



This is to certify that the
dissertation entitled
The Controlled Release of
Water Soluble Herbicides
presented by

Bruce D. Riggle

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Crop & Soil Sciences

A handwritten signature in dark ink, appearing to read "Donald Penner", written over a horizontal line.

Major professor

Donald Penner

Date 2-21-85



RETURNING MATERIALS:
Place in book drop to
remove this checkout from
your record. FINES will
be charged if book is
returned after the date
stamped below.

FEB 26 '80
~~MAR 1 1980~~
MAR 2 1980
33 K185

CONTROLLED RELEASE OF WATER
SOLUBLE HERBICIDES

By

Bruce Dale Riggle

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Crop and Soil Sciences

1985

© 1985

BRUCE DALE RIGGLE

All Rights Reserved

ABSTRACT

THE CONTROLLED RELEASE OF WATER SOLUBLE HERBICIDES

By

Bruce Dale Riggle

Pine kraft lignin was used to control the release of metribuzin (4-amino-6-tert-butyl-3-(methythio)-as-triazin-5(4H)-one) and alachlor (2-chloro-2',6'-diethyl-N-methoxymethyl acetanalide). Soil thin layer chromatography (TLC) analysis using ^{14}C -metribuzin and ^{14}C -alachlor demonstrated that NB-5203-58 series and PC940 series kraft lignins could retard the mobility of both herbicides after multiple soil TLC plate developments with water. Soil column chromatography analysis demonstrated that PC940C could retard the mobility of both herbicides after soil column water leaching by positioning the herbicides in the top portion of the soil column where the PC940C-herbicide mixture had been applied. There was a concentration effect where, as more PC940C was used, more ^{14}C -labelled herbicide was retained in the top

portion of the soil columns. Soil column chromatography and soil TLC plate analysis demonstrated that ^3H -PC940C was immobile. Finally, PC940C significantly reduced metribuzin related phytotoxicity to field and greenhouse grown soybeans (Glycine max (L.) Merr.) which had been treated with PC940C rates of 0.77 and 1.15 L/ha and metribuzin rates of 0.42 and 0.84 kg/ha. The results for ^{14}C -metribuzin and ^{14}C -alachlor as well as the reduction in metribuzin related phytotoxicity to soybeans suggests that PC940C can effectively control the release of metribuzin and alachlor.

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to his major professor, Dr. Donald Penner, for his guidance throughout this study and his friendship. The experience received through involvement in the controlled release project was very rewarding and appreciated. The assistance of Dr. A.R. Putnam, Dr. G.L. Hosfield, and Dr. M.E. Zabik as Guidance Committee members is gratefully acknowledged. A special thanks to Mr. Frank Roggenbuck for his technical assistance in the laboratory and greenhouse.

TABLE OF CONTENTS

	<u>PAGE</u>
LIST OF TABLES	v
LIST OF FIGURES	vii
INTRODUCTION	1
CHAPTER 1. LITERATURE REVIEW	3
LITERATURE CITED	17
CHAPTER 2. CONTROLLED RELEASE OF METRIBUZIN AND ALACHLOR BY KRAFT LIGNINS AS MEASURED BY SOIL THIN LAYER CHROMATOGRAPHY	24
ABSTRACT	24
INTRODUCTION	26
MATERIALS AND METHODS	28
RESULTS AND DISCUSSION	33
LITERATURE CITED	43
CHAPTER 3. CONTROLLED RELEASE OF METRIBUZIN AND ALACHLOR BY PC940C AS MEASURED BY SOIL COLUMN CHROMATOGRAPHY	46
ABSTRACT	46
INTRODUCTION	48
MATERIALS AND METHODS	50
RESULTS AND DISCUSSION	55
LITERATURE CITED	66

	<u>PAGE</u>
CHAPTER 4. PC940C PROTECTION OF FIELD AND GREENHOUSE GROWN SOYBEANS FROM METRIBUZIN INJURY	69
ABSTRACT	69
INTRODUCTION	70
MATERIALS AND METHODS	72
RESULTS AND DISCUSSION	76
LITERATURE CITED	87

LIST OF TABLES

	<u>PAGE</u>
 CHAPTER 2	
1. Effect of lignins on the percentage of ¹⁴ C-metribuzin retained at the point of origin on soil TLC plates after three developments	34
2. Effect of NB-5203-58B on the percentage of ¹⁴ C-metribuzin retained at the point of origin on soil TLC plates after three developments	35
3. Effect of lignins on the percentage of ¹⁴ C-metribuzin retained at the point of origin on soil TLC plates after three developments	37
4. Effect of formulated and nonformulated PC940C on the percentage of ¹⁴ C-metribuzin retained at the point of origin on soil TLC plates after two developments	39
5. Effect of lignins on the percentage of ¹⁴ C-alachlor retained at the point of origin on soil TLC plates after three developments	41
 CHAPTER 3	
1. The effect of PC940C on ¹⁴ C-metribuzin distribution in a Wando sandy loam soil column following one or two leaching periods with 2.54 cm of water	56
2. The effect of PC940C on ¹⁴ C-alachlor distribution in a Wando sandy loam soil column following one or two leaching periods with 2.54 cm of water	57

3.	Percentage of ^{14}C -metribuzin in various depth sections of a Wando sandy loam soil column following application of a metribuzin-alachlor mixture leached with 2.54 cm water over a 2 h time period	58
4.	Percentage of ^{14}C -alachlor in various depth sections of a Wando sandy loam soil column following application of a metribuzin-alachlor mixture leached with 2.54 cm water over a 2 h time period	60
5.	The influence of PC940C on the recovery of ^{14}C -metribuzin from Wando sandy loam soil columns following the two leaching and drying treatments	61
6.	Percentage of ^3H -PC940C in various depth sections of a Wando sandy loam soil column following leaching with 2.5 cm of water	64

CHAPTER 4

1.	Rainfall and irrigation data for 1984 at East Lansing, Michigan after 22 June	74
2.	Soybean injury ratings as affected by metribuzin and PC940C at 32 D.A.E.	77
3.	Soybean injury ratings as affected by metribuzin and PC940C at 46 D.A.E.	78
4.	Soybean injury ratings as affected by metribuzin and PC940C for greenhouse grown plants at the third trifoliar stage	84
5.	Effect of PC940C on metribuzin injury to soybeans grown in greenhouse as measured in dry weight of third trifoliar plants	86

LIST OF FIGURES

	<u>PAGE</u>
CHAPTER 4	
1. Soybeans treated with 0.42 kg/ha metribuzin and 0 L/ha PC940C and rated at 32 D.A.E.	80
2. Soybeans treated with 0.42 kg/ha metribuzin and 0.77 L/ha PC940C and rated at 32 D.A.E.	82

INTRODUCTION

A basic problem with the use of several water soluble preemergence herbicides is their rapid dissipation and subsequent dilution as water is added to the soil. Excessive water can result in reduced weed control and in the herbicide being positioned in the root zone of the crop species and/or movement to the ground water. These disadvantages are associated with metribuzin (4-amino-6-tert-butyl-3-(methythio)-as-triazin-5(4H)-one) and alachlor (2-chloro-2',6'-diethyl-N-methoxymethyl acetanilide). Metribuzin is mobile in neutral and alkaline pH soils and can cause injury to soybeans (Glycine max (L.) Merr.). Alachlor, while not phytotoxic to corn (Zea mays L.) or soybeans, could, over time, be more effective if leaching was reduced.

Controlled release agents used in combination with herbicides such as metribuzin and alachlor could potentially increase herbicide efficacy. This could be achieved by reducing herbicide dissipation and dilution in the soil zone containing weed seeds. The result would be an increase or extension of weed control, a reduction in crop plant phytotoxicity, and a reduction in ground water contamination.

The objectives of this study were: (1) to test pine kraft lignins for controlled release of metribuzin and alachlor by soil thin layer chromatography, (2) to test the most promising lignin for controlled release of metribuzin and alachlor by soil column chromatography, and (3) to test the most promising lignin for controlled release of metribuzin using greenhouse and field grown soybeans.

CHAPTER ONE

LITERATURE REVIEW

A basic problem with the use of several water soluble preemergence herbicides is their rapid dissipation and subsequent dilution as water is added to the soil. Even though water is essential to mobilize these surface-applied herbicides and move them into the soil to control germinating weed species, the addition of water over time can establish a diffusion gradient. This can result in the removal of a majority of the herbicide from the top portion of the soil and consequently reduce weed control. Herbicide activity may be further reduced by soil microorganism metabolism of the herbicide and the adsorption of the herbicide on soil clay and organic matter colloids. Excessive water leaching can also result in the herbicide being positioned in the root zone of the crop species and/or movement to the ground water. This may further result in phytotoxicity to non target plants and pollution of ground water.

A possible modification to the conventional approach of water-soluble preemergence herbicide application is the use of controlled release agents to control or delay the

movement of herbicide from the soil surface. This approach could reduce herbicide dissipation and dilution into the soil zone containing weed seeds and consequently increase or extend weed control, reduce crop plant phytotoxicity, and reduce ground water contamination.

Other goals of a controlled release strategy include increased herbicide efficacy throughout the growing season as well as the possible expansion of the weed control spectrum. Because the efficacy is usually dependent upon a dose response, a reduction in the dose or amount of herbicide present in the soil will reduce the potential weed control. The amount that will microbially or chemically degrade is generally dependent upon the first order rate law (9) and thus the persistence of herbicide activity may be increased by a reduction of the first order rate constant (9). This could be achieved by reducing the amount of free herbicide in the soil as compared to the amount of herbicide that would be currently adsorbed to the controlled release agent. The rate of herbicide release from the controlled release agent would also have a first order rate constant (26) which would determine, depending upon the magnitude, how quickly or slowly the herbicide would be released. Ideally for herbicides with short half-lives, a large rate constant for release is desirable. This approach might require more herbicide than the conventional approach (8),

however, this cost would be offset by the potential to increase the herbicide efficacy.

For the control release agent or polymer to successfully extend the half-life of a herbicide, it would have to serve as a barrier to microbial or chemical degradation. This degradation or dissipation of herbicide could be due to conversion to a nonphytotoxic substance by either some form of partial metabolism or by a conjugation process. There may also be nonbiological processes involved such as an interaction with clay surfaces resulting in conversion of the herbicide to a nonphytotoxic material.

The theoretical amount of herbicide that would be needed in conjunction with a controlled release agent would not be less than the conventional amount necessary to achieve the desired weed control (8). Furthermore, the amount needed could be more than that used for multiple applications but less than that needed for a single application (8). The predicted savings would be the possible elimination of multiple or split applications of herbicide.

Various approaches have been tried to find effective controlled release polymers for water-soluble herbicides. Combinations of cross-linked starch and 2,4-D (2,4-dichlorophenoxy acetic acid) which form 2,4-D esters of high acyl content have resulted in the controlled release of varying amounts of 2,4-D and water-soluble 2,4-D esters (28).

