course greens").

Table 1. Water contamination potential (WCP) for herbicides used on golf course greens (USGA specifications).

Herbicide	HLP	WCP
Bensulide	M	**Risky**
2,4-D DMA	H	**Risky**
Dicamba DMA	H	**Risky**
Dithiopyr	L	Safe
Ethofumesate	H	**Risky**
Fenarimol	L	Safe
MCPP, DMA	H	**Risky**
MSMA	L	Safe

Only minute quantities of 2,4-D were detected in the effluent from the lysimeters containing the two rooting media (Figure 1)(data reported in the 1992 semi-annual report). The extraction and analytical methods were developed to give a minimum concentration detection limit MCDL for 2,4-D at 0.005 mg L^{-1} and the peak areas equated to 0.002 mg 2,4-D L^{-1} effluent or less indicating that only trace quantities of 2,4-D percolates through the rooting media and it's aqueous concentration is an order of magnitude less than the MCL standard of 0.07 mg L^{-1} established by the Office of Drinking Water U.S. EPA (1990). Additionally, The GLEAMS model overestimated the actual values received from the lysimeters for the potential of 2,4-D to move through rooting media profiles containing 85:15 or 80:20 (sand:peat) rooting medium (Figure 1). The data would indicate that the equations for determining the WCP and the GLEAMS model overestimate the potential for 2,4-D DMA to enter the surface drainage and ground water following treatment of golf course greens.

The contrasting results of these reports indicate the need for the development of a data bank from treatments and simulated treatments of golf course greens and fairways to determine the potential for pesticides to move into water systems. The popular theme of recent origin is for there to be ZERO pesticides in the potable water systems. As technological proficiency increases yesterday's zero is no longer zero and today's zero will not be zero tomorrow. We will eventually have methods, capable of measuring a few molecules in a L of water allowing for the identification of some of everything in all water systems.

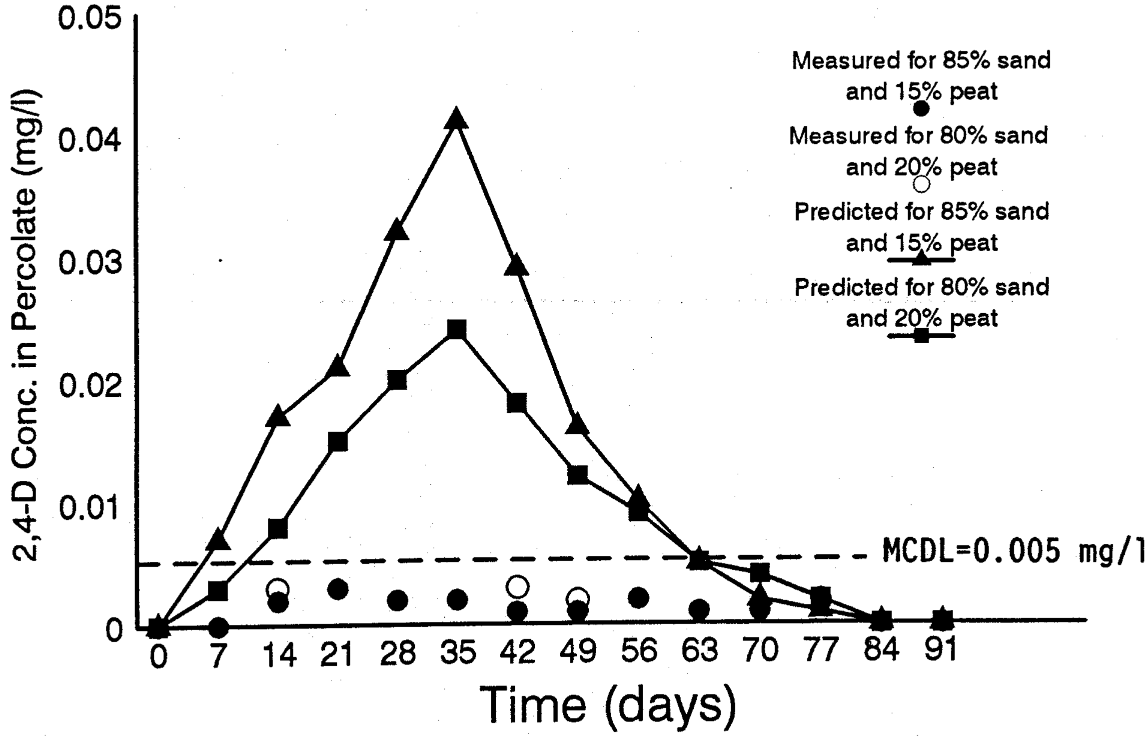

Figure 1. Predicted and measured 2,4-D transport in water percolated from lysimeters containing soil mixtures of 85:15 or 80:20 (sand:peat).

