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THE POTENTIAL OF LIGNIN AS A MONOLITHIC CONTROLLED RELEASE MATRIX FOR TRIFLURALIN, QUINCLORAC, AND METOLACHLOR

By

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ABSTRACT

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Laboratory, greenhouse and field studies were used to explore the potential of lignin as controlled release agent for various herbicides. The controlled release properties of lignins on the volatility of **trifluralin** (α, α, α-trifluoro-2,6-dinitropropyl-p-toluidine), **ethalfluralin** (*N*-ethyl-*N*-(2-methyl-2-propenyl)-2,6-dinitro-4-(trifluoromethyl) benzenamine), **EPTC** (*S*-ethyl dipropyl carbamothioate), and **triallate** (*S*-(2,3,3-trichloro-2-propenyl) bis(1-methylethyl) carbamothioate) were tested. In greenhouse studies tank-mixing slurried lignins with a commercial EC (emulsifiable concentrate) of EPTC yielded no observable controlled release. Non-soil-incorporated mixtures of dried lignin with technical grade trifluralin or ethalfluralin yielded extended weed control in greenhouse studies when compared to ECs of the same herbicides applied with an aqueous carrier. Non-soil-incorporated lignin-trifluralin, and lignin-ethalfluralin

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tank-mixes failed to provide weed control of comparable longevity to the soil-incorporated commercial EC formulations. Similar results were observed in field studies when the ECs of trifluralin and triallate were tank-mixed with slurried lignin. The reduced release of trifluralin and ethalfluralin observed in the greenhouse studies was not verified in laboratory assays. The leaching of **quinclorac** (3,7-dichloro-8-quinolinecarboxylic acid), **metolachlor** (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide), and **chloramben** (3-amino-2,5-dichlorobenzoic acid) was reduced when formulated with acetone-soluble lignin fractions. The lignin-herbicide matrix remained intact, retaining more than 50% of the herbicide under the mild weathering conditions of the laboratory. Results from greenhouse studies supported the laboratory findings. The lignin appeared to reduce leaching by encasing the herbicide in a lignin-herbicide matrix. The level of metolachlor released was increased when water responsive swelling materials were added to the lignin-herbicide matrix. The enhanced release occurred on a delayed basis and was initiated when exposed to water. Field results conflicted with laboratory and greenhouse studies. Leaching increased and the duration of weed control decreased for the lignin-metolachlor treatments when compared to the plots treated with the EC of metolachlor

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A thanks to those who are no longer with us. To Warren, Don, Janet and Gene all of whom played important parts in setting my priorities. Most importantly to Maggie for her commitment, patience, encouragement and love.

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CHAPTER ONE

LITERATURE REVIEW

INTRODUCTION

The percentage of applied pesticides that do not reach the targeted pests have caused concern for decades. This concern was expressed prior to the publication of **Silent Spring** by Rachel Carson in 1962 and the debate has intensified as analytical chemists have decreased the lower detection limit and cost of pesticide residue analysis. As the lower detection level has decreased the number of positive findings has increased (45, 53). These detections have triggered questions regarding the human health and environmental impact of chronic exposure to low levels of pesticides (17, 18, 21, 23, 41, 42, 43, 48). The analytical results have stirred debate among toxicologist and society regarding their relative importance (2, 29, 32).

Low level pesticide residue findings and the inability of scientist to conclusively define safe levels of exposure present considerable problems for policy makers (40, 44, 51, 52, 66). Various regulatory agencies on the State and Federal levels routinely publish documents that advocate extreme and opposite positions regarding the safety of pesticides and the ability of the government to protect the

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public (6, 22, 44, 45). The scientific community is no less divided over the issue (9, 49, 50, 61).

Public demand for abbreviated answers, the inability of the experts to condense complex issues, the speed that information is disseminated by the press and the lack of confidence in regulatory agencies all contribute to public confusion and fear (34, 55).

A number of policy makers and researchers believe that the debate is miss-focused (2, 6, 9,). Many indicate that resources devoted to eliminating and determining the human health effects of low level chronic exposure to pesticides is a poor allocation of limited resources (29). Health experts generally indicate that pesticide residue exposure is a minor health issue (30). These observations have failed to reduce the pressure on politicians, regulatory officials, and businesses. Each group is forced to address the concerns of their constituents and clients long before a consensus can be obtained in the scientific community.

The growing concern over contamination of food, surface-water and ground-water by pesticides has resulted in considerable regulatory activity in agriculture. The Endangered Species Act, the Wet-lands Act, the Clean Air Act, the proposed Food Safety bill by Waxmen and Kennedy, and other state and Federal laws are changing agriculture. Few regulatory policies hold the potential for changing farming

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farming practices to the degree that the Environmental Protection Agency's Pesticides and Ground-Water Strategy does (10, 46). Rather than impacting isolated areas or fine tuning specific practices it promises to drastically change farming practices in large regions.

A recent EPA well water survey found DCPA (dimethyl 2,3,5,6-tetrachloro-1,4-benzenedicarboxylate), the primary metabolite of DCPA, and atrazine (6-chloro-*N*-ethyl-*N*'-(1-methylethyl)-1,3,5-triazine-2,4-diamine) to be the most commonly found pesticide contaminates (67). Both are herbicides. Surprisingly, these contaminates have low water solubility and high octanol water partitioning coefficients (12, 13, 14, 15, 27). Not so surprising, atrazine and DCPA's primary metabolite have relatively long half-lives. The new regulatory attention given the pesticide issue has forced agricultural researchers and growers to reevaluate research and production objectives. No longer are yield optimization practices devised by agricultural researchers implemented without raising questions regarding economic and environmental impacts. The need to reconsider the objectives and methods of farming was emphasized in **Alternative Agriculture** a National Academy of Science publication (1). Peer review journals and popular publications similar to the **Journal of Sustainable**

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Agriculture[1] and **New Farm**[2] give some indication of the growing acceptance and in some situations the concession to change. Yet, by far the strongest incentive for changing agricultural practices is the market.

Detection of ethylene dibromide (1,2-dibromoethane) in cake mixes in 1984, the illegal use of aldicarb (2-methyl-2-(methyl thio) propionaldehde *O*-methyl carbamoyloxime) on California grown watermelons in 1985, the questions raised in 1989 by the National Resources Defense Council regarding the exposure of children to diamidazide (butandioic acid mono-(2,2-dimethylhydrazine)), concern raised by the uneven distribution of aldicarb in bananas first observed 1991 and other negative events have cost the United State's food industry in terms of money and credibility. Politicians, regulators and businesses are being pressured for immediate solutions.

No-till farming presents a potential solution for reducing soil erosion and associated pollution (1). No-till also limits the use of volatile herbicides. Many of which are inexpensive, efficacious, and possess desirable

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[1] Journal of Sustainable Agriculture published by Food Products Press, an imprint of The Haworth Press, Inc. Bringhamton, NY

[2] New Farm a publication of Rodale Press, Inc. PA

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environmental qualities (11). Altering the formulation of existing pesticides may be the most economical means of complying with the regulatory requirements and still providing weed control materials for minor use crops (16, 38). Controlling the delivery of a pesticide also holds promise as a possible means of improving performance (39, 56).

Off-site movement of pesticides and subsequent contamination of food, ground-water or surface-water need not be the prerequisite for banning a given pesticide. Alterna-tives to current farming practices can be utilized to improve the delivery of a pesticide (19, 26, 58, 65). The use of contour farming can reduce run-off, adjuvants can reduce aerosol formation retarding drift, and altered formulations can be developed to alter leaching or volatility (56).

Successful development of adjuvants or altered formulations to reduce off-site movement of agricultural chemicals is limited by cost constraints (33). The early developmental work in controlled release of bio-active chemicals occurred primarily in the pesticide field (7, 8, 25). More recently the development of most new controlled release technologies has occurred in the pharmaceutical field (25). The consistency of the physical environment, the small amount of material required and the greater ease

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of passing on the cost have contributed to the shift of basic research in controlled release technology from agriculture to the pharmaceutical industry. Low cost, ample supply and consistent quality will be common characteristics required in any commercially successful pesticide controlled release material.

Soil-pesticide interactions may reveal clues regarding possible source materials for pesticide controlled release materials (36, 47, 62, 63, 64). Pesticides have been noted to interact with the inorganic and organic constituents of the soil (3, 4, 5, 35, 59). Binding properties depend on specific pesticide and soil composition. Binding is attributed to cation exchange, hydrogen bonding, van der Waals forces, hydrophobic bonding, ligand exchange, partitioning, covalent bonding or any combination of these forces. The use of soil-incorporation has been a long-established means of reducing the off-site movement of many volatile herbicides and fumigants (3, 4, 56). For a nearly equal period of time pesticide manufacturers have adjusted application rates based on soil type and percent soil organic matter. Higher levels of soil organic matter are associated with greater binding of herbicides. This binding often reduces pesticide leaching and efficacy (37). Within the last ten years the EPA has established a prohibition on the use of pesticides identified as potential ground-water contaminates. The program is implemented on a county basis and is enforced depending on local soil properties. Limitations are common in sandy soils and uncommon in soils high in organic matter and clay.