Amylose-metribuzin (4-amino-6-tert-butyl-3-(methylthio)-as-triazin-5(4H)-one) polymers have been demonstrated to release metribuzin in a zero order manner as measured by HPLC analysis (26). However, amylose-metribuzin polymers have not been tested with soil and plants in field or greenhouse environments. Starch xanthide combinations with chloramben (3-amino-2,5-dichlorobenzoic acid) methyl ester salts have been tested and did not differ in weed control from chloramben ester formulations (33). Plaster of Paris tablet encapsulated alachlor (2-chloro-2',6'-diethyl-N-methoxymethyl acetanalide) has been shown to successfully control weeds and protect ornamental flowering plants from alachlor injury (39). Linear and cross-linked copolymers of polyvinyl alcohols were substituted with pendent metribuzin which resulted in varying release rates of metribuzin (17,25). Pine kraft lignin combined with 2,4-D esters has successfully controlled the release of 2,4-D at a zero order rate for use as a plant growth regulator (11). Multiple pesticide-lignin polymer combinations have been attempted, such as combining 2,4-D and 3,4,5,6-tetrachlorophthalic anhydride with kraft lignin polymers by the use of triazine functional groups which were covalently linked to the lignin polymer (2).

Problems can arise from using most of these controlled release polymers and combinations. Polysaccharides such as starch and amylose are readily available carbon sources for

soil microorganisms and thus would not be a good barrier to protect herbicides from microbial decomposition. In addition, the presence of polysaccharides in holding tanks or spray tanks would risk fermentation with resulting by-products which could result in clogged lines and nozzles. Polyvinyl polymers of pendent substituted herbicides is a very expensive technique and has not yet been successfully tested in greenhouse or field situations for weed control or crop plant protection from metribuzin phytotoxic effects. Furthermore, these pendent formulations would require enormous sums of money to test the toxicological effects of the chemically altered herbicide as well as the effectiveness of the new compounds as herbicides. Plaster of Paris tablet encapsulated herbicide would not be a practical formulation for field grown crops but may be suitable for ornamentals and perennial horticultural crops.

One of the most promising controlled release polymers is kraft lignin. The material is relatively cheap compared to polyvinyl polymers and not rapidly degraded as polysaccharides. Because of the multifunctionality (14) and adsorptive capacity of kraft lignin (12), it should be capable of readily adsorbing compounds such as metribuzin and alachlor.

Lignin has been referred to as the most abundant aromatic source in nature (11) and is produced in the cell walls of higher plants via the shikimic acid pathway (36).

Lignin's function appears to be to provide both structural and turgor-stress counteracting strength as well as serving as an anti-microbial agent (42). The anti-microbial properties are thought to be due to the multi-hydroxyl functional groups that are abundant in lignin (42). The natural structure has been defined by milling woody tissue (27). In addition there are differences in lignin structure that vary according to the location in the cell wall and middle lamella (27). How lignin is associated with cellulose and hemicellulose is not clear although some research has described this association as 'snake cages' in which polymers of lignin are wrapped around the cellulose and hemicellulose fibers which in turn imparts strength to the cell wall (14).

Lignin is persistent and remains in the soil for long periods of time because of the presence of multifunctional groups (36). It is slowly degraded by white rot fungi, Basidiomycetes sp., (36) and is believed to be the source of aromatic groups used in the formation of soil organic matter components such as humic and fulvic acid (40).

Lignin is very similar in structure to humic acid and both have been found to have a high adsorptive capacity for atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) (12). Atrazine adsorption to humic acid has been found to be mainly due to hydrogen bonding with carboxylic and hydroxyl groups of the humic acids to amine groups of

the triazine as measured by infrared spectrometry (41). Because of the similarity in structure between lignin and humic acid, the findings suggest that lignin would adsorb triazine herbicides in a similar manner.

The concept of using natural unaltered lignin for a lignin herbicide complex or as a controlled release mixture is impractical since unaltered lignin can only be obtained under laboratory conditions and only in small amounts. A more plentiful and realistic source is industrial grade lignin which is a by-product of the paper pulping industry.

The two major types of industrial lignin are sulfite and alkaline kraft lignin. The source of these lignins is typically from conifer trees and the differences between the two lignins depend upon differences in the chemical pulping processes. Sulfite pulping includes sulfonation, hydrolyses, and condensation which in turn produces highly water-soluble lignin, sulfate and sulfite salts, alcohols, aldehydes, and carbohydrates (13). Sulfite lignin is not suitable as a controlled release agent for water soluble herbicides due to the water solubility factor and the accompanying impurities. Alkaline pulping is a more complex method which utilizes sodium sulfite and sodium hydroxide to solubilize and strip lignin away from wood chips. The lignin is then precipitated out of the pulping liquors by acidification. The most popular form of alkaline pulping is the kraft process which uses sodium polysulfide, sodium thiosulfate, and sodium

carbonate, in addition to sodium sulfide and sodium hydroxide (27). The result is a relatively pure methoxylated water-insoluble lignin which contains approximately 1.5% sulfur (27).

The exact physical nature of kraft lignin is not fully known because of the distribution of functional groups and the cross linkage of the basic carbon six to carbon three (C6-C3) lignin units. The major C6-C3 units in pine lignin is sinapyl alcohol (31). Methoxyl groups make up approximately 14% of pine kraft lignin and for every 100 C6-C3 units there are approximately 120 OH groups and 16 COOH groups. The average pine kraft lignin is thought to have 20 or more C6-C3 units for an average molecular weight of 1800. Some researchers have found molecular weights as high as 50,000 or more. These large molecular weight fractions consist of smaller units held together by secondary linkages to form larger units (11). Viscosity analysis suggests spherical shapes but other research suggests small plate-like structures (11). There are free unattached low molecular weight catechol derivatives such as vanillin and protocatechuic acid in the lignin and these are produced by the time-controlled precipitation in the kraft process; the exact percentage composition of these water soluble compounds is not known but estimates are about as much as 1% of the total weight (27).

The following laboratory techniques can be employed to test the potential of kraft lignin as a controlled release agent for water-soluble herbicides such as metribuzin and alachlor in soil systems. Two standard methods that can be used to measure the movement of radio-labelled compounds are soil thin-layer chromatography (TLC) and soil column chromatography.

Soil thin-layer chromatography has been extensively used to study the mobility of ^{14}C -labelled pesticides (15,18,19,22,35,37,48). A change in the soil pH can effect the mobility of herbicides such as metribuzin which can be easily detected using the soil TLC plate method (22). Differences in herbicide mobility can also be observed by altering the organic matter or clay content percentages of the tested soil (35,37). Neither the soil layer thickness, nor the removal of coarse sand, nor the amount of radiolabelled material used affect the R_f or mobility of the tested pesticides (15).

The mobility of a compound can be easily tested by developing soil TLC plates with water and measuring radio-labelled herbicide movement by autoradiography, radiochromatogram scanning, and zonal extraction of radio-label (15). The resulting R_f values from soil TLC plates corresponds very closely to those of inverted soil columns (16,35). Unfortunately, an important factor missing in soil TLC plate analysis is the gravitational effect on

the movement of herbicides in soil systems. The only force measured in soil TLC plate systems is diffusion or capillary movement.

Soil column chromatography has been used to study the movement of radio-labelled pesticides (46). This method includes both the gravitational effect and diffusion. The initial moisture status of the soil column can have a pronounced effect on the mobility of the tested herbicide. Saturated flow conditions, prior to herbicide addition to the column, can sometimes lead to a greater displacement of the herbicide in the column (1,10). With unsaturated flow, such as intermittent watering, there is both a downward and upward movement of the herbicide in the column due to the soil drying effect (46). This last approach appears to be the most realistic of the two since saturated flow is rarely encountered in agricultural conditions.

Two herbicides which could potentially benefit from the use of a controlled release agent such as kraft lignin are metribuzin and alachlor. The former is typically used in soybean (Glycine max (L.) Merr.) production and may injure soybeans due to downward mobility in soil (23). The latter is also mobile in the soil. By controlled release it may be possible to position both compounds in the upper zone of the soil for longer periods of time.

Metribuzin has a molecular weight of 214.3, a water solubility of approximately 1200 ppm at 20 C, and relative

stability when exposed to ultraviolet radiation (47). Alachlor has a molecular weight of 269.8 and a water solubility of 242 ppm at 25 C (47).

Both compounds are typically tank-mixed for preemergence application for soybean production while alachlor is also used in corn (Zea mays L.) production. Metribuzin is used for the control of many annual dicotyledonous weed species and alachlor is used for the control of many of the annual monocotyledonous weed species.

Both herbicides are absorbed by germinating weed seedlings. Alachlor is believed to prevent protein synthesis by interference with transfer RNA (21). Alachlor is also believed to inhibit growth of epicotyl segments by controlling the function of GA₃ at the molecular level (29). A consequence of alachlor exposure is a reduction in cell division in the developing root system. Metribuzin inhibits plant growth by blocking electron transport in photosystem II at the B protein complex (3,32). This can result in the formation of free radicals which in turn can cause the disruption of the chloroplasts membrane and necrosis of the surrounding cell.

Many crop species are able to detoxify these two compounds. Corn and soybean are able to conjugate alachlor with glutathione and thiol containing compounds (24). Many soybean varieties are able to metabolize metribuzin to a nonphytotoxic compound called deaminated diketo metribuzin

(DADK) (38) and then conjugate the DADK with glycosides (38).

Alachlor and metribuzin have some similarities as well as differences in their behavior in soils. Both compounds are adsorbed and desorbed from soil clay and organic fractions.

Alachlor has a greater affinity for organic matter than for clay (45). The adsorption of alachlor to calcium-saturated organic matter has been reported to be 3 μm alachlor/g of organic matter at a alachlor mole equivalent of 3×10^{-5} . The adsorption of alachlor to calcium saturated montmorillonite clay has been reported to be 3 μm alachlor/g of montmorillonite at a alachlor mole equivalent concentration of 1×10^{-5} (45). Results from acetanilide adsorption studies suggest strong hydrogen bonding between the imino hydrogen of the adsorbate and the carbonyl oxygen or alternate site of the adsorbent (43). However, the level of organic matter in the soil does not appear to affect weed control with alachlor (30).

The half-life for alachlor has been found to vary from 9 days in a clay loam to 11 days in a sandy loam as measured by a sorghum bioassay (Sorghum bicolor (L.) Moench) (49). Other research has found the half-life to vary from 2 to 14 days with the majority of the dissipation due to microbial activity (5). A half-life of 2 to 14 may not provide long term weed control. An additional problem in the field is

the loss of alachlor due to leaching and this problem could be exacerbated in soils with low organic matter and clay content.

Metribuzin is predominately adsorbed by organic matter rather than by clay (34) with a reduction in herbicide mobility (37). Maximum adsorption of triazines usually occurs in soils with low pH levels (22,44). It has been suggested that the protonation of the amine group of the compound at the lower pH values gives the compound a positive charge which is then attracted to the negatively charged organic matter clay colloids (22,41). As the pH of the soil is increased, the metribuzin becomes more mobile (22) and in the case of soybean production, this could result in an increase in phytotoxicity to soybean (23). Additions of organic matter with a low pH to greenhouse grown potted soybeans resulted in a reduction in phytotoxicity to the soybeans as well as a reduction in giant foxtail (Setaria faberi Herrm.) control (7). These results demonstrate that metribuzin is very mobile in neutral and alkaline soils, especially those with sandy textures and low organic matter content.

The half-life of metribuzin has been reported to be from 5 to 20 days (4,6,20,34). Lower half-life values were obtained when the soil was warmed from 20 C to 35 C indicating the importance of microbial activity (20,34).