Research was initiated in the spring of 1992 to determine the potential movement of 2,4-D, dicamba, and MCPP through golf course greens using the greenhouse and field lysimeter facilities described in the 1991 annual report and appended publications.

MATERIALS AND METHODS.

Greenhouse lysimeters: The greenhouse facility is described in the appended manuscript submitted to the Journal of Environmental Science for review toward publication. Growth boxes containing bentgrass grown on 85:15 and 80:20 (sand:peat) rooting media were used for the treatments. The bentgrass was seeded into the growth boxes on September 13, 1991. During March of 1992 the growth boxes were mounted on the lysimeter tubes containing the respective rooting mixtures beneath the track watering system. The watering system was programmed to deliver an irrigation simulation of 0.625 cm water daily for 6 days and a rainfall simulation of 2.5 cm on the seventh day of the week. Due to a disease problem the irrigation simulation was limited to alternate days during weeks 3-7. The turf was mowed and clippings removed thrice weekly with a greens (reel-type) mower to a stubble height of 0.4 cm. Herbicide treatments (Table 3) were applied on June 29, 1992. Each herbicide treatment was in 3 replications for each rooting media. The herbicides were applied to the growth boxes, moved to a spray booth, in 204 L ha^{-1} water diluent at 18 psi under compressed air.

Table 2. Herbicide treatments applied to the growth boxes containing 'Pencross' bentgrass in the greenhouse facility on June 29, 1992.

Herbicide	Rate (kg ha^{-1})	Herbicide over lysimeter[6] (μg)
2,4-D DMA[1] + X77	0.28	511
2,4-D LV[2]	0.28	511
dicamba[3] + X77	0.07	123
MCPP[4] + X77	0.56	1022
Control	----	0

[1]2,4-D DMA; Weedar 64; 46.8% Active ingredient Dimethylamine salt of (2,4-dichlorophenoxy)acetic acid. EPA Reg. No. 264-2AA; EPA EST. No. 264-Mo-01 Rhone-Poulenc Ag Co. RP-4500-148-000-031.
[2]2,4-D LV; Weedone LV4; 60.8% Active ingredient butoxyethyl ester of (2,4-dichlorophenoxy)acetic acid. EPA Reg. No. 264-20ZA EPA Est. No. 264-MO-01 Rhone-Poulenc Ag. co. RP-4500-155-118.
[3]Dicamba; Banvel 4S; 48.2% Active Ingredient Dimethylamine salt of 3,6-dichloro-2-methoxybenzoic acid. Sandoz Crop Protection Corp.
[4]MCPP; Mecomec 4; 48.2% Active Ingredient Potassium Salt of 2-(2-methyl-4-chlorophenoxy)propionic acid. EPA Reg. No. 2217-674 EPA Est. No. 2217-KS-1. PBI/Gordon Corp. 841/1087.
[5]X-77 surfactant (Contains alkylarylpolyoxyethylene glycols, free fatty acids, isopropanol); product 5463, Valent U.S. A. Corp., P.O. Box 8025, Walnut Creek, CA.
[6]Lysimeter surface area = 0.012 m^2.