Similarities between lignin and soil humic acids, a major component of soil organic matter, raise the possibilities of using lignin to control the off-site movement of herbicides (28, 31, 57, 60). Lignin, a by-product of the wood pulping process is a low cost material in ample supply, that can be consistently delivered within specified quality guidelines (20, 57). Theoretically, lignin should possess similar sorptive properties to humic acid. Chemically altering the lignin may provide enhance sorptive properties.

Riggle[3] reports that various lignin fractions demonstrated varying controlled release properties with a number of water-soluble herbicides (54). These observations appear to support the reports that the nature of the soil organic matter significantly affects the sorptive properties of a soil (24).

Lignin possess many of the properties referred to earlier as essential in an agricultural chemical controlled

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[3] Riggle, B. D. 1985. The controlled release of water soluble herbicides. Ph.D. Dissertation. Michigan State University, East Lansing. 88 pp.

release material. The natural origin and similarities to naturally occurring sorptive soil constituents makes lignin an ideal candidate for additional research. The objective of this thesis was to explore the controlled release properties of lignin in association with herbicides known to be subject to off-site movement. Increasing the delivery of the herbicide to weeds while reducing off-site movement of the herbicides was the goal of this research.

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CHAPTER TWO

CONTROLLED RELEASE PROPERTIES OF LIGNIN FOR TRIFLURALIN

ABSTRACT

Laboratory, greenhouse, and/or field studies were used to explore the potential of lignin as a controlled release material for trifluralin (α, α, α-trifluoro-2,6-dinitropropyl-p-toluidine) and other volatile herbicides. No controlled release properties were observed during preliminary studies with herbicides with vapor pressures greater than trifluralin (i.e. EPTC (S-ethyl dipropylthiocarbamate) and triallate (S-(2,3,3-trichloroallyl) diisopropyl thiocarbam-ate)). A commercially available emulsifiable concentrate of trifluralin (Treflan)[1] was mixed with various lignin fractions slurried in water. The slurried lignins and emulsifiable concentrate were tank-mixed with water just prior to application. Dry lignin fractions and technical grade trifluralin were mixed while grinding. Alterations in the formulation procedures and lignin to trifluralin ratios were tested. Bio-assays were used in the field and greenhouse tests to measure the phytotoxic effects of the herbicides. Barnyardgrass (*Echinochloa crus-galli* (L.) Beauv.) shoots or the roots of

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[1] Treflan is the trade name for the commercial emulsifiable concentrate marketed by Elanco.

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corn (*Zea mays* L.) seedlings were used in the greenhouse studies. The weights of oat (*Avena sativa* L.) inter-cropped with soybeans (*Glycine max*) seedlings were used as the assay species in the field trial. Trifluralin displaced by a constant stream of N_2 was used to measure the control release properties in the laboratory studies. Under greenhouse conditions surface applications of various lignin-trifluralin fractions when surface applied provided extended weed control when compared to a similarly applied emulsifiable concentrate of trifluralin. In all experiments the duration of weed control provided by the non-soil-incorporated lignin-trifluralin formulations was shorter than the soil incorporated treatments. The extended weed control observed in greenhouse studies was not duplicated in the field or laboratory test. Controlled release properties of lignin with regard to trifluralin appear to be limited to physical encasement and not the result of chemical interaction between lignin and trifluralin.

INTRODUCTION

Numerous herbicides control emerging weed seedlings. Often these herbicides are applied prior to planting a crop (41, 42). Many pre-plant applied herbicides require soil incorporation within a prescribed period of time after application (3, 5, 27, 37, 50). Soil-incorporation for many herbicides is essential for weed control. Incorporation disperses the herbicides throughout the upper layer of soil. This provides better coverage and contact with emerging seedlings (2, 18, 28, 42). Soil-incorporation also reduces exposure to direct sunlight. This reduced exposure lowers the level of photodegradation for photosensitive herbicides (64). Off-site movement of volatile herbicides is reduced with soil-incorporation (10, 21, 22, 25, 30, 38, 45, 59, 64).

Reducing off-site movement of pesticides has recently been given a higher priority by the EPA (16, 38, 39, 61). Most point pollution sources have been identified and regulations implemented and refined. This has freed agency staff to focus on the more diffuse and regulatory challenging issue of non-point pollution sources. The EPA has identified agriculture as the nation's largest non-point polluting industry (1).

A primary form of agriculturally derived non-point pollution occurs with soil erosion. Minimizing or eliminating soil preparation for seed beds has developed as one possible solution for soil erosion. Reduced soil erosion holds promise as a means of limiting surface water contamination from pesticides and fertilizers.

Defining and solving the issue of ground water contamination is less clear. Soil properties and fauna are dominate factors impacting the movement of herbicides in soils. Increased activity of soil organisms in no-tillage operations appears to enhance the movement of some herbicides through the upper soil layers. Once a compound reaches the vadose zone continued movement becomes more dependent on the movement of soil water and specific properties of the herbicide and soil (12, 29, 30, 31, 32, 62). Questions remain regarding the positive or negative impact of no-tillage or minimum-tillage operations on ground-water contamination. Changes in tillage practices are unlikely to alter the compound specificity of the ground-water contamination problem (39).

Negative factors associated with no-tillage operations include the cost of new equipment, soil compaction, elimination of mechanical cultivation and lose of herbicides requiring soil-incorporation (4). Mechanical cultivation offers low cost, weed control practice that appears to be less environmentally insulting then many alternatives (1). Many soil-incorporated herbicides have historically provided a reliable low cost weed control.

With the increase of no-tillage farming and the loss of soil-incorporated herbicides growers have limited alternative weed control measures. Pre-emergence herbicides provide one alternative. Similar to soil-incorporated herbicides pre-emergence materials are used in a preventative manner. Use is based on predicted weed pressures verse actual evaluations. Unlike soil-incorporated herbicides pre-emergence materials require rainfall or irrigation (3). Efficacy is reduced or lost without adequate surface applications of water. A second alternative to soil-incorporated herbicides are the post-emergence herbicides. Their use is limited to responses to identified weed infestations. Post-emergence herbicides provide little or no residual weed control, allow weed crop competition to exist during the early growth of the crop, and at this time are a relatively expensive alternative to cultivation and most pre-plant soil-incorporated herbicides. In irrigated crops the delivery of some soil-incorporated herbicides provides a third alternative (37).

Future advances in application equipment, adjuvants or formulations may offer assistance in maintaining effective herbicides while adopting no-till farming practices (11, 16, 26, 35, 63). Considerable effort has been expended on the development of controlled release formulation of trifluralin using starch xanthides and related chemistries (9, 10, 24, 46, 51, 57). Much of the starch xanthate formulation work has been based on developing a granular formulation of trifluralin. Grower acceptance of a non-aqueous application technology is questionable. The ease, convenience and familiarity of the pesticide formulations applied in a water carrier will make convincing growers to change formulations difficult. In addition the limited soil movement of trifluralin leaves some question regarding the efficacy of granular formulations (9, 27, 28, 35, 46, 58).

Various synthetic and naturally occurring materials have been used to control or retard the release of pesticides or pheromones for decades (6, 7, 11, 13, 19, 36, 52, 54, 55).

Early aquatic controlled release materials included paints designed to retard the release molluscicides (6, 7, 19). More recently aquatic pest control materials have been release from various polymers utilizing a serious of shapes, sizes, and densities. Design changes can optimize efficacy by adjusting the placement and release rate for the targeted pest (7, 52, 53).

The success of controlled release aquatic pesticides is do in part to the relatively stable environment offered by the water. In contrast terrestrial pest controlled release materials operate in a more dynamic environment. Temperature, humidity, wind and other climatic conditions change drastically and frequently. Soil types and plant-back restrictions are additional considerations. These changes impact most controlled release materials

The success achieved in developing controlled release formulations for pheromones or growth regulators was in part a result of the low volume of material utilized (13, 60). Until recently, most herbicides have been applied at 0.25 kg/ha or greater. The pheromone controlled release materials can be composed out of more exacting and expensive materials.

The development of the No-Pest strip[2] by Shell Co. a polyvinyl chloride with appropriate plasticizer, stabilizers, and 20% dichlorvos (dimethyl-2,2-dichloro-vinyl phosphate) was the first long lasting controlled release material of commercial success (6, 7, 19). A series of similar protects designed to control ticks and fleas on dogs and cats were developed soon after the introduction of the No-Pest strip (7, 47).