Controlled release of both metribuzin and alachlor could benefit users by keeping more of each compound in the upper 'weed seed zone' portion of the soil for an extended period of time. Also, less of each herbicide would migrate into the lower horizons of the soil profile where it could be absorbed by non target crop species or enter the ground water supply.

LITERATURE CITED

1. Abernathy, J.R. and J.M. Davidson. 1971. Effect of calcium chloride on prometryne and fluometuron adsorption in soil. *Weed Sci.* 19:517-521.
2. Allan, G.G., J.W. Beer, M.J. Cousin, and R.A. Mikels. 1980. The biodegradative controlled release of pesticides. Pages 7-20 in *Controlled Release Technologies: Methods, Theory, and Applications*. Vol. II. ed. A.F. Kydonieus. CRC Press. Boca Raton, Florida.
3. Ashton, F.M. and A.S. Crafts. 1981. Mode of action of herbicides. Wiley-Interscience, New York.
4. Banks, P.A. and E.L. Robinson. 1982. The influence of straw mulch on the soil reception and persistence of metribuzin. *Weed Sci.* 30:164-165.
5. Beestman, G.B. and J.M. Deming. 1974. Dissipation of acetanilide herbicides in soils. *Agro. J.* 66:308-311.
6. Bouchard, D.C., T.L. Lavy, and D.B. Marx. 1982. Fate of metribuzin, metolachlor, and fluometuron in soil. *Weed Sci.* 30:629-632.
7. Coble, H.D. and J.W. Schrader. 1973. Soybean tolerance to metribuzin. *Weed Sci.* 21:308-309.

8. Collins, R.L., S. Doglia, R.A. Mazak, and E.T. Samulski. 1973. Controlled release of herbicides - theory. Weed Sci. 21:1-5.
9. Collins, R.L. and S. Doglia. 1973. Concentration of pesticides slowly released by diffusion. Weed Sci. 21:343-349.
10. Davidson, J.M. and J.R. McDougal. 1973. Experimental and predicted movement of three herbicides in a water-saturated soil. J. Environ. Qual. 2:428-433.
11. DelliColli, H.T. 1980. Pine kraft lignin as a possible delivery system. Pages 225-234 in Controlled Release Technologies: Methods, Theory, and Application. Vol. II. ed. A.F. Kydonieus. CRC Press, Boca Raton, Florida.
12. Dunigan, E.P. and T. MacIntosh. 1971. Atrazine soil organic matter interaction. Weed Sci. 19:279-282.
13. Glennie, D.W. 1971. Reactions in sulfite pulping. Pages 597-631 in Lignin Occurrence, Formation, Structure, and Reactions. ed. K.U. Sarkanen and C.H. Ludwig. Wiley Interscience, New York.
14. Goring, D.A.I. 1971. Polymer properties of lignin and lignin derivatives. Pages 697-761 in Lignin Occurrence, Formation, Structure, and Reactions. ed. K.U. Sarkanen and C.H. Ludwig. Wiley Interscience, New York.

15. Green, R.E. and J.C. Corey. 1971. Pesticide adsorption measurement by flow equilibrium and subsequent displacement. Soil Sci. Soc. Am. Proc. 35:561-565.
16. Harris, C.I. 1967. Movement of herbicides in soil. Weeds 15:214-216.
17. Harris, F.W. 1980. Polymers containing pendent pesticide substituents. Pages 63-82 in Controlled Release Technologies: Method, Theory, and Applications. Vol. II. CRC Press, Boca Raton, Florida.
18. Helling, C.S. and B.C. Turner. 1968. Pesticide mobility: Determination by soil thin-layer chromatography. Science 162:562-563.
19. Helling, C.S. 1971. Pesticide mobility in soils. I. Parameters of thin-layer chromatography. Soil Sci. Soc. Amer. Proc. 35:731-737.
20. Hyzak, D.L. and R.L. Zimdahl. 1974. Rate of degradation of metribuzin and two analogs in soil. Weed Sci. 22:75-79.
21. Jaworski, E.G. 1969. Analysis of the mode of action of herbicidal α -chloroacetamides. J. Agri. and Food Chem. 17:165-170.
22. Ladlie, J.S., W.F. Meggitt, and D. Penner. 1976. Effect of soil pH on microbial degradation, adsorption, and mobility of metribuzin. Weed Sci. 24:477-481.

23. Ladlie, J.S., W.F. Meggitt, and D. Penner. 1976. Effect of pH on metribuzin activity in the soil. *Weed Sci.* 505-507.
24. Leavitt, J.R.C. and D. Penner. 1978. In vitro conjugation of glutathione and other thiols with acetanilide herbicides and EPTC sulfoxide and the action of the herbicide antidote R-25788. *J. Agri. Food Chem.* 27:533-536.
25. McCormick, C.L. and M.M. Fooladi. 1980. Controlled activity polymers with labile bonds to pendent metribuzin. Pages 317-330 in *Controlled Release of Bioactive Materials.* ed. R. Baker. Academic Press, New York.
26. McCormick, C.L., K.W. Anderson, J.A. Pelezo, and D.K. Lichatowich. 1981. Controlled release of metribuzin, 2,4-D, and model aromatic amines from polysaccharides and poly (vinyl alcohol). Pages 147-158 in *Controlled Release of Pesticides and Pharmaceuticals.* ed. D.H. Lewis. Plenum Press, New York.
27. Marton, J. 1971. Reactions in alkaline pulping. Pages 639-689 in *Lignins Occurrence, Formation, Structure, and Reactions.* ed. K.U. Sarkanen and C.H. Ludwig. Wiley-Interscience, New York.
28. Mehlretter, C.L., W.B. Roth, F.B. Weakley, T.A. McGuire, and C.R. Russell. 1974. Potential controlled-

- release herbicides from 2,4-D esters of starch. *Weed Sci.* 22:415-418.
29. Narsaiah, D.B. and R.G. Harvey. 1977. Alachlor and gibberellic acid interaction on corn tissues. *Weed Sci.* 25:197-199.
30. Parochetti, J.U. 1973. Soil organic matter effect on activity of acetanilides, CDAA, and atrazine. *Weed Sci.* 21:157-160.
31. Pearl, I.A. 1964. Lignin chemistry. *Chemistry and Engineering News*. July 6 issue :81-92.
32. Pfister, K. and C.J. Arntzen. 1979. The mode of action of photosystem II. Specific inhibitors in herbicides-resistant weed biotypes. *Z. Naturforsch* 34C:966-1009.
33. Raboy, U. and H.J. Hopen. 1982. Effectiveness of starch xanthide formulations of chloramben for weed control in pumpkin (Cucurbita moschata). *Weed Sci.* 30:169-174.
34. Savage, K.E. 1976. Adsorption and mobility of metribuzin in soil. *Weed Sci.* 24:525-528.
35. Savage, K.E. 1977. Metribuzin persistence in soil. *Weed Sci.* 25:55-59.
36. Schubert, W.J. 1965. Lignin Biochemistry. Academic Press, New York.

37. Sharom, M.S. and G.R. Stephenson. 1976. Behavior and fate of metribuzin in eight Ontario soils. *Weed Sci.* 24:153-160.
38. Smith, A.E. and R.E. Wilkinson. 1974. Differential absorption, translocation, and metabolism of metribuzin 4-amino-6-tert-butyl-3-(methylthio)-as-triazin-5(4H)-one by soybean cultivars. *Plant Physiol.* 32:253-257.
39. Smith, A.E. and B.P. Verma. 1977. Weed control in nursery stock by controlled release of alachlor. *Weed Sci.* 25:175-178.
40. Stevenson, F.J. 1982. *Humus Chemistry Genesis, Composition, Reactions.* Wiley and Sons, New York.
41. Sullivan, J.D., Jr. and G.T. Felbeck, Jr. 1968. A study of the interaction of s-triazine herbicides with humic acids from three different soils. *Soil Sci.* 106:42-52.
42. Swain, T. 1979. Tannins and lignins. Pages 674-681 in *Herbivores Their Interaction with Secondary Plant Metabolites.* ed. G.A. Rosenthal and D.H. Jansen. Academic Press, New York.
43. Ward, T.M. and R.P. Upchurch. 1965. Role of the amido group in adsorption mechanisms. *J. Agr. Food Chem.* 13:334-340.
44. Weber, J.B., S.B. Weed, and T.M. Ward. 1969. Adsorption of s-triazines by soil organic matter. *Weed Sci.* 17:417-421.

45. Weber, J.B. and C.J. Peter. 1982. Adsorption, bioactivity, and evaluation of soil tests for alachlor, acetochlor, and metolachlor. *Weed Sci.* 30:14-20.
46. Weber, J.B. and D.M. Whitacre. 1982. Mobility of herbicides in soil columns under saturated and unsaturated conditions. *Weed Sci.* 30:579-584.
47. Weed Science Society of America. 1983. *Herbicide Handbook*, 5th Ed. WSSA, Champaign, IL 131-318 pp.
48. Wu, C.H. and P.W. Santelmann. 1975. Comparison of different soil leaching techniques with four herbicides. *Weed Sci.* 23:508-511.
49. Zimdahl, R.L. and S.K. Clark. 1982. Degradation of three acetanilide herbicides in soil. *Weed Sci.* 30:545-548.

CHAPTER TWO

CONTROLLED RELEASE OF METRIBUZIN AND ALACHLOR BY KRAFT LIGNINS AS MEASURED BY SOIL THIN LAYER CHROMATOGRAPHY

ABSTRACT

The controlled release of metribuzin (4-amino-6-tert-butyl-3-(methythio)-as-triazin-5(4H)-one) and alachlor (2-chloro-2',6'-diethyl-N-methoxymethyl acetanilide) from pine kraft lignin was studied using ^{14}C -labelled herbicides and ^3H -labelled lignin on soil thin layer chromatography. NB-5203-58 series and PC940 series kraft lignins adsorbed and desorbed metribuzin as soil plates were developed with water. PC671, a former kraft lignin commercial control release product, did not show control release properties with metribuzin. NB-5203-58B and PC940C were the most promising of their respective series of kraft lignins. PC940C appeared to be the most suitable of the two since NB-5203-58B was obtained by a complicated and costly method of ultrafiltration. PC940C, when formulated with surfactant agents, was less active as a controlled release agent for metribuzin than nonformulated PC940C. PC940C was also found

to be an excellent controlled release agent for alachlor. The mechanism of adsorption possibly involved hydrogen bonding.

INTRODUCTION

The advantage of a controlled release agent for readily degradable water-soluble herbicides would be to increase the period of activity of the compound (2). Furthermore, if the bound herbicide is slowly released with the addition of water, potentially less herbicide would be leached through the soil. The possible savings would be in a reduction or elimination of multiple applications of the same or other herbicides (1).