The leachate was collected twice weekly, the samples were stored at 4 °C and the leachate volumes were determined on weekly intervals except on weeks 4 and 6. Due to disease problems the watering regimen was reduced to irrigating on alternate days, during weeks 3-7, reducing the volume of water accumulated. Therefore leachate samples for weeks 4 and 6 were included in samples 5 and 7, respectively. Subsamples were taken from the samples for analyte extraction and quantification by electron-capture GLC. Subsamples (100 mL) were acidified and the acid analytes were partitioned into 200 mL diethyl ether using a separatory funnel. Following evaporation of the ether, the analytes were esterified with diazomethane and the methyl esters were dissolved in 10 mL ethyl acetate for injection into the Tracor 565 chromatograph for quantification of the analytes using 2,4,5-T as the internal standard. The method was developed to yield a minimum concentration detection level (MCDL) for 2,4-D and dicamba were 1 μg L^{-1}, respectively. The experiment was conducted for ten weeks. The clipped foliage was collected from each treated growth box, immediately frozen, freeze-dried, and ground to pass a 40 mesh screen. At the termination of the experiment, soil cores were collected from the columns for analysis of analytes remaining in the rooting media. The analytes will be extracted from the soil and plant material and analyzed at a future date.

Field lysimeter experiment. The field lysimeter facility contained 10 lysimeters under each of the turfgrass cultivars. 'Pencross' bentgrass was seeded during September 1991 into the lysimeters filled with the 85:15 (sand:peat) rooting mix and 'Tifdwarf' bermudagrass was sodded onto the lysimeters filled with 80:20 soil mix during April 1992. The lysimeters were automatically covered with a rainout shelter during rain events.

The turfgrass was mowed and the clippings were removed with a greens (reel-type) mower to a height of 0.4 cm three times per week. A complete fertilizer (20 N:20 P:20 K) was applied in water to an N rate of 2.44 g m^{-2}. Fungicides and insecticides were applied as needed. The herbicide treatments (Table 4) were applied on July 3, 1992. The herbicides were applied with a CO_2 backpack sprayer in 252.1 L ha^{-1} water diluent. Water was applied through an automatically-timed irrigation system of full-jet nozzles (FL-5VS) operated at 25 psi to simulate irrigation and rainfall events on the same schedule as the greenhouse lysimeter experiment.

Table 3. Herbicide treatments applied to 'Pencross' bentgrass and 'Tifdwarf' bermudagrass turf over the lysimeters in the field lysimeter facility.

Turf	Herbicide	Rate (kg ha^{-1})	Herbicide over lysimeter[1] (μg)
bentgrass	2,4-D DMA + X77	0.28 + 0.5%	8,181
	dicamba + X77	0.07 + 0.5%	1,963
	MCPP + X77	0.56 + 0.5%	16,362
bermuda- grass	2,4-D DMA + X77	0.56 + 0.50 (2 week) 0.5%	32,723
	dicamba + X77	0.28 + 0.5%	8,181
	MCPP + X77	1.40 + 0.5%	40,904

[1]Lysimeter surface area = 0.283 m^2.

The effluent water was collected thrice weekly and the combined collections were quantified and subsampled once weekly for extraction and quantification of the analytes in the effluent water. All samples and subsamples were stored at 4 °C from the time of collection until they were extracted. The subsamples were extracted and the analytes were analyzed as described for the greenhouse experiment. This experiment was terminated after 10 weeks.

RESULTS AND DISCUSSION

The salt formulations of MCPP, dicamba, and 2,4-D have similar numerical HLPs indicating that their potential for transport from the lysimeters are similar and all three are assigned a HLP rating of high (Weber, 1990). However, the potential for the butoxyethyl ester formulation of 2,4-D is low because of the low water solubility and high affinity to organic matter. All numerical data in the tables denoted as <1 indicates that an integration was developed for the analyte but the calculated concentration was less than 1 μg L^{-1} established as the MCDL for our procedures. Data, for total herbicide transport, were subjected to the analyses of variance to test for influence of 2,4-D formulation and rooting soil mixture on analyte transported and no differences were identified for the data obtained from the greenhouse and field lysimeters.

Greenhouse lysimeters: Data from this research indicate that similar amounts of both formulations of 2,4-D were transported from the greenhouse lysimeters through similar rooting media (Tables 4,5,6, and 7). The butoxyethyl ester of 2,4-D was not identified in the leachate and 2,4-D was the only analyte identified in the leachate from lysimeters treated with 2,4-D LV indicating that the ester is hydrolyzed in the system and the acid/salt molecular form is transported from the lysimeter. Only 0.35 and 1.16% of the 2,4-D was transported from the lysimter tubes containing 85:15 soil moisture for the DMA and LV formulations, respectively, over the 10 week period. Generally, the small quantities of the analyte was found in 1 or 2 of the replications. The percentages of the applied 2,4-D transported from the lysimeters containing the 80:20 rooting media was less than 0.5% and the influence of 2,4-D formulation on the total herbicide transported was not significant (Tables 6 and 7).