Recently commercial formulations of microencapsulated herbicides have been introduced. Test on the microencapsulated formulation of metolachlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide) have revealed that the product provides questionable controlled release advantages (4, 63). The release cycle

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[2] The trade name for the dichlorvos formulation used to control houseflies developed by Shell Co.

appears to be strongly related to wetting-drying cycles. A larger release rate is observed on drying rather then wetting. This sequence fails to take advantage of the potential soil-incorporation and weed seedling germination occurring during or after a rainfall event.

The focus on developing synthetic polymeric controlled release materials may be ignoring a low cost substitute that has been used indirectly for years. The effect of soil organic matter on the retention and efficacy of various herbicides has been well established for decades (49, 56). Numerous herbicide labels describe limitations regarding use or adjustments in rates that are made as a result of soil organic matter levels.

The soil organic matter is composed primarily of two materials humic and fulvic acids (22, 50). Each has numerous similarities to the wood pulping by-product lignin (23, 44). Garbarini reports that the oxygen and carbon content of soil organic matter are more relevant than simple soil organic matter levels when attempting to predict the sorption properties of soils for various herbicides (19). This conclusion appears to collaborate the findings of Riggle and Penner(40), and Dellcolli (14). Each has reported that specific lignin fractions have a greater controlled release properties than others.

The studies were designed to explore the potential of lignin as a control release material for volatile herbicides.

MATERIALS AND METHODS

General greenhouse materials and methods. An air dried Spinks loamy sand soil was used as the growing media for the greenhouse studies. The Spinks loamy sand's organic matter was 0.8% and the pH 6.5. Soil was screened prior to each study. A soil sieve with 2 mm square openings was used to standardize soil structure from study to study. After herbicide application the pots were sub-irrigated until the soil surface moistened. The soil surface was maintained in a moisten state throughout the studies.

Herbicide applications consisted of three types: none treated controls, soil incorporated treatments, and none soil incorporated surface applications. One-liter plastic pots were used as growing containers. All herbicide applications were applied to the soil surface and not incorporated unless otherwise stated. After allowing for a prescribed period of time the indicator plants were sown on top of the treated soil and covered with 3 cm of non-treated soil.

Five hundred-milliliter pots containing 5 cm of soil were used when treating the soil that was to be incorporated. Each 500 ml pot was inverted ten times after the application to assure uniform incorporation of the herbicides. The treated

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soil was placed above non-treated soil in the 1 liter plastic pots.

Herbicides and herbicide-slurried lignin tank mixes were applied with an aqueous spray. The carrier and formulated products were applied at 375 L ha^{-1}. The spray was maintained at 10.25 kg cm^{-1}. Pots were placed in single or double rows under an SS8002E nozzle. A 50 mesh screen inserted prior to the nozzle prevented blockage of the orifice and a distortion of the spray pattern. The boom was attached to a motorized belt system and passed over the pots.

For the barnyardgrass bio-assays twenty seeds were sown per pot. Shoot lengths were measured when the shoot length of the controls were 20 to 25 cm long. The average shoot length of the barnyardgrass seedling per pot were used for the analysis of variance (ANOVA).

An ANOVA was run on the averages and differences between means was determined using a Duncan's Multiple Range test at the 5% level of significance.

EPTC (Table 1). EPTC (S-ethyl dipropylthiocarbamate) and individual lignin fractions slurried in water were tank-mixed at a 1:3 ratio of, 1 part dry weight lignin and 3 parts active herbicidal ingredient. The active material was applied at a rate of 1.7 kg ha^{-1}. Twenty hours after EPTC application barnyardgrass seeds were sown.

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Trifluralin study using low levels of slurried lignins (Table 2). Trifluralin and various slurried lignin fractions were tank mixed at a 1:3 ratio, 1 parts dry weight lignin and 3 parts active herbicidal ingredient. The active material was applied at 0.84 kg ha^{-1}. Zero, 17 and 36 days after herbicide application barnyardgrass seeds were sown.

Direct verses greenhouse filtered sunlight. (Table 3). An emulsifiable concentrate of trifluralin and various slurried lignin fractions were tank mixed with equal parts of lignin and active herbicide. The active material was applied at 0.84 Kg ha^{-1}. The following lignin fractions blocked the 50 mesh screen: PC951, PC951C, PC955A, PC955B, PC955C and PC950. All six of these trifluralin lignin fraction solutions are passed through four layers of cotton fiber. A marked loss of lignin was noted in fraction PC950.

The tank mix combinations were replicated eight times. Four replications were placed under direct sunlight for 12 hour. After 12 hours of direct sunlight the pots were moved into the greenhouse. Four replications were retained in the greenhouse throughout the study. Weather conditions on the day of direct exposure were: RH 34%, wind 9 MPH, temperature high and low 22 C and 1 C respectively.

Bean and beet farm field study (Table 4). Field studies established near Saginaw, Michigan measured the efficacy of

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various lignin slurry solutions tank mixed with either triallate (S-(2,3,3-trichloroallyl)diisopropylthiocarbamate) or the trifluralin. Applications were made using a four nozzle boom attached to a backpack sprayer. Triallate was applied at 1.12 kg ha^{-1} and trifluralin at 0.86 kg ha^{-1}. Tank mixes were made at a 3:1 ratio of lignin to active ingredient. Treatments were replicated four times on 1.8 by 6 m-plots. Treatments consisted of non-treated control, trifluralin, triallate and one of the preceding herbicides mixed with slurries of PC950W, PC940 or REAX. The commercial formulation treatments were replicated eight times with four replications having the treatments incorporated and four unincorporated.

After application the herbicides were incorporated with a springtime harrow. Oats and soybeans were seeded into all plots. Thirty days after treatment and planting quadrants were randomly placed within each plot. The oat foliage within the quadrant was harvested and weighed. The weights from the treated plots were divided by the average weight from the non-treated control to give a percent of control value.

Barnyardgrass coleoptile node bio-assays (Tables 5 and 6). The studies were designed to allow multiple planting dates each spaced at varying intervals from a single application. The bottoms of 500 ml plastic pots were removed and replaced with a double layer of cheese cloth. The smaller pots were filled with air dried and screened Spinks sandy loam soil. Applications were made to the smaller pots which were then placed on top of 1-L pots filled with the same soil.

By assuring good contact between the cheese cloth and the soil of both pots the surface of the smaller pot was moistened by sub-irrigation. Seeds were sown by lifting the 500 ml pots and placing 20 seeds on the surface of the lower pot. The barnyardgrass seedlings were then allowed to grow through the treated soil.

The study was carried out in the greenhouse under natural lighting supplemented from high pressure sodium lights. Supplemental lighting provided 500 uE m^{-2} s^{-1} of light and combined with natural lighting would reach 1200 uE m^{-2} s^{-1}. Supplemental lighting was run for 12 hrs from 6 AM until 6 PM.

The lignin-trifluralin formulations were made by combining technical grade trifluralin with dry lignin fractions. The dried lignins were ground with the herbicide, heated to temperatures ranging from 70 to 80 degrees Celsius for 30 to 50 minutes and ground again. All lignin-trifluralin treatments used 0.84 kg ha^{-1} of the herbicide and a 2.52 kg ha^{-1} rate of lignin.

All lignin and lignin-herbicide applications were made by spreading 13 mg of the formulation across the soil surface.

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The commercial emulsifiable concentrate of trifluralin was applied with a aqueous carrier. Application parameters were as stated in the general methods.

Barnyardgrass seedlings were sown on four different dates. Treatments were replicated four times in a completely randomized design. Evaluations were taken approximately 3 weeks after the seeding and entailed measuring the length of the shoots.

The impact of cross-linking, and oxidizing on control release properties of the lignins was explored by testing the fractions 5528-60 C, D, 5528-61 A, B and C (Table 4). The fractions were altered prior to the addition of trifluralin.

The lignin fractions utilized in study results presented in table 5 include lignins derived from peat, hardwood, pine or altered by methylation or cross-linking.

Corn bio-assays (Tables 7 through 13). All corn bioassay studies used Pioneer 3320 as the assay species. Four seeds were planted per pot directly on the treated soil surface. The seed was planted with the radical facing the center of the pot and the embryo facing up. For all applications involving lignin formulations and commercial formulations applied to the soil surface the seeds were placed directly on top of the treated soil, then covered with non-treated soil. Corn seeds were planted in a 3 to 4 cm bed of treated soil placed above none treated soil for the incorporated studies. Applications were made to dry soils but soils were sub-irrigated after application moistening the surface within 1 to 2 hours of application. The herbicide applications were made on dry soil in study presented in Table 13. In a deviation from the previous studies the soils in study 13 were left dry until seeding.