The controlled release of water-soluble herbicides has been extensively studied. Polysaccharides have been tested as control release agents with metribuzin (11), chloramben (3-amino-2,5-dichlorobenzoic acid) (13), and 2,4-D (2,4-dichlorophenoxy acetic acid) (12). Unfortunately, polysaccharides can also serve as a readily available carbon source for microorganisms, and, consequently, the controlled release agent will have a short half-life. Alachlor has been encapsulated in plaster of Paris for effective weed control in perennial ornamentals (13), however, this concept would not be suitable for agronomic purposes. The mobility of metribuzin has been successfully reduced when formulated in polymers of polyvinyl alcohols (5,10). Because there are

covalent linkages formed between metribuzin and the controlled release polymer, the product is a series of compounds similar in structure to metribuzin. Kraft lignins have successfully controlled the release of 2,4-D (3). Pine kraft lignin has been shown to bind atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) (4). Although little is known about the physical properties of kraft lignin, they have a large number of hydroxyl, carboxylic, and carbonyl keto groups (3), which may participate in hydrogen bonding herbicides.

The purpose of this research was to evaluate various commercial and experimental kraft lignins in both formulated and nonformulated forms for controlled release properties with metribuzin and alachlor as measured by soil thin layer chromatography techniques (6,7,8) using ¹⁴C-labelled herbicides and ³H-labelled kraft lignin.

MATERIALS AND METHODS

Materials Used. Thin layer soil plate analysis was done in the following fashion. Glass plates with dimensions of 20 by 20 cm and 0.4 cm thick were cleaned with soap and water, dried, and then coated with a slurry of 106 mm sieved soil using a Desage Heidelberg plate spreader. The soil type used was a Spinks sandy loam with an organic matter content of 0.8% and a pH of 6.5.

Materials tested as possible controlled release agents were the following pine kraft lignins: NB-5203-58A, NB-5203-58B, NB-5203-58C, INDULIN AG, PC940A, PC940B, and PC940C¹. The NB-5203-58 series was prepared by ultra-filtration of INDULIN AG to three molecular size classes which were less than 10,000, 10,000-100,000, and greater than 100,000. The corresponding codes for the NB-5203-58 series were A, B, and C. INDULIN AG was a commercial kraft lignin. PC940A was a high surface kraft lignin which was prepared by chemical alterations and PC940B and PC940C were prepared from caustic solutions.

¹Obtained from Westvaco Corp.

PC671, which is a combination of INDULIN AG and surfactants, was also tested. Two different mixtures of surfactants, designated as WP8 and WP10, were also used to formulate PC940C.

Radio-labelled materials used were: ^{14}C -metribuzin with a specific activity of 21.9 mCi/mM, ^{14}C -alachlor with a specific activity of 1.76 mCi/mM, and ^3H -PC940C with an activity of 0.73 mCi/mg.

Stock solutions of metribuzin and alachlor were made using 90% pure technical grade metribuzin and 95% pure technical grade alachlor. The metribuzin stock was 1800 ppm and the two stocks of alachlor were 200 ppm and 2400 ppm. All stocks were made in distilled water and refrigerated.

NB-5203-58, PC671, INDULIN AG, and surfactants with ^{14}C -metribuzin. The first study was designed to determine the controlled release effect of the NB-5203-58 series, PC671, INDULIN AG, and the surfactant mix of PC671 on metribuzin. Five ml of metribuzin stock solution was added to 25 mg of solid lignin, or in the case of PC671 or the surfactant mix, 78 mg of liquid. These materials were placed in a 10 ml test tube and the tube was shaken using a table top mixer for approximately 15 sec; 250 μl of this mixture was transferred to a vial containing 5 μl of ^{14}C -metribuzin. This vial was then shaken for 1 hr and then stored for 24 h prior to application. After 24 h, the vial

was again shaken and 10 μ l subsamples were withdrawn and spotted on the soil plates. The brown colored lignin was easily detected on the soil plates. Subsamples were also radioassayed via liquid scintillation spectrometry which showed that a 10 μ l sample contained approximately 90,000 disintegrations per minute (DPM). Soil plates were developed in holding tanks with distilled water to an approximate height of 12.5 cm and then dried. Soil plates were then scanned using a Berthold 2D-TLC-Scanner LB276 using methane as the carrier gas. Disintegrations were integrated to determine how much of the ^{14}C remained at the point of application and how much had migrated with the water. The following studies also used the same procedures as described above and all studies had two replications and were repeated.

NB-5203-58B with ^{14}C -metribuzin. This study used only NB-5203-58B and the surfactants found in PC671. Rates of NB-5203-58B to metribuzin stock were 5 mg/ml (1X) and 12.5 mg/ml (2.5X). The rate of surfactant was 15.6 mg/ml of liquid and this contained approximately 460 μ g/ml of solid material. The purpose of this study was to determine how NB-5203-58B's potential as a controlled release agent would be effected by the addition of surfactants.

PC940 with ^{14}C -metribuzin. The PC940 series was used with metribuzin at a ratio of 10 mg/ml. An exception to the first study was a storage period of only 1 h prior to application. The rest of this study was identical to the first. The purpose was to test the controlled release properties of the PC940 series and identify the most suitable for the controlled release of metribuzin.

PC940 with surfactants and ^{14}C -metribuzin. A study was designed to test the effect of formulation on the controlled release potential of the most effective lignin in the PC940 series. The lignin was mixed with the surfactants used to make the commercial formulations WP8 and WP10². The materials were mixed as dry powders which were 93.7% lignin. The rates of nonformulated and formulated lignin used were 9.59 mg/ml and 19.17 mg/ml to the metribuzin stock. The remainder of this study was identical to the first study.

PC940 with ^{14}C -alachlor. A study was also done to test the potential of the PC940 series for the controlled release of alachlor. Five ml of 200 and 2400 ppm alachlor stock solution were added to 25 mg of PC940 lignin. After a 15 sec mixing period as described above, 100 μl was transferred to a vial with 10 μl of ^{14}C -alachlor. This vial was shaken and stored for 1 h and then 10 μl subsamples were spotted on

²Products of the Westvaco Corp.

the soil plates. Subsamples were radio-assayed by liquid scintillation spectrometry, which showed that a 10 μ l sample had approximately 17,000 DPM. The rest of the procedures used were identical to those of the first study.

^3H -PC940C. The last study was done to examine the mobility of PC940C when analyzed separately. PC940C was tritiated by New England Nuclear using a straight tritium gas exchange method. Two ml of distilled water plus 19.2 mg of PC940C were mixed together and shaken for 15 sec and 100 μ l of this was transferred to a vial containing 0.3 mg of ^3H -PC940C. The vial was shaken for 1 h and 1 μ l subsamples were spotted on soil thin layer plates. Each 1 μ l sampled contained approximately 4.8×10^6 DPM as determined by liquid scintillation radioassay. The remaining procedures were identical to those used with ^{14}C -labelled materials.

RESULTS AND DISCUSSIONS

PC671, the PC671 surfactants, and INDULIN AG did not retard the movement of metribuzin from the point of origin (Table 1).

However, the NB-5203-58 series significantly retarded the movement of metribuzin. NB-5203-58C was the most effective in retarding the movement of metribuzin for all three developments than NB-5203-58A and NB-5203-58B. However, NB-5203-58C did not release metribuzin after subsequent developments. There was approximately a 50% decrease in the percentages retained for NB-5203-58A and NB-5203-58B after the third development. There was a direct relationship between the amount of metribuzin immobilized and the molecular size of the three NB-5203-58 lignins with the largest size, greater than 100,000 molecular size, having the highest percentage retained and the smallest size, less than 10,000 molecular size, having the lowest percentage retained.

Since the NB-5203-58 series was derived from ultrafiltration of INDULIN AG, this may have exposed active sites for the adsorptive process.

As the concentration of NB-5203-58B increased (Table 2), the amount of metribuzin immobilized at the point of

Table 1. Effect of lignins on the percentage of ^{14}C -metribuzin retained at the point of origin on soil TLC plates after three developments.

Treatments	Developments ^a		
	1	2	3
	----- (% of Total) ^b -----		
NB-5203-58A	10.9 bc	4.2 c	3.8 c
NB-5203-58B	17.6 b	8.7 bc	8.6 bc
NB-5203-58C	36.3 a	33.5 a	33.9 a
PC-671	0 d	0 d	0 d
INDULIN AG	0 d	0 d	0 d
PC671 Surfactants	0 d	0 d	0 d
Metribuzin Control	0 d	0 d	0 d

^aDevelopments are multiples of approximately 12.5 cm.

^bNumbers followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

Table 2. Effect of NB-5203-58B on the percentage of ^{14}C -metribuzin retained at the point of origin on soil TLC plates after three developments.

Treatments	Developments ^a		
	1	2	3
	----- (% of Total) ^b -----		
NB-5203-58B (1X)	17.6 bc	8.7 de	8.6 de
NB-5203-58B (2.5X)	33.3 a	19.2 bc	13.7 cd
NB-5203-58B (2.5X) + PC671 Surfactants (1X)	21.5 b	11.1 de	7.2 e

^aDevelopments are multiples of approximately 12.5 cm.

^bNumbers followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

origin also increased after the first two developments. With the addition of the surfactants found in PC671, there was a significant reduction in the percentage of metribuzin retained at the point of origin for the 2.5X rate. This would suggest that there was a competitive effect between the surfactant mixture and metribuzin for the adsorptive sites of NB-5203-58B.

INDULIN AG did not desorb metribuzin but could be altered via ultrafiltration to produce new materials which could desorb metribuzin, this would suggest that INDULIN AG had been chemically or physically altered during manufacture.

To test whether or not INDULIN AG had been altered, three other kraft lignins were tested which had been produced from the INDULIN AG precursor. PC940A was a chemically altered high surface area kraft lignin and PC940B and PC940C were made from INDULIN AG subjected to caustic treatment.

All lignins of the PC940 series were able to desorb metribuzin from the point of origin on the soil plates (Table 3). PC940C was the superior of three tested in terms of the greatest amount of metribuzin retained at the origin after each of the three developments. PC940B had similar but significantly lower percentages for metribuzin retained at the point of origin than did PC940C. The differences between PC940B and PC940C may be due to PC940C being treated

Table 3. Effect of lignins on the percentage of ^{14}C -metribuzin retained at the point of origin on soil TLC plates after three developments.

Treatments	Developments ^a		
	1	2	3
	----- (% of Total) ^b -----		
PC940A	17.1 d	8.5 fg	5.3 g
PC940B	41.6 b	21.6 d	11.4 ef
PC940C	47.4 a	29.2 c	16.2 de

^aDevelopment are multiples of approximately 12.5 cm.

^bNumbers followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

under caustic conditions for a longer period of time than PC940B. The lowest percentages for each development were those of PC940A. This may suggest that an increase in surface area may not have been the best way to restore the potential of INDULIN AG to desorb metribuzin.

Whereas both PC940B and PC940C similarly retained metribuzin at the point of origin after a single development as NB-5203-58B, NB-5203-58C did not desorb additional metribuzin with the second and third developments. NB-5203-58B desorbed similar amounts of metribuzin with subsequent developments as PC940B and PC940C.

The adjuvants of WP8 and WP10 decreased the performance of PC940C by interfering with desorption of metribuzin (Table 4). The nonformulated PC940C had significantly higher percentages of metribuzin retained at the point of origin after the first two developments than PC940C with the WP8 and WP10 surfactants; only half as much PC940C was used with the nonformulated treatment as compared to the two adjuvant treatments. This reduction in the performance of PC940C was very similar to the reduction in the performance of NB-5203-58B when it was mixed with the adjuvants found in PC671 (Table 2). The WP8 and WP10 surfactants were dry materials, whereas PC671 was in a liquid state. Since the only major difference between the two WP formulations and PC671 was water, it may be assumed that the negative responses of PC940C and NB-5203-58B to the surfactants was

Table 4. Effect of formulated and nonformulated PC940C on the percentage of ^{14}C -metribuzin retained at the point of origin on soil TLC plates after two developments.