Table 4. Weekly water elutriated and herbicide transported from greenhouse lysimeters containing bentgrass in 85:15 (sand:peat) rooting media and treated with 2,4-D DMA. Data are averages for 3 replications.

Week	Weekly water volume (mL)	Herbicide transported ($\mu g\ L^{-1}$)	Total (μg)
1	903	ND[1]	------
2	590	ND	------
3	220	ND	------
5	80	3.7	0.30
7	215	<1	------
8	335	1.0	0.34
9	320	3.6	1.15
10	320	<1	------

[1]Not detected

Table 5. Weekly water elutriated and herbicide transported from greenhouse lysimeters containing bentgrass in 85:15 (sand:peat) rooting media and treated with 2,4-D LV. Data are averages for 3 replications.

Week	Weekly water volume (mL)	Herbicide transported ($\mu g\ L^{-1}$)	Total (μg)
1	960	ND	-----
2	653	ND	-----
3	263	<1	-----
5	90	1.31	0.12
7	283	2.82	0.80
8	400	5.20	2.08
9	446	6.60	2.94
10	137	<1	-----

Table 6. Weekly water elutriated and herbicide transported from greenhouse lysimeters containing bentgrass in 80:20 (sand:peat) rooting media and treated with 2,4-D DMA. Data are averages for 3 replications.

Week	Weekly water volume (mL)	Herbicide transported ($\mu g\ L^{-1}$)	Total (μg)
1	767	ND	------
2	667	ND	------
3	343	1.1	0.38
5	117	2.4	0.28
7	447	ND	------
8	557	ND	------
9	567	3.2	1.81
10	380	<1	------

Table 7. Weekly water elutriated and herbicide transported from greenhouse lysimeters containing bentgrass in 80:20 (sand:peat) rooting media and treated with 2,4-D LV. Data are averages for 3 replications.

Week	Weekly water volume (mL)	Herbicide transported ($\mu g\ L^{-1}$)	Total (μg)
1	680	ND	-----
2	510	<1	-----
3	243	<1	-----
5	70	5.0	0.35
7	363	ND	-----
8	475	ND	-----
9	420	ND	-----
10	150	ND	-----

Only small quantities of dicamba were found in the leachate collections from the greenhouse lysimeters containing both rooting media (Tables 8 and 9). Assuming all of the water collected contained the minimum detectible concentration of 1 $\mu g\ L^{-1}$ dicamba, the fraction of the dicamba available for transport, that would have been transported would be 3.9 and 3.3% for the 85:15 and 80:20 rooting media, respectively. That is to say that only a very small portion of the added dicamba could have been transported and not detected.

Table 8. Weekly water elutriated and herbicide transported from greenhouse lysimeters containing bentgrass in 85:15 (sand:peat) rooting media treated with dicamba. Data are averages for 3 replications.

Week	Weekly water volume (mL)	Herbicide transported ($\mu g\ L^{-1}$)	Total (μg)
1	960	ND	-----
2	860	ND	-----
3	453	ND	-----
5	142	ND	-----
7	517	ND	-----
8	727	<1	-----
9	763	<1	-----
10	385	ND	-----

Table 9. Weekly water elutriated and herbicide transported from greenhouse lysimeters containing bentgrass in 80:20 (sand:peat) rooting media treated with dicamba. Data are averages for 3 replications.

Week	Weekly water volume (mL)	Herbicide transported ($\mu g\ L^{-1}$)	Total (μg)
1	927	ND	-----
2	752	ND	-----
3	320	<1	-----
5	177	<1	-----
7	518	ND	-----
8	517	ND	-----
9	573	ND	-----
10	383	ND	-----

Field lysimeters: Only small quantities of 2,4-D and dicamba were found to have elutriated from the lysimeters below both species of turfgrass, in the greenhouse (Tables 10 and 11) and in the field experiments (Tables 12 and 13). Only two leachate collections contained dicamba at a concentration above the MCDL. A concentration of 1.22 $\mu g\ L^{-1}$ dicamba was determined for the leachate collected for week 6 from the lysimeters under bentgrass and 2.58 $\mu g\ L^{-1}$ dicamba was found in the leachate collected during week 6 from the lysimeters under bermudagrass. Small concentrations of dicamba were found in collections made following week 6 but the level of dicamba in the leachate was below the MDCL of 1 $\mu g\ L^{-1}$.