Lignin, sand or rosins were combined with the technical grade herbicides in a 3:1 ratio (matrix to herbicide) unless specified differently in the table. Lignin-trifluralin formulations used in the study presented in Table 13 examined the shelf life of the lignin-trifluralin formulation. The older formulation was formed on 10/8/85, the treatment titled new was formulated on 10/31/85.

The dried lignin or sand was ground with the herbicide, heated to temperatures ranging from 70 to 80 degrees C for 30 to 50 min and ground again. The results provided in Table 11 describe the effects of combining technical grade trifluralin with lignins without heating the mixture. Treatments designated by a lignin fraction description but followed by data collected on a single date were tests designed to identify the phytotoxicity of the lignin fraction.

All lignin studies used a 0.84 kg ha^{-1} rate of trifluralin or ethalfluralin and a 2.52 kg ha^{-1} rate of lignin. All lignin and lignin-herbicide applications were made by evenly spreading 13 mg of the formulation across the surface of the pot. Concentrations varied depending on the ratio of inert material to herbicide, for mixtures requiring less than 13 mg, talc was added to facilitate handling. The commercial formulation of trifluralin was applied as stated in the general methods.

Micro column test. A glass wool plug was placed at the base of a Pasteur pipet to hold 50 mg of 3:1 mixture of lignin-trifluralin or sand-trifluralin added to the pipet. A steady stream of N_2 was passed through a water bath maintained at room temperature and then through the column. The Pasteur pipets were kept in a growth chamber maintained at 38 C. The flow rate of the N_2 was maintained at 100 ml min^{-1} as possible. The concentration of trifluralin released was linear in this system over a range of 60 to 240 ml min^{-1}. The flow rates were measured at the beginning and end of each time period. The average time was used to determine the amount of trifluralin released per 100 ml N_2 min^{-1}.

The tapered end of the Pasteur pipet was passed though a polyurethane plug. The plug was placed in the neck of a scintillation vial. The N_2 vented into the vial was collected in the polyurethane. The polyurethane plug was removed from the vial and placed in a glass tube. Three 5 ml aliquots of acetone were passed through the tube and each collected separa

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separately. Preliminary studies demonstrated that the trifluralin was completely removed after the second 5-ml aliquot.

The acetone solution was injected into an HPLC system equipped with a 25 cm ODC column The column was run under isocratic conditions with an acetonitrile:water (80:20) mobile phase set at 1 ml min^{-1}. Data was reported as ug trifluralin (100 ml N_2 $min^{-1})^{-1}$.

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RESULTS AND DISCUSSION

The surface application of the lignin fraction PC955A tank mixed with EPTC reduced barnyardgrass shoot length to a greater degree than the similarly applied non-tank mixed EPTC (Table 1). All non-incorporated applications of EPTC either tank mixed with lignins or not, gave poor barnyardgrass control. As a result of the large gap in phytotoxicity between the best lignin-EPTC surface and the incorporated EPTC application future studies focused on a pesticides with lower vapor pressures.

Differences in phytotoxicity appeared to be attributable to the lignin fractions in the initial lignin trifluralin study (Table 2). The first planting was done the same day as the application and in 100 percent control for all treatments (data not shown). Two surface applied lignin-trifluralin treatments (PC950 and PC58C) yielded results comparable to the incorporated treatments when seeds were sown 17 days after treatment (DAT). At the conclusion of the third planting incorporated treatments were providing a superior control when compared to all non-incorporated treatments. Differences between surface treatments not noted at the 17 DAT planting developed at the conclusion of the third planting. Lignin trifluralin formulations; PC952, and 58C reduced barnyardgrass shoot growth more than the similarly applied trifluralin treatment.

The third study was designed to continue exploring the controlled release properties of lignin and to determine if the lignins might enhance the photodegradation of trifluralin (Table 3). Ten of the 1. Eleven of the 20 least effective treatment were left in the greenhouse throughout the study and ten of the 19 most effective treatment were left in the greenhouse throughout the study. The exposure to the sun did not impact the efficacy of trifluralin. Though, differences were observed between lignin fractions the spread from the greenhouse control and the surface treatment yielding the greatest control (PC952) was 3.2 cm. In contrast, the spread form the best surface treatment (PC952) to the incorporated trifluralin was 4.5 cm. The probability of any given lignin yielding dissimilar results appear about even. Comparing direct and indirect light exposed treatments to one another 10 of 19 were significantly different. Under these conditions the observed differences between lignins though significant fail to demonstrate consistency or a comparable degree of efficacy to the incorporated treatments.

The field study confirmed that the slurried lignins failed to yield weed control comparable to the incorporated treatments (Table 4). The response of triallate to tank mixes was similar to that observed for EPTC and trifluralin. In contrast to previous studies no absolutely no differences could be distinguished between the lignins used (PC940 and PC950W).

By allowing the barnyardgrass to grow through, rather than on top of, treated soil the next set of studies more closely imitated actual field conditions (Table 5 and 6). It was assumed that talc would demonstrate little or no adsorptive properties. Thus the trifluralin formulated with talc provided a comparison between the application techniques. The commercial formulation of trifluralin was applied with water as the carrier. The lignin and talc formulations were applied as a dry powder by hand. The phytotoxicity resulting from the talc formulation was statistically identical to that caused by surface applied commercial trifluralin formulation. The lignin appeared to extend the effectiveness of the trifluralin through 8 days. Certain lignins were more effective than others but at no time did the lignin formulations approach the effectiveness of the incorporated treatments.

In the next 8 studies corn was used as the bioassay species. Lignin's lack of phytotoxicity is verified in the first study (Table 7). No differences between the lignin formulations and the commercial formulation were observed when applied in an identical manner.

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The controlled release properties of PC950W on ethalfluralin were explored in the next study (Table 8). At 14 days after application all four treatments were statistically distinct with PC950W providing extended control over the comparably applied commercial ethalfluralin formulation.

The controlled release properties observed in PC950W resulted from the formulation process (Table 9). The slurried PC950W when tank mixed with ethalfluralin produce a negative impact on the efficacy of the surface application. The newly formulated lignin ethalfluralin slightly improved the efficacy of the surface application.

The extended efficacy noted in the last experiment was not duplicated when trifluralin was substituted for ethalfluralin (Table 10). Altering the ratio of PC950W to trifluralin failed to consistently extended weed control (Table 11). Liquefying the trifluralin in the presence of PC950W by applying heat failed to improve the controlled release properties of the formulation. The relatively low melting point of trifluralin and the ability of the liquified technical grade material to dissolve most lignin fractions aided the formulation processes. The lignin trifluralin formulation treatments in this study once again demonstrated a slight extension of the efficacy of trifluralin. Once again no lignin trifluralin formulation approached the efficacy provided by the incorporated treatments. Differences between

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the surface applications were not observable when the loamy sand was replaced with a clay soil (Table 12). Differences were not observed when a new preparation of PC950W was compared to a month old formulation (Table 13).

The lignins appeared to provide an extension of the efficacy of trifluralin in the greenhouse studies. The extension could not be linked to a specific lignin, the intensity varied from weak to negligible, never approaching the results yielded by incorporated treatments. The controlled release properties noted were not apparent in reproducible form in the tank mixes involving slurried lignin and herbicide. Greater consistency was observed when technical grade herbicide was formulated with dry lignins. Attempts to extend the efficacy by increasing the concentration of lignin or the formulation process under these conditions failed.

Results of the corn bioassay indicate that mixing rosin with technical grade trifluralin results in complete or nearly complete retention of the herbicide (Table 14). All lignins examined to date originated from the Kraft pulping process. The lignin identified as BEC was derived from a pulping process using organic solvents. BEC when formulated with trifluralin yielded results similar to the Kraft lignins.

The laboratory study partially confirmed the greenhouse results. A sand trifluralin mixture yield a similar level of the he

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the herbicide as a three lignin trifluralin formulations. The laboratory test lacked the sensitivity of the greenhouse studies but confirmed that the degree of controlled release was at best slight.

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Table 1. Controlled release properties of lignins tank mixed with EPTC.

Treatment (lignin)	Barnyardgrass Shoot length (cm)
Nontreated control	10.1 A[1]
PC951A[2]	9.9 A
37D	9.7 AB
PC953	9.6 AB
PC949	9.2 ABC
EPTC[3] (surface)[4]	8.8 ABC
PC951	8.7 ABC
PC955B	8.7 ABC
PC954	8.4 BC
PC951C	8.3 BCD
PC950	8.3 BCD
PC952	8.3 BCD
PC955C	7.9 CD
PC955A	6.9 D
EPTC (incorporated)	0 E

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1. Means followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.
2. All lignin fractions were tank mixed with the EPTC formulation at a 1:3 ratio lignin dry weight to active ingredient weight of the herbicide.
3. Trade name for the ICI Americas emulsifiable concentrate of EPTC was EPTAM.
4. EPTC applications were either incorporated in the soil immediately after application or surface applied without incorporation as were the lignin applications.