Treatments	Developments ^a	
	1	2
	---- (% of Total) ^b ----	
WP8 Surfactant Formulation	24.0 bc	6.9 d
WP10 Surfactant Formulation	17.3 c	3.6 d
Nonformulated	47.4 a	29.2 b

^aDevelopments are multiples of approximately 12.5 cm.

^bNumbers followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

due to a similar type of competitive interaction between a component in the surfactant mixture for the adsorptive sites of the two lignins.

The PC940 series desorbed alachlor from the point of origin (Table 5). As was the case with metribuzin, PC940C was superior to PC940B with significantly higher percentages of alachlor with the first two developments. PC940A had percentages that were not significantly different from PC940B, but the PC940A treatment had twice as much lignin material used than either the PC940B or the PC940C treatment.

Comparisons of the PC940 series for desorption of metribuzin and alachlor (Tables 3 and 5) were very similar. PC940A was used at identical rates for both metribuzin and alachlor and the percentages for each were very similar. Twice the amount of PC940B and PC940C were used for the metribuzin analysis (Table 3) as compared to the alachlor analysis (Table 5). Consequently, if the amount of lignin is taken into consideration, the response of these two lignins was almost identical with each herbicide.

Although there is little resemblance between the chemical structures of metribuzin and alachlor, desorption percentages of each compound were almost identical for the PC940 series. This is probably due to an abundance of hydrogen bonding possibilities that exist between the lignins and the herbicides. These possibilities are the

Table 5. Effect of lignins on the percentage of ^{14}C -alachlor retained at the point of origin on soil TLC plates after three developments.

Treatments	Developments ^a		
	1	2	3
	----- (% of Total) ^b -----		
PC940A	19.4 b	6.7 de	2.1 e
PC940B	15.1 bc	10.7 cd	6.4 de
PC940C	29.1 a	21.0 b	10.1 cd

^aDevelopments are multiples of approximately 12.5 cm.

^bNumbers followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

keto and primary amine group of metribuzin and the keto and tertiary amine group of alachlor being hydrogen bonded to the hydroxyl, carboxylic, and carbonyl groups of the tested kraft lignins. Similar observations have been reported with different materials such as humic acids (15,16).

Tritiated PC940C was not mobile since most of the radiolabel was detected at the point of origin. After two developments, only from 3 to 5% of the ^3H had moved from the origin and the majority of this was at the water solvent front on the soil TLC plates. This small percentage is similar to that calculated to be the amount of water-soluble small molecular weight materials found in kraft lignin (9). However, there is also the possibility that there was some ^3H exchange that took place between the lignin and the water or water-soluble materials in the soil. If there was ^3H exchange taking place, this would mean that the percentages of ^3H -PC940C measured at the point of origin were underestimated.

In summary, PC940C appeared to be the most suitable pine kraft lignin of the lignins tested to be used as a controlled release agent for metribuzin and alachlor. It had the highest retention percentages of the PC940 series. It appeared to be equal to the performance of NB-5203-58B but NB-5203-58B required a costly and time consuming filtration process while PC940C only required a caustic treatment.

LITERATURE CITED

1. Colins, R.L., S. Doglia, R.A. Mazak, and E.T. Samulski. 1973. Controlled release of herbicides-theory. Weed Sci. 21:1-5.
2. Collins, R.L. and S. Doglia. 1973. Concentration of pesticides slowly released by diffusion. Weed Sci. 21:343-349.
3. DelliColli, H.T. 1980. Pine kraft lignin as a pesticide delivery system. Pages 225-234 in Controlled Release Technologies: Methods, Theory, and Application. Vol. II. ed. A.F. Kydonieus. CRC Press. Boca Raton, Florida.
4. Dunigan, E.P. and T. MacIntosh. 1971. Atrazine-soil organic matter interaction. Weed Sci. 19:279-282.
5. Harris, F.W. 1980. Polymers containing pendent pesticide substituents. Pages 63-82 in Controlled Release Technologies: Methods, Theory, and Application. Vol II. ed. A.F. Kydonieus. CRC Press. Boca Raton, Florida.
6. Helling, C.S. and B.C. Turner. 1968. Pesticide mobility: determination by soil thin-layer chromatography. Science 162:562-563.

7. Helling, C.S. 1971. Pesticide mobility in soils. I. Parameters of thin-layer chromatography. Soil Sci. Soc. Amer. Proc. 35:731-737.
8. Ladlie, J.S., W.F. Meggitt, and D. Penner. 1976. Effect of soil pH on microbial degradation, adsorption, and mobility of metribuzin. Weed Sci. 24:477-481.
9. Marton, J. 1971. Reactions in alkaline pulping. Pages 639-689 in Lignins Occurrence, Formation, Structure, and Reactions. ed. K.U. Sarkanen and C.H. Ludwig. Wiley-Interscience. New York.
10. McCormick, C.L. and M.M. Fooladi. 1980. Controlled activity polymers with labile bonds to pendent metribuzin. Pages 317-330 in Controlled Release of Bioactive Materials. ed. R. Baker. Academic Press, New York.
11. McCormick, C.L., K.W. Anderson, J.A. Pelezo, and D.K. Lichatowich. 1981. Controlled release of metribuzin, 2,4-D, and model aromatic amines from polysaccharides and polyvinyl alcohol. Pages 147-158 in Controlled Release of Pesticides and Pharmaceuticals. ed. D.H. Lewis. Plenum Press, New York.
12. Mehltrittter, C.L., W.B. Roth, F.B. Weakley, T.A. McGuire, and C.R. Russell. 1974. Potential controlled-release herbicides from 2,4-D esters of starches. Weed Sci. 22:415-418.

13. Raboy, V. and H.J. Hopen. 1982. Effectiveness of starch xanthide formulations of chloramben for weed control in pumpkin (Cucurbita moschata). Weed Sci. 30:169-174.
14. Smith, A.E. and B.P. Verma. 1977. Weed control in nursery stock by controlled release of alachlor. Weed Sci. 25:175-178.
15. Sullivan, J.D., Jr. and G.T. Felbeck, Jr. 1968. A study of the interaction of s-triazine herbicides with humic acids from three different soils. Soil Sci. 106:42-52.
16. Ward, T.M. and R.P. Upchurch. 1965. Role of the amido group in adsorption mechanisms. J. Agr. Food Chem. 13:334-340.

CHAPTER THREE

CONTROLLED RELEASE OF METRIBUZIN AND ALACHLOR BY PC940C AS MEASURED BY SOIL COLUMN CHROMATOGRAPHY

ABSTRACT

PC940C, a pine kraft lignin, controlled the release of ^{14}C -metribuzin (4-amino-6-tert-butyl-3-(methythio)-s-triazin-5(4H)-one) and ^{14}C -alachlor (2-chloro-2',6'-diethyl-N-methoxymethyl acetanilide) as measured by leaching soil columns with water. As more PC940C was used, a concentration effect was found with more of the two herbicides being retained in the top portions of the soil columns. Combinations of alachlor and metribuzin applied with PC940C did not alter the retention of either ^{14}C -metribuzin or ^{14}C -alachlor as compared to each herbicide applied with PC940C alone. This would suggest that, at the rate of PC940C used, there was no competition between either herbicide for the controlled release sites on PC940C. The percentage of ^{14}C -metribuzin and ^{14}C -alachlor retained by PC940C in the top portion of the columns was very similar. Since the compounds are not similar in structure, this would

suggest that the mechanism involved in controlled release is hydrogen bonding. Combinations of metribuzin and alachlor without PC940C retarded the mobility of both ^{14}C -metribuzin and ^{14}C -alachlor. This would suggest that hydrogen bonding also occurred between metribuzin and alachlor which resulted in a larger, less water-mobile molecule. Finally, ^3H -PC940C was found to be very immobile in soil columns leached with water. There was a beneficial effect of combining PC940C with either metribuzin or alachlor; however, a three way combination of PC940C, metribuzin, and alachlor resulted in the lowest amount of ^3H -PC940C remaining in the top portion of the soil columns.

INTRODUCTION

A controlled release agent applied with triazine and acetanilide herbicides could increase weed control as more herbicide would remain in the top portion of the soil. It would also extend the activity of the herbicide (1). The advantages of a controlled release mechanism would be the reduction in herbicide injury to deeper rooted crop species as well as the possibility of increasing the weed control spectrum of the herbicide over time. The potential would be to reduce or even eliminate multiple applications of the same or other expensive herbicides (2). In addition, a controlled release strategy would have the potential environmental benefit of having less herbicide leached through the soil and into the ground water.

These advantages would appear to be applicable to metribuzin and alachlor. Metribuzin is mobile in neutral and alkaline pH soils (7) and can cause injury to soybean (Glycine max (L.) Merr.) (8). Alachlor, while not phytotoxic to corn (Zea mays L.) or soybean, could over time be more effective if leaching was reduced.

Several controlled release methods have been tested with metribuzin and alachlor. Pendent metribuzin attached

to polyvinyl alcohol polymers have resulted in a reduction in metribuzin mobility (6,9). However, this approach necessitates covalent bonding of metribuzin to the polymers and results in a series of compounds which incorporate a portion of the metribuzin molecule and have questionable herbicidal value. Metribuzin has also been tested with polysaccharides (10), but unfortunately polysaccharides are short termed readily available carbon sources for soil microorganisms. Alachlor has been successfully tested in encapsulated forms with plaster of Paris for weed control in azalea (Rhododendrum sp.) planting (13). However, this technique would not be a practical one to use with current agronomic practices.

A material that would have the potential to control the release of both metribuzin and alachlor is pine kraft lignin. Lignin has already been successfully used as a controlled release agent for 2,4-D (2,4-dichlorophenoxy acetic acid) (3) and has been shown to have a high adsorptive capacity for atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) (4), possibly via hydrogen bonding (5).

The purpose of this study was to determine the controlled release properties of the pine kraft lignin PC940C with metribuzin and alachlor.

MATERIALS AND METHODS

Soil columns were prepared using polyvinyl chloride tubing with dimensions of 4.6 cm diameter and 36 cm length. The columns were packed uniformly with air dried 2 mm mesh sieved soil. Tubes were split lengthwise and taped back together and the bottom end of the columns were covered with cheese cloth to keep the soil in the columns. Soil used was a Wando sandy loam with 1.7% organic matter, 79.6% sand, 7.2% silt, 13.2% clay, 7.1 pH, and a low 4.2 m.e.q./100 g of soil cation exchange capacity.

The controlled release agent was PC940C¹. This is a dry pine kraft lignin prepared from caustic treated INDULIN AG².

Stock solutions of metribuzin (1800 ppm) and alachlor (9600 ppm) were made using 90% technical grade metribuzin and 15% granular LASSO^{®3} form of alachlor.

¹Provided by the Westvaco Corp.

²Product of the Westvaco Corp.

³Product of the Monsanto Corp.