Table 10. Weekly water elutriated and herbicide transported from field lysimeters containing bentgrass in 85:15 (sand:peat) rooting media treated with 2,4-D DMA. Data are averages for 3 replications.

Week	Weekly water volume (L)	Herbicide transported ($\mu g\ L^{-1}$)	Total (μg)
1	98.8	<1	-----
2	96.3	ND	-----
3	91.7	<1	-----
4	117.0	<1	-----
5	113.7	ND	-----
6	103.5	ND	-----
7	108.2	ND	-----
8	120.0	ND	-----
9	98.3	ND	-----
10	94.7	ND	-----

Table 11. Weekly water elutriated and herbicide transported from field lysimeters containing bentgrass in 85:15 (sand:peat) rooting media treated with dicamba. Data are averages for 3 replications.

Week	Weekly water volume (L)	Herbicide transported ($\mu g\ L^{-1}$)	Total (μg)
1	104.5	ND	-----
2	91.3	ND	-----
3	117.5	ND	-----
4	135.0	ND	-----
5	116.5	ND	-----
6	87.0	1.22	106.1
7	106.2	<1	-----
8	166.7	<1	-----
9	108.2	ND	-----
10	111.2	ND	-----

Table 12. Weekly water elutriated and herbicide transported from field lysimeters containing bermudagrass in 80:20 (sand:peat) rooting media treated with 2,4-D DMA. Data are averages for 3 replications.

Week	Weekly water volume (L)	Herbicide transported (μg L^{-1})	Total (μg)
1	67.2	<1	-----
2	65.3	<1	-----
3	110.0	ND	-----
4	101.7	ND	-----
5	98.7	ND	-----
6	73.1	ND	-----
7	103.2	ND	-----
8	113.3	ND	-----
9	98.0	ND	-----
10	80.8	ND	-----

Table 13. Weekly water elutriated and herbicide transported from field lysimeters containing bermudagrass in 80:20 (sand:peat) rooting media treated with dicamba. Data are averages for 3 replications.

Week	Weekly water volume (L)	Herbicide transported (μg L^{-1})	Total (μg)
1	71.7	ND	-----
2	77.4	ND	-----
3	125.0	ND	-----
4	114.5	ND	-----
5	105.3	<1	-----
6	75.8	2.58	195.6
7	121.7	<1	-----
8	135.0	ND	-----
9	106.7	ND	-----
10	95.0	ND	-----

PROGRESS OF PROPOSED RESEARCH

1. The subsamples collected from the greenhouse and field lysimeters treated with MCPP are presently being analyzed and should be completed by November 15, 1992. The plant clippings and soil samples will be extracted and analyzed for analytes prior to December 20, 1992.

2. The treatments for a repetition of the greenhouse experiment will be made to bermudagrass on November 2, 1992. These treatments will be conducted for 10 weeks. The second repetition of the field experiment will be treated next spring to duplicate the studies reported in this report.

3. The field installation for the run-off studies will be completed by next spring in time for treatment and determination of the potential for herbicides to be transported in surface run-off water during rain events.

4. The new gas chromatograph equipped with mass spectrometer and EC detectors will be installed during the week of November 2, 1992. This system will be utilized for the continuation of this research and the peaks will be verified by mass spectrometry.

5. A visiting scientist, from Korea, will be joining our laboratory staff for one year to assist in adapting the Enzyme Linked Immunoassay (ELISA) methodology to this research project. The intended use will be to use the ELISA methodology for screening all samples and analyzing the samples determined to have the analyte present in the leachate by GC-MS. Although the system will be of little assistance on this project, it will allow for the testing of the potential use of the ELISA method for field determinations of certain pesticides in surface and ground water systems. Ohmicron Corporation, developer of the ELISA methodology, has agreed to assist in this research and will develop the antibodies, if possible, for pesticides commonly used on turfgrass. The method is simple, sensitive and molecule-specific and should allow for an excellent tool to be used in testing for water contamination at golf courses.

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