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Table 2. Controlled release properties of lignin tank mixed with trifluralin[1].

	17 DAT Planting		36 DAT Planting
Treatment (lignin)	--Shoot length-- ---(cm)---	Treatment (lignin)	--Shoot length-- ---(cm)---
Nontreated cont.	9.6 A	Nontreated cont.	9.5 A
22D	5.0 B	37DSL	9.1 AB
PC949	4.8 B	19	8.5 ABC
PC954	4.1 BC	PC949	8.2 BCD
PC957	3.7 CD	Treflan (surf.)	8.2 BCD
PC922	3.0 DE	PC956	7.9 CDE
PC954	2.9 DE	22D	7.8 CDE
PC956	2.8 DE	58A	7.7 CDE
58B	2.7 EF	37D	7.6 CDE
Trifluralin(surf.)[3]	2.6 EFG	PC922	7.6 CDE
PC925	2.5 EFG	PC957	7.6 DEF
37DSL	2.4 EFGH	PC953	7.1 DEF
37D	2.3 EFGH	58B	6.9 EFG
58A	2.2 EFGHI	PC954	6.8 FGH

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1. Trade name for the DowElanco emulsifiable concentrate of trifluralin.
2. Average values followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level. The data is analyzed using a two way ANOVA comparisions between dates are not intended.
3. All lignin fractions were tank mixed with the Treflan formulation at a 1:3 ratio lignin dry weight to active ingredient weight of the pesticide.
4. EPTC applications were either incorporated in the soil immediately after application or surface applied without incorporation as were the lignin applications.

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Table 2 continued. Controlled release properties of lignin tank mixed with Trifluralin[1].

Treatment (lignin)	17 DAT Planting --Shoot length-- ---(cm)---	Treatment (lignin)	36 DAT Planting --Shoot length-- ---(cm)---
37DSL	2.4 EFGH	PC953	7.1 DEF
37D	2.3 EFGH	58B	6.9 EFG
58A	2.2 EFGHI	PC954	6.8 FGH
37DSL (incorp.)	1.7 FGHI	PC952	5.9 GH
PC825 (incorp.)	1.6 GHI	Treflan (incorp.)	1.6 I
Treflan (incorp.)	1.4 HIJ	37DSL (incorp.)	1.5 I
PC58C	1.4 HIJ	PC954 (incorp.)	1.3 I
PC950	1.3 IJ		
PC954 (incorp.)	0.6 J		

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1. Trade name for the DowElanco emulsifiable concentrate of trifluralin.
2. Average values followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level. The data is analyzed using a two way ANOVA comparisions between dates are not intended.
3. All lignin fractions were tank mixed with the Treflan formulation at a 1:3 ratio lignin dry weight to active ingredient weight of the pesticide.
4. EPTC applications were either incorporated in the soil immediately after application or surface applied without incorporation as were the lignin applications.

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Table 3. Controlled release properties of lignin as impacted by direct sunlight.

Treatment (lignin)	--Shoot length-- ---(cm)---	Treatment (lignin)	--Shoot length-- ---(cm)---
Control[2] G[3]	9.4 A	PC922HW O	7.3 G-O
58C O[4]	9.3 A	PC950N O	7.3 G-O
PC955C G	8.8 AB	PC955B G	7.3 G-O
PC922HW G	8.7 AB	PC955B O	7.3 G-O
PC949 O	8.5 BC	PC951A G	7.3 G-O
PC955C O	8.2 B-E	PC951B G	7.3 G-O
PC940C G	8.1 B-F	PC952 O	7.2 H-O
5528 60A G	8.0 C-G	PC922H O	7.1 I-O
PC950 G	7.9 C-H	PC940C O	7.1 J-O
58C G	7.9 C-H	PC950 O	7.1 J-O
PC949W O	7.9 C-I	5528 60A O	7.1 J-O
PC922H G	7.8 C-J	PC949 G	7.0 K-O
Treflan (surf.) O	7.8 D-J	PC950W G	7.0 L-O
PC951B O	7.7 E-K	PC922L O	6.9 L-O

---

1. Trade name for the DowElanco emulsifiable concentrate of trifluralin.
2. Average values followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.
3. All lignin fractions were tank mixed with the Treflan formulation at a 1:1 ratio lignin dry weight to active ingredient weight of the pesticide.
4. EPTC applications were either incorporated in the soil immediately after application or surface applied without incorporation as were the lignin applications.

Table
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Table 3 continued. Controlled release properties of lignin as impacted by direct sunlight.

Treatment (lignin)	--Shoot length-- ---(cm)---	Treatment (lignin)	--Shoot length-- ---(cm)---
Control O	7.6 E-L	PC955A G	6.8 L-O
PC951C O	7.5 E-L	PC949N G	6.8 M-P
PC922LW O	7.5 F-M	PC922L G	6.7 NOP
Treflan (surf.) G	7.4 G-N	PC922LW G	6.6 OP
PC949W G	7.4 G-N	PC952 G	6.2 Q
PC951C G	7.4 G-O	Treflan (inc.)	1.7 R
		Treflan (inc.)	1.5 R

1. Trade name for the DowElanco emulsifiable concentrate of trifluralin.
2. Average values followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.
3. All lignin fractions were tank mixed with the Treflan formulation at a 1:1 ratio lignin dry weight to active ingredient weight of the pesticide.
4. EPTC applications were either incorporated in the soil immediately after application or surface applied without incorporation as were the lignin applications.

Table
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Trefl
REAX:
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PC940
Trefl
Far G

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Table 4. Oat-field study testing the controlled release properties of tank mixes lignin with triallate or trifluralin.

Treatment	Shoot weight (% of control)
PC040:Treflan	92[3] A
PC950W:Treflan	92 A
Treflan[4] (surface)	91 A
REAX:Treflan	86 A
Far Go (surface)	82 A
PC950WP:Far Go	71 A
PC940:Far Go	71 A
Treflan (incorporated)	34 B
Far Go (incorporated)	9 B

[1] Triallate was applied or added in tank mixes with the lignins as the commercial product Far Go an emulsifiable concentrate marketed by Monsanto.

[2] Trifluralin was applied or added in tank mixes with the lignins as the commercial product Treflan an emulsifiable concentrate marketed by DowElanco

[3] Average values followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

[4] Lignin herbicide tank mixes were not soil incorporated.

Table
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Table 5. Release rate of trifluralin form crosslinked (5528 - 60 B-E) and oxidized (5528-61 A-B) Kraft lignins.

	----- Shoot length (cm/plant) -----				
Treatment	2 DAT	5 DAT	8 DAT	14 DAT	24 DAT
Nontreated control	10.0A[1]	14.8A	14.9A	14.0A	26.9A
Trifluralin (surf)	1.2AB	2.2BC	6.8AB	11.8AB	17.8A
Talc:trifluralin	4.0AB	2.6B	5.2AB	10.7AB	11.7ABC
5528-60 C	0.2CD	0.7DE	0.8D	3.2AB	5.2C
5528-60 D	0.7BC	1.1BCD	1.6CD	4.7AB	11.7ABC
5528-60 E	2.0AB	1.1BCD	1.3CD	0.1C	17.0AB
5528-61 A	2.6AB	0.4DE	0.6D	2.1AB	9.8ABC
5528-61 B	3.6AB	0.7CDE	3.0BC	8.1AB	5.9BC
5528-61 C	0.1D	0.3E	0.5D	1.2B	13.8A
Trifluralin (inc.)	0.0E	0.0F	0.0E	0.0D	0.0D

1. Values with a single column (DAT) are comparable. Means followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

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Table 6. The release rate of trifluralin form lignin series 531-75 (A-E) and Indulin W.