Labelled materials used were the following: ^{14}C -metribuzin (specific activity of 21.9 mCi/mM), ^{14}C -alachlor (specific activity of 1.76 mCi/mM), and ^3H -PC940C (specific activity of 0.73 mCi/mg).

Two leaching treatments were used. The first, a single leaching of 51 ml (equivalent of 2.54 cm) of distilled water, was uniformly applied to the soil surface over a 2 h time period. The second was identical to the first but with a 6 day drying period followed by an additional 51 ml of water which was also uniformly applied to the soil surface over a 2 h time period; for the drying period, the leached columns were placed under sodium halide lamps located in the greenhouse. The height of the lamps was approximately 30 cm above the soil surface and the illumination was approximately $1000 \mu\text{E}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ with the lamps set for a 15 h illumination period.

Radio-labelled material distribution in the soil columns was determined by the following. The columns were split open and the moist soil removed at 2.54 cm increments with the first increment split in 1.27 cm portions. The water front was typically 15 cm from the soil surface. The entire segments of collected soil were transferred to long necked 250-ml Erlenmeyer ground glass flasks. Fifty ml of extraction solvent was added and the flasks were shaken for 2 h using a table top wrist action shaker at 200 reciprocations/min. Samples from each flask were transferred to

50-ml glass centrifuge tubes and centrifuged at 1000 rpm for 10 min. Between 1 to 5 ml of collected supernatant was removed by using a 5-ml disposable glass pipette and added to a 20-ml glass vial which contained 10 ml of liquid scintillation radioassay fluid. Samples were radioassayed with a liquid scintillation spectrometer.

The extraction solvent used for ^{14}C -alachlor and ^{14}C -metribuzin was acetone and methanol was used for ^3H -PC940C. The extraction efficiency was over 90% for all three radio-labelled materials.

Controlled Release of Metribuzin by PC940C. A study was done to evaluate the potential of PC940C to control the release of metribuzin in soil columns. PC940C was used at 0, 2X, 4X, and 16X levels and these were multiples of 2.6 mg PC940C/ml of metribuzin stock solution. These rates simulated the concentration equivalents of 0, 2.24, 4.48, and 17.92 kg/ha of PC940C in 94.6 L of water with 0.42 kg/ha of metribuzin.

The corresponding amount of PC940C, depending upon the rate tested, was weighed out and mixed with 1 ml of metribuzin stock solution in a 10-ml glass test tube. This was shaken for 15 sec using a table top shaker and 200 μl transferred to a vial which contained 5 μl of ^{14}C -metribuzin. The vial was shaken for 1 h using the same

shaker and then the entire contents of the vial was transferred to the soil surface of the column.

Both leaching treatments were used in this study and following treatment, the columns were sampled for ^{14}C -label distribution patterns. The study had two replications and was repeated two times.

Controlled Release of Alachlor by PC940C. A study was designed to measure the potential of PC940C to control the release of alachlor in soil columns. The same four levels of PC940C were used as in the metribuzin study and identical procedures employed.

Possible Competitive Effect Between Alachlor and Metribuzin.

A study was designed to test the possible competitive effect between metribuzin and alachlor for the controlled release potential of PC940C. PC940C was used at rates of 0, 2X, and 4X with multiples of 5.2 mg PC940C added to 1 ml of metribuzin stock solution plus 1 ml of alachlor stock solution. Mixtures were shaken for 15 sec using a table top shaker and 200 ml samples were transferred to a vial containing 5 μl of ^{14}C -metribuzin or ^{14}C -alachlor. Only the single leaching treatment was used. Extraction procedures and method of analysis were identical to those already described. This study also had two replications and was repeated two times.

Mobility of PC940C. The last study was designed to test the mobility of ^3H -PC940⁴ after a single leaching and if this mobility or lack of mobility was affected by the addition of one or both of the tested herbicides. Consequently the following four treatments were used: PC940C, PC940C + metribuzin, PC940C + alachlor, and PC940C + metribuzin + alachlor. A 2X rate of nonlabelled PC940C was used which corresponded to 2.6 mg PC940C/2 ml of herbicide stock solution. For the PC940C treatment, 2 ml of distilled water was added, while, with the PC940C + metribuzin + alachlor treatment, 1 ml of each herbicide stock solution was used. For the PC940C treatments with each individual herbicide, 2 ml of metribuzin or alachlor stock solution was used. These mixtures were shaken for 15 sec as previously described and 100 μl samples were transferred to vials which contained 0.1 mg ^3H -PC940C. Vials were shaken for 1 h and a 10 μl sample was transferred from the vial to the soil surface. Extraction and analysis were identical to other studies. This study had two replications and was repeated two times.

⁴Tritiated by New England Nuclear using a straight tritium gas exchange method.

RESULTS AND DISCUSSION

PC940C controlled the release of metribuzin in the Wando sandy loam soil columns and kept more of the ^{14}C -metribuzin in the top portion of the columns (Table 1) with less moving to the lower portion of the column. The effect occurred in both single and double leaching treatments and was linear as the concentration of PC940C increased. Although there was a significant decrease in the percentages of ^{14}C -label from ^{14}C -metribuzin that remained in the top 1.27 cm of soil at the 2X and 4X rate of PC940C with the double leaching, the double leaching did not increase the movement of ^{14}C -label with the 16X rate of PC940C.

The effect of PC940C on the controlled release and mobility of ^{14}C -alachlor was similar to that observed with metribuzin (Table 2). However, ^{14}C -metribuzin was more mobile in the columns than was ^{14}C -alachlor, possibly because metribuzin is almost five times more water soluble than alachlor (14).

Combination of alachlor with metribuzin did not interfere with ^{14}C -metribuzin retention and release from PC940C at the 2X and 4X rates of PC940C (Table 3). This

Table 1. The effect of PC940C on ¹⁴C-metribuzin distribution in a Wando sandy loam soil column following one or two leaching periods with 2.54 cm of water.

Sample Depth	Treatments ^{ab}							
	Metribuzin Leaching		Metribuzin + PC940C (2X) Leaching		Metribuzin + PC940C (4X) Leaching		Metribuzin + PC940C (16X) Leaching	
	1 ^c	2	1	2	1	2	1	2
(cm)	-----(% of Total)-----							
0-1.27	5.6 E d	4.5 E d	11.2 CD d	7.8 DE cd	18.6 B b	12.7 C b	48.5 A a	47.4 A a
1.27-2.54	3.2 A d	3.9 A d	5.1 A e	4.3 A d	5.6 A c	4.8 A c	6.2 A d	6.8 A d
2.54-5.08	11.4 A c	11.1 A c	14.3 A c	13.5 A b	15.4 A b	15.6 A b	10.7 A c	15.0 A b
5.08-7.62	31.1 AB b	28.2 B b	35.1 A a	30.1 AB a	31.3 AB a	26.5 B a	17.4 C b	18.0 C b
7.62-10.16	44.0 A a	38.5 AB a	32.1 BC b	33.7 BC a	28.1 C a	30.2 C a	16.3 D b	10.9 D c
10.16-12.70	4.6 BC d	13.4 A c	2.3 C e	10.6 AB bc	1.0 C c	10.2 AB bc	1.0 C e	1.5 C e

56

^aNumbers followed by the same capital letter in the same row are not significantly different according to Duncan's multiple range test at the 0.05 level.

^bNumbers followed by the same lower case letter in the same column are not significantly different according to Duncan's multiple range test at the 0.05 level.

^cLeaching rates are as follows: 1 = 2.54 cm of water and 2 = two 2.54 cm of water separated by a six day drying period.

Table 2. The effect of PC940C on ^{14}C -alachlor distribution in a Wando sandy loam soil column following one or two leaching periods with 2.54 cm of water.

Sample Depth	Treatments ^{ab}					
	Alachlor Leaching	Alachlor + PC940C (2X) Leaching		Alachlor + PC940C (4X) Leaching		Alachlor + PC940C (16X) Leaching
		1	2	1	2	1
	1 ^c	2				2
-----(% of Total)-----						
0-1.27	7.3 D c	5.7 D d	15.2 C c	9.7 D cd	24.3 B b	57.0 A a
1.27-2.54	5.8 C c	9.8 AB c	6.1 C d	8.5 B d	6.0 C c	9.5 AB c
2.54-5.08	22.4 B b	34.3 A b	23.3 B b	29.7 A b	22.4 B b	31.9 A a
5.08-7.62	57.4 A a	38.6 C a	48.5 B a	38.6 C a	42.8 C a	32.3 D a
7.62-10.16	7.1 BC c	11.5 AB c	7.0 BC d	13.3 A c	4.6 CD c	8.6 ABC c
						53.4 A a
						8.5 B c
						16.4 C b
						13.9 E b
						0.3 D d
						5.0 CD c

^aNumbers followed by the same capital letter in the same row are not significantly different according to Duncan's multiple range test at the 0.05 level.

^bNumbers followed by the same lower case letter in the same column are not significantly different according to Duncan's multiple range test at the 0.05 level.

^cLeaching rates are as follows: 1 = 2.54 cm of water and 2 = two 2.54 cm of water separated by a six day drying period.

Table 3. Percentage of ^{14}C -metribuzin in various depth sections of a Wando sandy loam soil column following application of a metribuzin-alachlor mixture leached with 2.54 cm water over a 2 h time period.

Sample Depth	Treatments				
	Metribuzin ^{ab}	Metribuzin + Alachlor	Metribuzin + PC940C (2X)	Metribuzin + Alachlor + PC940C (2X)	Metribuzin + Alachlor + PC940C (4X)
(cm)	-----(% of Total)-----				
0-1.27	5.6 C d	6.3 C c	11.2 B d	13.3 B c	18.6 A b
1.27-2.54	3.2 B d	5.5 A c	5.1 A e	5.7 A d	5.6 A c
2.54-5.08	11.4 D c	19.2 AB b	14.3 CD c	21.4 A b	15.4 BC b
5.08-7.62	31.1 D b	52.7 A a	35.1 CD a	39.2 BC a	31.3 D a
7.62-10.16	44.0 A a	16.3 D b	32.1 B b	20.2 CD b	28.1 BC a
10.16-12.70	4.6 A d	0.1 C d	2.3 B e	0.1 C e	1.0 BC c
					16.7 A b
					6.5 A c
					18.0 ABC b
					40.5 B a
					18.0 D b
					0.2 C d

^aNumbers followed by the same capital letter in the same row are not significantly different according to Duncan's multiple range test at the 0.05 level.

^bNumbers followed by the same lower case letter in the same column are not significantly different according to Duncan's multiple range test at the 0.05 level.

would suggest that alachlor did not compete with ^{14}C -labelled and non-labelled metribuzin for the active binding sites on PC940C, or if it did, the PC940C binding sites were not over-saturated at the 2X rate. Since a rate response was observed for ^{14}C -metribuzin retention between the 2X and 4X PC940C rates, the latter is not probable.

Combination of metribuzin with alachlor also did not interfere with ^{14}C -alachlor retention and release from PC940C at the 2X and 4X rates (Table 4). This would suggest that metribuzin did not interfere with ^{14}C -alachlor for the active sites on PC940C.