	----- Shoot length (cm/plant) -----				
Treatment	4 DAT	8 DAT	12 DAT	16 DAT	26 DAT
Nontreated control	17.2A[1]	11.3A	11.2A	18.7A	31.6A
PC951A	1.3E	1.3C	1.2E	1.8D	24.5AB
Trifluralin(surface)	1.4E	1.6B	8.6AB	12.1AB	29.5A
Talc:trifluralin	7.7B	1.6B	3.4BCD	7.4ABC	23.4AB
5528-60 A	1.4E	1.4B	3.1CD	7.5ABC	26.9AB
Indulin W	5.8BC	1.6B	3.8BCD	7.5ABC	18.6AB
5531-75 A	1.6DE	1.3B	4.9ABC	2.9CD	18.2AB
5531-75 B	6.3BC	1.8B	3.0CD	7.0ABC	18.2AB
5531-75 C	3.5CD	1.7B	2.8CD	4.1CD	24.0AB
5531-75 D	5.9BC	1.2B	4.9ABC	5.7BC	22.4AB
5531-75 E	2.4DE	1.1B	1.5DE	3.2CD	-----
Trifluralin(incorp.)	0.0F	0.0D	0.0F	0.0E	0.0B

---

1. Values with a single column (DAT) are comparable. Numbers followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

Table 7. F
PC922:trif

Treatment
Nontreated
PC 940[2]
PC 922
PC922:trifl
PC940:trifl
Treflan[3](su
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Table 7. Phytotoxic properties of PC940, PC922, PC940:trifluralin, PC922:trifluralin as evaluated by corn root assay.

	----- Root length in cm -----					
Treatment	1 DAT	2 DAT	4 DAT	5 DAT	7 DAT	11 DAT
Nontreated control	16.7A[1]	27.13A	24.6A	19.4A	21.1A	24.9A
PC 940[2]	24.5A					
PC 922	23.2A					
PC922:trifluralin	3.9B	3.4BC	3.5B	9.1B	9.2B	14.6C
PC940:trifluralin	2.8B	6.0B	3.7B	6.0BC	8.5B	17.8BC
Treflan[3](surface)	2.3B	3.5BC	3.4B	5.3BC	8.2B	19.1B
Treflan (incorporated)	2.3B	2.3C	2.4C	3.0C	3.1C	3.5D

1. All analysis done on the log transformed root length data. Values with a single column (DAT) are comparable. Means followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

2. PC950W and PC940 applications made without trifluralin to evaluate the lignin phytotoxicity

3. Trade name for the DowElanco emulsifiable concentrate of trifluralin

Table 8.
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Treatment

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Table 8. The rate of release of ethalfluralin from the Kraft lignin fraction PC950W.

	Root length					
		Time				
	0 DAT	3 DAT	5 DAT	8 DAT	14 DAT	21 DAT
Treatment		---(cm)---				
Control (nontreated)	15.4[1]A	12.5 A	13.3 A	20.4 A	15.0 A	17.7 A
PC950W: ethalfluralin	2.0 B	2.6 C	4.2 B	5.1 B	4.9 C	5.9 C
Sonalan (surface)	1.7 B	2.4 C	6.0 B	5.4 B	6.9 B	11.8 B
Sonalan (incorporated)	1.2 B	3.9 B	3.2 B	3.3 C	3.1 D	3.7 D

1. Values with a single column days after treatment (DAT) are comparable. Numbers followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

2. Trade name for the DowElanco emulsifiable concentrate of ethalfluralin.

Table 9. C
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Treatment
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PC950W S[1]:e
PC950W D[2]:e
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Table 9. Controlled release properties of dry and slurried lignins for ethalfluralin.

	Root length	
	Time	
Treatment (formulation)	1 DAT	2 DAT
Non-treated control	21.6[3]A	15.0 A
PC950W S[1]:ethalfluralin	10.8 B	14.5 A
PC950W D[2]:ethalfluralin	3.7 C	3.1 C
Ethalfluralin[4](surface)	2.6 CD	4.5 B
Ethalfluralin(incorporated)	2.0 D	1.9 D

1. Lignin is mixed as a slurry. The slurry was mixed at a ratio that provides a 3:1 ratio of lignin (dry weight) to ethalfluralin.

2. Lignin is mixed as a dry material to ethalfluralin by grinding, heating and grinding.

3. Values with a single column (DAT) are comparable. Numbers followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

4. Trade name for the DowElanco emulsifiable concentrate of ethalfluralin was Sonalan.

Table 10.
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Treatments
Non-treate control
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Table 10. Controlled release properties of dry and slurried lignins for ethalfluralin.

Treatments	1 DAT	2 DAT	3 DAT	5 DAT	14 DAT	21 DAT
	Root length in cm					
Non-treated control	14.9A[1]	21.7A	18.0A	15.0A	19.8A	20.5A
PC950W	12.5A[2]	----	----	----	----	----
PC950W:trifluralin	3.1B	3.6B	3.2C	3.4B	9.5B	12.6B
Treflan[3](surface)	2.6B	3.6B	4.5B	3.2B	8.8B	10.8B
Treflan (incorporated)	2.1C	3.1B	2.1D	2.1B	3.4C	3.9C

1. All analysis done on the log transformed root length date. Values with a single column (DAT) are comparable. Numbers followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

2. PC950W application made without trifluralin to evaluate the lignin phytotoxicity

3. Trade name for the DowElanco emulsifiable concentrate of trifluralin.

Table 11.
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Treatment
Nontreated
PC 950W Tr heated 6
PC 950W Tr not heat
PC 950W Tr not heat
PC950W Tri heated 3
Treflan[2](s
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[2] Trad
triflural

Table 11. Controlled release properties of lignin for trifluralin as effected by ratio and formulation procedures.

Treatment (formulation)	5 DAT	6 DAT	11 DAT	12 DAT
	----------- Root length on cm -------------			
Nontreated control	20.0[1]A	21.6 A	16.7 A	17.6 A
PC 950W Trifluralin heated 6:1	9.0 BC	4.0 BC	10.4 BC	15.0 AB
PC 950W Trifluralin not heated 3:1	7.7 BCD	5.5 B	12.1 B	15.7 AB
PC 950W Trifluralin not heated 6:1	6.1 CDE	3.4 C	8.7 BC	11.1 B
PC950W Trifluralin heated 3:1	4.8 DE	3.5 C	7.8 C	12.1 B
Treflan[2](surface)	11.4 B	6.0 B	17.3 A	14.5 AB
Treflan (incorporated)	3.9 E	3.5 C	3.6 D	3.5 C

1. All analysis done on the log transformed root length data. Values with a single column (DAT) are comparable. Numbers followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

2. Trade name for the DowElanco emulsifiable concentrate of trifluralin.

Table 12. Controlled release properties of lignin for trifluralin on a moist clay surface.

Treatments (formulation)	3 DAT	6 DAT	10 DAT	15 DAT
	----- Root length in cm -----			
Nontreated control	21.1 A[1]	21.8 A	25.5 A	24.8 A
PC950W:trifluralin	7.3 C	6.9 B	13.4 B	13.8 B
Treflan[2](surface)	12.0 B	5.3 B	16.4 B	12.6 B
Treflan (incorporated)	4.3 C	4.1 B	4.2 C	4.6 C

1. All analysis done on the log transformed root length data. Values with a single column (DAT) are comparable. Numbers followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

2. Trade name for the DowElanco emulsifiable concentrate of trifluralin.

Table 13. Shelf life of lignin trifluralin formulations.

Treatment	----- Root length ----- 3DAT	 7DAT	 14DAT	 19DAT
	----- (cm/plant) -----			
Non-treated control	24.1A[1]	27.9A	17.8A	25.6A
PC950W:trifluralin old[2]	2.6C	2.2C	2.2B	2.2B
PC950W:trifluralin new[3]	2.5C	2.4C	2.7B	2.3B
Treflan surface	2.7C	2.3C	2.5B	2.4B
Treflan incorporated	3.6B	3.4B	3.2B	4.0B

1. All analysis done on the log transformed root length data, values with a single column (DAT) are comparable. Numbers followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

2. Formulation prepared on 10-8-85.

3. Formulation prepared on 10-31-86.

Table 14
organosol

Treatment
Non-treat
Rosin:tri
Rosin:tri
Rosin:tri
BEC:trifl
BEC:trifl
Talc:tri
PC951:tri
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Table 14. Release rates of trifluralin from lignins (Kraft and organosolvent derived) and other inert materials.

	----- Root length -----			
	9 DAT	13 DAT	17 DAT	22DAT
Treatment	----- (cm/plant) -----			
Non-treated control	11.2A[1]	10.2A	9.1A	9.1A
Rosin:trifluralin 2:1	11.7AB	11.7A	9.8A	10.0A
Rosin:trifluralin 1000:1	12.6A	9.5A	9.5A	9.3A
Rosin:trifluralin 10:1	10.7AB	9.5A	9.1A	8.5A
BEC:trifluralin 1:1	0.9D	2.4BC	5.5B	8.7A
BEC:trifluralin 3:1	1.1CD	1.1C	5.2B	8.5A
Talc:trifluralin 3:1	3.3BC	4.1B	5.2BC	8.5A
PC951:trifluralin 3:1	0.9D	2.9B	3.2C	7.8A
Treflan (surface)	11.0AB	9.8A	9.5A	8.9A

1. All values with a single column (DAT) are comparable. Numbers followed by the same letter are not significantly different according to Duncan's multiple range test at the 0.05 level.

Table 15.
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Treatment	
Sand[1]	3
PC950W	3
PC940	3
PC922	3

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Table 15. The release rate of trifluralin from lignin and other inert materials as measured by a laboratory assay.

	Time (min)					Total Released
	1-13	13-25	25-37	37-49	49-56	
Treatment	ug/(100/ml N_2/min)					(%)
Sand[1]	36(7)[2]	48(3)	44(4)	40(6)	37(2)	76.3
PC950W	34(1)	45(1)	46(1)	45(1)	48(2)	74.9
PC940	34(3)	41(2)	41(4)	38(1)	41(5)	68.8
PC922	34(2)	49(3)	47(2)	48(2)	55(3)	78.9

1. Sand and lignins are prepared by mixing at a 3:1 ratio inert matrix to trifluralin.

2. The average value of three replicates is followed by the standard deviation of the three values.

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CHAPTER THREE

LIGNIN AS A CONTROLLED RELEASE MATERIAL FOR QUINCLORAC

ABSTRACT

Quinclorac (3,7-dichloro-8-quinolinecarboxylic acid) provides effective pre and postemergence weed control in rice. Reports indicate that quinclorac is effective on a number of Midwestern weeds of agronomic significance. Questions exist regarding the phytotoxicity of the herbicide on crops grown in this region. Quinclorac when placed in the root zone inhibits the root growth of corn (*Zea mays* L), soybean (*Glycine max* L), barnyardgrass (*Echinochloa crus-galli* (L) Beauv.), ivyleaf morningglory (*Ipomoea wrightii* Gray) and several cereal grains. Foliar and soil applications of ^{14}C labeled quinclorac were absorbed by weeds and crops. Once adsorbed the herbicide translocated acropetally and basipetally to the actively growing regions of the plants. Despite root and foliar uptake, specific placement and retention of the herbicide results in selective phytotoxicity. Under identical conditions quinclorac leached twice as far as metolachlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide) in the Spinks loamy sand. This propensity to leach makes retention in the soil above the seeds difficult. Effective placement and retention of the herbicide was enhanced by the use of a quinclorac-lignin formulation. A dry flowable formulation was created by incorporating technical grade quinclorac into a lignin matrix. By physically binding the quinclorac in the lignin less was available to be leached during any irrigation or rainfall event. The lignin formulation also extended herbicidal activity in leaching studies. The lignin formulation shows promise in reducing the vertical off-site movement of quinclorac.

Additional index words. Quinclorac acid, BAS 514, controlled release

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INTRODUCTION

Quinclorac (3,7-dichloro-8-quinolinecarboxylic acid) controls a number of weeds commonly found in the Midwest (15, 14). The chemical is a chlorinated organic molecule with the molecular formula of $C_{10}H_5O_2NCl_2$ and a molecular weight of 242. Pure quinclorac is a colorless crystalline material with a vapor pressure less than 1.1×10^{-7} mm Hg at 25°C. Quinclorac is soluble in: acetone at 0.2 g, xylene at 1.0 g, and water at 6.2 g, all at 100 g of solvent (1). Phytotoxicity varies from plant species to species. Preliminary results indicate that the pesticide has herbicidal activity when applied pre-plant incorporated, pre-emergence or postemergence (data not presented). A few weed species appear to be more susceptible to root uptake of the pesticide. Quinclorac shows promise as a herbicide in rice (*Oryza sativa*), oats (*Avena sativa*), hard red spring wheat (*Triticum aestivum*), winter wheat and broccoli (*Brassica oleracea* var. *botrytis*) production (1, 12, 13, 15).

The commercial development of a selective herbicide is not limited to those pesticides that exploit plant differences in morphology, metabolic degradation, rates of metabolism, selective uptake or sites of action (17). A number of physiologically nonselective herbicides have been commercially marketed as selective by utilizing innovative application methods. For example the selective application of glyphosate (*N*-(phosphonomethyl) glycine) utilizing wicks, paraquat (1,1'-dimethyl-4,4'-bipyridinium ion) with shields, or 2,4-D ((2,4-dichlorophenoxy)acetic acid) by avoiding application during various formative stages of grain development (7).

Innovations designed to optimize selectivity are often discovered late in the development of an herbicide. At times they develop from the efforts of growers and extension specialist working with minor crops. Variations in the formulation of a pesticide can reduce or enhance the selectivity of a chemical (20). Modifications of pesticide formulations can also be used to reduce the acute toxicity of a pesticide formulation (6). For example, the formulation of parathion (O,O-diethyl-O-(4-nitrophenyl) phosphorothioate) in polymeric encapsulated beads reduces mixer and applicator exposure to the insecticide (2, 3). The early use of molescides in paints extended the delivering and the effectiveness of these pesticides to their intended targets (4, 7).

The unintended movement of herbicides away from their targets and into groundwater has been highlighted by recent ground water surveys. Altering formulations have addressed concerns regarding efficacy and toxicity (5, 6, 8, 16). Altering formulations may hold similar answers for a number of environmental concerns (19). Controlled release materials may provide a means of reducing or eliminating contamination of ground waters by herbicides, while retaining an economically and efficaciously desirable material.

Guidelines developed by the Environmental Protection Agency require the review of the leaching properties of a pesticide as part of the registration process. The regulatory agency also limits or eliminates the use of chemicals known to leach when used in regions with sandy soils. These policies reduce the weed control options available to growers. The development of controlled release formulations could address the concerns of the EPA while providing the growing community with options.

Cost is the most serious limitations affecting the development of controlled release pesticides in agriculture. During the nineteen fifties and sixties pest control researchers in agriculture were at the forefront of controlled release research (2, 3, 10, 11, 18). Cost limitations have shifted the development of control release technology from agriculture to the pharmaceutical industry. The development of a commercially viable control release material in agriculture must be based on a readily available inexpensive raw material. Even a readily available low cost material may fail as a result of increases in transportation cost. A marked changed in the percentage of active ingredient can negatively impact transportation cost resulting in the product being economically nonviable. The objectives of these studies were to; determine the site of uptake of quinclorac, study methods of exploiting phytotoxic differences between crops and weeds, to evaluate whether quinclorac might be used on other crops, explore the possibility of utilizing lignins to extend the time period for weed control, reduce the movement of quinclorac by using lignins as a controlled release agent.

MATERIAL AND METHODS

Rate and placement studies (Table 1 and 2) An air dried Spinks loamy sand soil was used as the growing media for all greenhouse studies. The Spinks loamy sand's organic matter was 0.8% and the Ph 6.5. Soil was screened prior to each study. A soil sieve with 2 mm square openings was used to standardize soil structure from study to study. After sieving the soil was placed in 1 L plastic pots.

The quinclorac was applied below the seeds, above the seeds, and postemergence at the two-leaf stage. All applications were made with water as the carrier at 375 L ha^{-1} with a flatfan SS8002E nozzle. Boom pressure was maintained at 10 kg cm^{-1}. Application rates of quinclorac were 1.4, 0.6, 0.1 and 0 kg. ha^{-1} of active ingredient. Soil applications were incorporated by pouring the contents of the treated pot into a non-treated pot 10 time and then pouring the inverted soil into the seeded pot.

Barnyardgrass was used as the bioassay species. Twenty seeds were evenly dispersed across the container and each treatment was replicated four times. The efficacy of quinclorac on barnyardgrass was determined by visual comparison relative to the non-treated controls. The impact of the herbicide on wheat and rye was evaluated using shoot weight, shoot length and emergence.

Barnyardgrass, wheat and rye seedlings used in the postemergence test were evaluated 8 days after application.

Watering and herbicide placement studies. Selective placement of quinclorac was accomplished by postemergence application and seed placement above or below treated soil. Subsequent movement of quinclorac to non-treated areas was restricted by using activated carbon or vermiculite. Quinclorac from the soil applications was isolated from the seeds by using activated carbon and soil. A 1 to 2-cm band of soil was placed between the 0.5-cm band of activated carbon and the treated area. A 1 to 2 cm-surface layer of vermiculite was placed on the soil to isolate the foliar applications. The vermiculite was removed 24 h after application. The movement of quinclorac into the carbon layer was minimized by supplementing surface irrigation with sub-irrigation. Post applications and above seed applications are sub-irrigated. Below seed applications were surface watered. After two weeks the soil was sub and surface irrigated.