An interaction between alachlor and metribuzin retarded the mobility of both ^{14}C -metribuzin and ^{14}C -alachlor at all levels of PC940C. This suggests that there was an interaction taking place between the two compounds which would result in both becoming less mobile in the soil columns. Hydrogen bonding may have occurred between the two compounds, possibly between the primary amine group of metribuzin and the carbonyl group of alachlor. This would result in a larger and probably less mobile molecule.

With the double leaching treatment for the ^{14}C -metribuzin treatment, there were significantly larger percentages of ^{14}C -label extracted from the 16X rate of PC940C than from the other three levels of PC940C (Table 5). The amount extracted was almost twice as much as compared to PC940C rates of 0, 2X, and 4X. Since metribuzin is very

Table 4. Percentage of ^{14}C -alachlor in various depth sections of a Wando sandy loam soil column following application of a metribuzin-alachlor mixture leached with 2.54 cm water over a 2 h time period.

Sample Depth	Treatments			
	Alachlor ^{ab}	Alachlor + Metribuzin	Alachlor + PC940C (2X)	Alachlor + Metribuzin + PC940C (2X)
			Alachlor + PC940C (4X)	Metribuzin + PC940C (4X)
(cm)	-----(% of Total)-----			
0-1.27	7.3 C c	7.3 C c	15.2 B c	15.1 B c
1.27-2.54	5.8 B c	7.5 B c	6.1 B d	7.7 B d
2.54-5.08	22.4 B b	34.1 A b	23.3 B b	33.3 A b
5.08-7.62	57.4 A a	50.2 B a	48.5 B a	40.0 C a
7.62-10.16	7.1 A c	1.0 A d	7.0 A d	3.9 A e
			24.3 A b	20.7 A b
			6.0 B c	10.9 A c
			22.4 B b	34.4 A a
			42.8 C a	30.5 D a
			4.6 A c	2.9 A d

^aNumbers followed by the same capital letter in the same row are not significantly different according to Duncan's multiple range test at the 0.05 level.

^bNumbers followed by the same lower case letter in the same column are not significantly different according to Duncan's multiple range test at the 0.05 level.

Table 5. The influence of PC940C on the recovery of ^{14}C -metribuzin from Wando sandy loam soil columns following the two leaching and drying treatments^a.

Treatments			
Metribuzin ^b	Metribuzin+ PC940C (2X)	Metribuzin+ PC940C (4X)	Metribuzin+ PC940C (16X)
----- (DPM Recovered) -----			
263,130 C	255,002 C	250,715 C	557,569 A

^aNote that each treatment received approximately 576,000 DPM of ^{14}C metribuzin.

^bNumbers followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

soluble in acetone, the lower values would suggest that there was metabolism of the ^{14}C -metribuzin during the 6-day drying period prior to the last leaching. Since the amount of ^{14}C -label extracted was higher at the 16X rate, there was little or no metabolism of metribuzin with this treatment. This type of analysis does not rule out the possibility that a non-phytotoxic metabolite of metribuzin was extracted by the acetone. However, the data suggests that PC940C at the high rate was able to increase the activity period of metribuzin. Because lignin has been found to be relatively impervious to microbial decomposition in a short period of time (12), PC940C may have served as a barrier between metribuzin and soil microorganisms.

There were no significant differences in the amount of ^{14}C -label recovered for the single leaching treatment of ^{14}C -metribuzin and of ^{14}C -alachlor between the rates of PC940C used. Because the single leaching treatment was done in such a short period of time, there was probably not enough time for any appreciable microbial decomposition of either herbicide.

There was also no significant difference in the amount of ^{14}C -label recovered after the double leaching treatment of ^{14}C -alachlor between the rates of PC940C used. This would suggest that alachlor was more persistent in the Wando sandy loam soil columns than metribuzin.

PC940C was not mobile in the soil columns as determined by the ^3H -labelled experiments (Table 6). The greatest portion of the applied ^3H -PC940C remained in the top 1.27 cm of the soil. This was also supported by visual observation since the material tended to remain on the soil surface after repeated leachings.

A combination of metribuzin and alachlor retained less ^3H -PC940C at the soil surface than did the treatments of ^3H -PC940C plus alachlor and ^3H -PC940C plus metribuzin. The treatment of ^3H -PC940C with no alachlor or metribuzin had a smaller percentage of ^3H -label remaining in the top 1.27 cm of the soil than did the treatments with alachlor or with metribuzin. However, the treatment with no alachlor or metribuzin had more retained in the top 1.27 cm of the soil than did the treatment with both metribuzin and alachlor.

The retention of more ^3H -label in the top 1.27 cm of the soil columns when PC940C was mixed with metribuzin or with alachlor may have been due to hydrogen bonding between the more mobile fractions of PC940C and either herbicide. This may have reduced the mobility of highly water-soluble ^3H -labelled fractions. However, an explanation for what happened with the three way interaction of ^3H -PC940C, alachlor, and metribuzin is more difficult. It was found that metribuzin and alachlor interacted with one another (Tables 3 and 4) and this interaction may be partially

Table 6. Percentage of ^3H PC940C in various depth sections of a Wando sandy loam soil columns following leaching with 2.5 cm of water.

Sample Depth	Treatments			
	PC940C (2X) ^{ab}	PC940C (2X)+ Metribuzin	PC940C (2X)+ Alachlor	PC940C (2X)+ Metribuzin+ Alachlor
(cm)	----- (% of Total) -----			
0-1.27	86.7 B a	91.2 A a	89.0 AB a	80.0 C a
1.27-2.54	2.3 B bcd	1.9 B bc	2.3 B bc	3.5 A bc
2.54-5.08	2.0 B cd	1.1 C c	1.7 BC c	2.7 A c
5.08-7.62	1.7 B d	0.9 D c	1.2 C c	3.1 A bc
7.62-10.16	3.5 B bc	2.1 B bc	2.0 B bc	5.5 A b
10.16-12.70	3.8 A b	2.8 A b	3.8 A b	5.3 A b

^aNumbers followed by the same capital letter in the same row are not significantly different according to Duncan's multiple range test at the 0.05 level.

^bNumbers followed by the same lower case letter in the same column are not significantly different according to Duncan's multiple range test at the 0.05 level.

responsible for less ^3H -label being retained in the top 1.27 cm of the soil columns.

The water solubility of ^3H -PC940C can be estimated. Previous soil plate analysis of ^3H -PC940C after multiple developments, showed that only 3 to 5% of the ^3H -label migrated with the water solvent front (11). If a value of approximately 4% is assigned for the water-soluble fraction of ^3H -PC940C, than the amount of ^3H -PC940C which percolated into the soil column ranged from 5 to 16%.

To summarize, PC940C effectively controlled the release of metribuzin and alachlor in soil columns with two leaching treatments. PC940C, at the 16X rate, appeared to inhibit the decomposition of metribuzin. PC940C was also found to be mostly non-mobile in the soil columns when leached with water. Water insolubility of PC940C is a prerequisite for a successful controlled release agent of water-soluble herbicides.

LITERATURE CITED

1. Collins, R.L., S. Doglia, R.A. Mazak, and E.T. Samulski. 1973. Controlled release of herbicides theory. *Weed Sci.* 21:1-5.
2. Collins, R.L. and S. Doglia. 1973. Concentration of pesticides slowly released by diffusion. *Weed Sci.* 21:343-349.
3. DelliColli, H.T. 1980. Pine kraft lignin as a pesticide delivery system. Pages 225-234 in *Controlled Release Technologies: Methods, Theory, and Application*. ed. A.F. Kydonieus. Vol. II. CRC Press. Boca Raton, Florida.
4. Dunigan, E.P. and T. MacIntosh. 1971. Atrazine-soil organic matter interaction. *Weed Sci.* 19:279-282.
5. Goring, D.A.I. 1971. Polymer properties of lignin and lignin derivatives. in *Lignins Occurrence, Formation, Structure, and Reactions*. ed. K.U. Sarkanen and C.H. Ludwig. Wiley Interscience, New York.
6. Harris, F.W. 1980. Polymers containing pendent pesticide substituents. Pages 63-82 in *Controlled Release Technologies: Methods, Theory, and Application*.

- ed. A.F. Kydonieus. Vol. II. CRC Press. Boca Raton, Florida.
7. Ladlie, J.S., W.F. Meggitt, and D. Penner. 1976. Effect of soil pH on microbial degradation, adsorption, and mobility of metribuzin. *Weed Sci.* 24:477-481.
 8. Ladlie, J.S., W.F. Meggitt, and D. Penner. 1976. Effect of pH on metribuzin activity in the soil. *Weed Sci.* 24:505-507.
 9. McCormick, C.L. and M.M. Fooladi. 1980. Controlled activity polymers with labile bonds to pendent metribuzin. Pages 317-330 in *Controlled Release of Bioactive Materials*. ed. R. Baker. Academic Press, New York.
 10. McCormick, C.L., K.W. Anderson, J.A. Pelezo, and D.K. Lichatowich. 1981. Controlled release of metribuzin, 2,4-D, and model aromatic amines from polysaccharides and poly (vinyl alcohol). Pages 147-158 in *Controlled Release of Pesticides and Pharmaceuticals*. ed. D.H. Lewis. Plenum Press, New York.
 11. Riggle, B.D. and D. Penner. Controlled release of metribuzin and alachlor by pine kraft lignins as measured by soil thin layer chromatography. (in preparation)
 12. Schubert, W.J. 1965. *Lignin Biochemistry*. Academic Press, New York.

13. Smith, A.E. and B.P. Verma. 1977. Weed control in nursery stock by controlled release of alachlor. Weed Sci. 25:175-178.
14. Weed Science Society of America. 1983. Herbicide Handbook, 5th Ed. WSSA, Champaign, IL. 13 and 318 pp.

CHAPTER FOUR

PC940C PROTECTION OF FIELD AND GREENHOUSE GROWN SOYBEANS FROM METRIBUZIN INJURY

ABSTRACT

PC940C, a pine kraft lignin, combined with metribuzin (4-amino-6-tert-butyl-3-(methylthio)-as-triazin-5(4H)-one), significantly reduced metribuzin related phytotoxicity to field and greenhouse grown soybeans (Glycine max (L.) Merr.). PC940C rates of 0.77 and 1.15 L/ha protected field grown soybeans treated with metribuzin rates of 0.42 and 0.84 kg/ha. PC940C rates of 1.15 and 2.30 L/ha also protected greenhouse grown soybeans treated with metribuzin of 0.64 kg/ha. PC940C did not interfere with the effective weed control of redroot pigweed (Amaranthus retroflexus L.) and common lambsquarters (Chenopodium album L.). PC940C did not appear to have any herbicidal activity and did not appear to injure soybeans. These results suggest that PC940C effectively controlled the release of metribuzin in field and greenhouse soil.

INTRODUCTION

A controlled release agent used with metribuzin could be most beneficial for use in soybean production. The net result would be a reduction in mobility of this highly water-soluble herbicide (11) in neutral and alkaline pH soils (4), and, consequently, a reduction in metribuzin related phytotoxicity of soybeans, since less herbicide would migrate into the soybean root zone.

Different controlled release materials have been tested with metribuzin. Pendent metribuzin, which was attached to polyvinyl alcohol polymers, resulted in a reduction of metribuzin mobility (3,6); however, this approach necessitates covalent bonding of metribuzin with the polymers and results in a series of compounds which incorporate a portion of the metribuzin molecule and have questionable herbicidal value. Metribuzin has also been tested with polysaccharides (7), but unfortunately polysaccharides are short term readily available carbon sources for soil microorganisms.

A material that would have the potential as a controlled release agent for metribuzin is pine kraft lignin. Pine kraft lignin has already been successfully

used with 2,4-D (2,4-dichlorophenoxy acetic acid) (1) and has been demonstrated to have high adsorptive capacity for atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) (2). In addition, pine kraft lignin has been shown to control the release of metribuzin and alachlor (2-chloro-2',6'-diethyl-N-methoxymethyl acetanilide) as demonstrated by soil thin layer chromatography (8) and soil column chromatography (9).

The purpose of this study was to evaluate PC940C as a controlled release agent for preemergence applied metribuzin as measured by the reduction of metribuzin related phytotoxicity to field and greenhouse grown soybeans.

MATERIALS AND METHODS

Material Studied. PC940C is a pine kraft lignin made from caustic treated INDULIN AG¹. PC940C was used in a 15% solid water slurry form which kept the water-insoluble lignin in a suspension.

Field Study. A field experiment was conducted in 1984 at East Lansing, Michigan. The soil was a Capac fine loam (fine loamy, mixed mesic Aeric Ochraqualfs) with 2.6% organic matter and pH of 7.8. The experiment was designed as a completely randomized block two factor factorial with four levels of metribuzin and four levels of PC940C for a total of sixteen treatments with four replications. The metribuzin rates were 0, 0.42, 0.64, and 0.84 kg/ha; PC940C rates were 0, 0.38, 0.77, and 1.15 L/ha. Four hours prior to application, metribuzin, and PC940C were mixed together in 1-L plastic bottles and allowed to stand. Treatments of metribuzin and PC940C were applied preemergence with a tractor-mounted sprayer that delivered 215 L/ha at 207 kPa

¹Product of Westvaco Corp.

pressure. Four rows of soybeans, Corsoy 79, were planted in each plot. Plot size was 9.1 m by 3 m with 0.76 row width spacing. Planting date was June 22, 1984. Rainfall (Table 1) was sparse for that year and so plots were periodically irrigated (Table 1). All plots were hand weeded as needed early in the growing season. Soybean injury ratings (0 = no injury; 100 = complete kill) was measured 32 and 46 days after emergence (D.A.E.). Weed control ratings were recorded (0 = no control; 100 = complete control) for redroot pigweed and common lambsquarters at 32 and 46 D.A.E. Due to technical difficulties, the 0.64 kg/ha metribuzin treatment was discarded.

Greenhouse Study. Greenhouse experiments were conducted in 1984 and 1985 at East Lansing, Michigan. Soil type used to pot plants was a Spinks sandy loam (sandy, mixed mesic Psammentic Hapludalfs) with 0.8% organic matter and pH of 6.5. Three soybean seeds (Corsoy 79) were planted in 1-L plastic pots with drainage holes. Pots were placed in 250-ml aluminum pans to allow for daily subirrigation with water. A combination of PC940C and metribuzin was applied preemergence and the experimental design was a two factor factorial with metribuzin applied at two rates and PC940C applied at three rates. The rates for metribuzin were 0 and 0.64 kg/ha; the rates for PC940C were 0, 1.15, and 2.30

Table 1. Rainfall and irrigation data for 1984 at East Lansing, Michigan after 22 June.

Month	Rainfall	Irrigation
	(cm)	(cm)
June	0	2.54
July	3.18	6.35
August	8.13	0

L/ha. Materials were mixed together in plastic 1-L bottles, shaken, and allowed to stand for 1 h prior to application. Materials were applied with a belt sprayer with a pressure of 104 kPa and a spray volume of 234 L/ha. All treatments were arranged in the greenhouse in a completely randomized design and six replications were used. Container-grown plants were kept in greenhouse at 20 to 30 C with natural illumination and sodium halide supplemental lighting at $500 \mu\text{E}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$. When plants were in the third trifoliar growth stage (approximately 35 D.A.E.), they were rated for injury (0 = no injury, 100 complete kill) and the dry weights measured. Data for dry weights is expressed as percentage of control.

RESULTS AND DISCUSSION

Irrigation was essential for the field experiment since enough water had to be present to insure that the metribuzin would be mobilized into the soil profile. Research has shown that the movement of water-soluble herbicides into the soil is necessary and is enhanced under high moisture conditions (10).

PC940C successfully reduced metribuzin related phytotoxicity to the soybeans in the field at 32 and 46 D.A.E. (Tables 2 and 3). There was a significant reduction in phytotoxicity at 32 D.A.E. when 0.77 and 1.15 L/ha rates of PC940C were used with a 0.42 kg/ha rate of metribuzin. However, only a 0.77 L/ha rate of PC940C significantly reduced phytotoxicity when a 0.84 kg/ha rate of metribuzin was used. There was also a significant reduction in phytotoxicity at 46 D.A.E. when PC940C was used with the two rates of metribuzin.

There was no apparent injury to the plants which had been treated with just PC940C. This would suggest that PC940C did not have any herbicidal activity.

The two week interval between the two injury rating dates was apparently enough time for the PC940C plus

Table 2. Soybean injury ratings as affected by metribuzin and PC940C at 32 D.A.E.^a.

PC940C	Metribuzin ^b (kg/ha)		
	0	0.42	0.84
(L/ha)	----- (%) -----		
0	0 d	48 ab	66 a
0.38	0 d	32 bc	52 ab
0.77	0 d	20 cd	38 bc
1.15	0 d	22 cd	43 abc

^aInjury index rating is based on the following: 0 = no injury, 100 = total kill.

^bNumbers followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

Table 3. Soybean injury ratings as affected by metribuzin and PC940C at 46 D.A.E.^a.

PC940C	Metribuzin ^b (kg/ha)		
	0	0.42	0.84
(L/ha)	----- (%) -----		
0	0 d	45 a	43 a
0.38	0 d	26 bc	28 b
0.77	0 d	12 cd	20 bc
1.15	0 d	16 bc	17 bc

^aInjury index rating is based on the following: 0 = no phytotoxicity, 100 = total kill.

^bNumbers followed by the same letter are not significantly different according the Duncan's multiple range test at the 0.05 level.

metribuzin treated plants to out-grow their metribuzin induced injury as compared to the non-PC940C metribuzin treated plants.

The protective effects of PC940C are readily apparent from photographs taken at 32 D.A.E. (Figures 1 and 2). There was an improvement in both height and vigor of the plants.

PC940C did not interfere with metribuzin related weed control at the two testing dates for both redroot pigweed and common lambsquarters which were the predominate broadleaf weed types present in the study. There was also no observed PC940C effect for either weed type.

The similarity in the degree of phytotoxicity for both the 0.42 and 0.84 kg/ha rate of metribuzin may have been due to the high pH of the soil which was 7.7. Research has shown that, as the soil pH increases, the degree of metribuzin related injury to soybeans also increases (5).

The results obtained in the greenhouse were very similar to those of the field study. There was a significant reduction in metribuzin related phytotoxicity with plants treated with PC940C; 0.64 kg/ha rate of metribuzin treated soybeans had a 50% reduction in injury when treated with PC940C at rates of both 1.15 and 2.30 L/ha (Table 4). Since there appeared to be no concentration effect of PC940C in terms of injury reduction, it can be assumed that some saturation point had

Figure 1. Soybeans treated with 0.42 kg/ha metribuzin and 0 L/ha PC940C and rated at 32 D.A.E.



Figure 2. Soybeans treated with 0.42 kg/ha metribuzin and 0.77 L/ha PC940C and rated at 32 D.A.E.



Table 4. Soybean injury ratings as affected by metribuzin and PC940C for greenhouse grown plants at the third trifoliar stage^a.

	Metribuzin ^b (kg/ha)	
	0	0.64
PC940C		
(L/ha)	----- (%) -----	
0	0 c	22 a
1.15	0 c	10 b
2.30	0 c	11 b

^aInjury index rating is based on the following: 0 = no injury, 100 = total kill.

^bNumbers followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

been reached at the 1.15 L/ha rate. PC940C did not appear to injury or alter the percentage dry weight of the container grown plants (Table 5).

In conclusion, PC940C successfully reduced metribuzin related phytotoxicity to both field and greenhouse grown soybeans and did not interfere with metribuzin related weed control as measured in the field. These results suggest that PC940C controlled the release of metribuzin both in the field and greenhouse.

Table 5. Effect of PC940C on metribuzin injury to soybeans grown in greenhouse as measured in dry weight of third trifoliar plants^a.

Metribuzin	PC940C	% Dry Weight of Control ^b
(kg/ha)	(L/ha)	(%)
0	1.15	95.6 a
	2.3	91.7 ab
0.64	0	73.0 c
	1.15	77.8 c
	2.3	81.4 bc

^aEffects on dry weights are as percentages of the untreated control.

^bMeans with common letters are not significantly different according to Duncan's multiple range test at the 0.05 level.

LITERATURE CITED

1. DelliColli, H.T. 1980. Pine kraft lignin as a pesticide delivery system. Pages 225-234 in Controlled Release Technologies: Methods, Theory, and Application. Vol. II. ed. A.F. Kydonieus. CRC Press, Boca Ration, Florida.
2. Dunigan, E.P. and T. MacIntosh. 1971. Atrazine soil organic matter interaction. Weed Sci. 19:279-282.
3. Harris, F.W. 1980. Polymers containing pendent pesticide substituents. Pages 63-82 in Controlled Release Technologies: Methods, Theory, and Application. Vol. II. ed. A.F. Kydonieus. CRC Press, Boca Raton, Florida.
4. Ladlie, J.S., W.F. Meggitt, and D. Penner. 1976. Effect of soil pH on microbial degradation, adsorption, and mobility of metribuzin. Weed Sci. 24:477-481.
5. Ladlie, J.S., W.F. Meggitt, and D. Penner. 1976. Effect of pH on metribuzin activity in the soil. Weed Sci. 24:505-507.
6. McCormick, C.L. and M.M. Fooladi. 1980. Controlled activity polymers with labile bonds to pendent

- metribuzin. Pages 317-330 in Controlled Release of Bioactive Materials. ed. R. Baker. Academic Press, New York.
7. McCormick, C.L., K.W. Anderson, J.A. Pelezo, and D.K. Lichatowich. 1981. Controlled release of metribuzin, 2,4-D, and model aromatic amines from polysaccharides and poly (vinyl alcohol). Pages 147-158 in Controlled Release of Pesticides and Pharmaceuticals. ed. D.H. Lewis. Plenum Press, New York.
 8. Riggle, B.D. and D. Penner. Controlled release of metribuzin and alachlor by kraft lignins as measured by soil thin layer chromatography. (in preparation)
 9. Riggle, B.D. and D. Penner. Controlled release of metribuzin and alachlor by PC940C as measured by soil column chromatography. (in preparation)
 10. Ritter, W.F., H.P. Johnson, and W.G. Lovely. 1973. Diffusion of atrazine, propachlor, and diazon. Weed Sci. 21:381-384.
 11. Weed Science Society of America. 1983. Herbicide Handbook, 5th Ed. WSSA, Champaign, IL. 318 pp.

MICHIGAN STATE UNIV. LIBRARIES



31293106565058