Soil treatments were incorporated by spraying an surface area of soil 5.0 cm deep and inverting the soil 10 times. The soil was added above or below the seeds The seeds would be planted on the opposite side of a 0.25 cm-layer of activate carbon. All seeds were sown the day of soil application. Postemergence applications were applied at the two leaf stage for the grasses or at the initiation of the first trifoliate leaf for soybean and morningglory. Treatments were replicated eight times with one-half of the pots in each treatment being either sprinkler or sub-irrigated. Sub-irrigation was accomplished by filling 40 ml aluminum pie pans placed beneath pots with water. Sprinkler irrigation was conducted by passing a boom with a single teejet 8004E nozzle over the pots until the required amount of water has been added (100 ml h^{-1} pot).

Barnyardgrass, corn, morningglory, soybean, rye and wheat were used to study the effect of herbicide placement on each species. The number of seeds sown per pot for each species were 4 corn, 6 soybean, 8 morningglory and 10 wheat and rye seeds. Shoot heights were measured for all species.

Use of a lignin mixture for controlled release of quinclorac. Attempts to introduce technical grade quinclorac into the lignin matrix by co-grinding in a mortar and pestle failed. Addition of both lignin and quinclorac in aqueous solutions adding lignin first or quinclorac allowing equilibration periods in excess of 144 h or heating the aqueous solutions were also unsuccessful. Attempts to co-melt the co-ground lignin-quinclorac combinations resulted in lignin liquefying prior to the quinclorac and the subsequent separation of the materials. Solubilization of the lignin with tetrahydrofuran, toluene, n-propyl failed to create a single phase. Efforts to use carbon disulfide yielded limited success. Solubilization of most lignins in acetone was successful. Introduction of lignin, quinclorac and acetone yield a single phase solution, with viscosity properties directly responsive to the proportion of acetone present. Subsequent volatilization of the acetone resulted in a solution of increasing viscosity, the matrix initially adopted liquid, then tar, and ultimately glass-like properties. The viscosity of the final product was temperature dependent. Successful preparation of the material required for application utilizing standard agricultural application equipment (Tee Jet nozzles, screens, etc.) required grinding under freezing or near freezing conditions. To avoid clogging the screens in application equipment the matrix was maintained in a cool environment until application. Warming of the formulation resulted in a congealing of the screen lignin-quinclorac mix. Increased stability may be enhanced by the more extensive removal of the acetone. The lignin-quinclorac matrix had a density greater than one and required constant agitation to avoid settling.

Soil column leaching studies. The leaching properties of quinclorac were tested by utilizing a soil column bioassay. Polyvinyl-chloride tubes were used. Columns were cut along two radial axis 30 cm apart. Radial openings have 7 cm diameters. Tubes were tangentially approximately 2 cm deep. The tangential cut allowed accurate selective removal of soil. Multiple layers of cheese cloth were used on the lower radial opening. Cheese cloth provided support to allow drainage.

An air dry Spinks loamy soil was screened to remove all material larger than 2 mm. Organic matter content of the soil was

0.8% and the Ph 6.5. Columns were dropped on the floor from 10 to 15 cm to facilitate equivalent settling.

Treatments applied to the columns were quinclorac, quinclorac:lignin (1:1 ratio), metolachlor and a non-treated control. All treatments were replicated on four columns. Metolachlor was used as a reference. All applications were made across the open air radial surface of the columns. Water applied at 375 L ha^{-1} was used as the carrier. Applications were made by passing the columns under a fixed position flatfan SS8002E nozzle. Boom pressure was maintained at 10:25 kg cm^{-1}. A 1.12 kg ha^{-1} rate of quinclorac was applied. Metolachlor was applied at 2.24 kg ha^{-1}.

All columns were sprinkler irrigated immediately after application. One hundred and fifty ml (3.9 cm) of water was applied over a 30-minute period. Rainfall was simulated by repeatedly passing a belt driven SS4004E nozzle over the columns. Sequential passes were timed to avoid puddling.

Forty-eight hours after the application the tangential cut on each column was removed. Columns were divided into 10 3-cm sections along the tangential surface. Soil was removed from each section and maintained distinct from the other nine sections.

Barnyardgrass was used as the bioassay species. The soil from each section was used to cover 20 barnyardgrass seeds. Barnyardgrass was then grown in the greenhouse under natural lighting. Once controls reach an average height of 10-cm the plants were harvested. Average shoot length defined as the length of the tallest leaf from soil to apex was used to measure efficacy. The individual pot values were then divided by the mean on the four controls. The percent of control value was used in the statistical evaluation of herbicidal efficacy.

Distribution of ^{14}C quinclorac in plant. Radiolabeled quinclorac was ^{14}C labeled at the third carbon with a specific activity of 40.4 uCi mg^{-1}. Plants were exposed to ^{14}C quinclorac in one of three locations. Plants were exposed by placing: the seeds above a treated band of soil, planting the seed below the treated band or by foliar application.

Movement of the soil applied quinclorac was restricted by using a layer of activated carbon. Seventy-five ml test tubes were used for the soil studies with 1 Uci of quinclorac being added to each test tube. Plants were grown in a growth chamber. Initial applications of ^{14}C quinclorac added formulated quinclorac 00 H (soil treated at 1.5 kg ha^{-1} into soil 3-cm deep) resulted in death of for all plants. All subsequent soil uptake studies were conducted using only ^{14}C quinclorac. The application rate of active material was 0.17 kg ha^{-1}. The acetone carrier was allowed to volatilize prior to planting. All applicable treatments were spiked with 1 Uci of quinclorac per test tube. Plants were removed from the test tubes and divided into foliage and roots. All plant material above the soil surface being foliage and all below the surface being classified roots.

The ^{14}C quinclorac was applied to the second leaf of corn plants after emergence of the fourth leaf. The third leaf of the barnyardgrass was treated after the emergence of the fourth leaf. The first leaf of the morningglory was treated after the emergence of the second leaf. All ^{14}C quinclorac applications were made immediately following the application of 0.5 kg ha^{-1} of quinclorac as a broadcast application. All ^{14}C quinclorac foliar applications were made by diluting the ^{14}C quinclorac with non-labeled quinclorac to a ratio of 1 to 33.7. So the concentration totaling 172,000 DPM were applied per plant in five 2 ul-drops. Applications were made with a 10 ul-syringe. Acetone was added to the labeled and non-labeled solution to facilitate stability. A surface layer of vermiculite 1.25 cm deep was used to restrict the movement of pesticide into the soil for all foliar applications. Movement of ^{14}C quinclorac in soil applications were restricted by placing a 3 to 5 mm band of activated carbon between the seed and the treated soil. All test tubes were wrapped with aluminum foil. Test tubes used in the soil applications were covered to reduce evaporation rates until the emergence of the seedlings.

RESULTS AND DISCUSSION

The visual phytotoxicity expressed in the barnyardgrass increased with the concentration of quinclorac (Table 1). During this initial study activated carbon and vermiculite were not used. Pots were surface watered and attempts to control the movement of quinclorac were not implemented. Above-seed applications gave the best barnyardgrass control. The below-seed applications yielded the least effective weed control. On termination of the study, root growth of the surface applied treatments were restricted to the upper zone of soil. Under the relatively mild conditions of the greenhouse (i.e. optimum water, etc.) seedlings with root growth limited to the top few centimeters of soil produced foliar growth comparable to the controls. The phytotoxicity differences observed between the lower and upper soil applications appear to be the result of the morphology of the barnyardgrass.

Under similar conditions, wheat and rye seedlings were not as sensitive to quinclorac as the barnyardgrass (Table 2). Above seed applications reduced the germination rate in wheat and rye but only significantly in wheat. No differences were observed in the foliar weight or length of the seedlings.

Shoot and root growth of both dicots, soybean and morningglory were reduced by foliar applications (Tables 7 and 8). These applications of quinclorac had the most significant phytotoxic effect on the morningglory and barnyardgrass (Tables 3 and 8).

Sprinkler irrigation enhanced the phytotoxicity of the foliar applications. This enhanced response of was most prevalent in the root measurements taken on corn and morningglory seedlings (Table 6). The sprinkler irrigation was presumed to have washed the quinclorac from the leaves and into the soil. The lack of activated carbon in the foliar applications and the removal of vermiculite 24 h after application allowed the herbicide to move through the soil unimpeded.

For the soil applications the herbicidal effects in most studies were reduced when the watering placed the herbicide between the activated carbon and the source of water. The response was most notable in barnyardgrass and morningglory (Table 3 and 6). This reduced phytotoxicity was assumed to result from the movement of the herbicide into the activated carbon.

When quinclorac was applied and retained in the upper soil horizon no visual or gravimetric damage was evident (Tables 4, 5, 6 and 7). In contrast, growth by both weed species were significantly arrested when quinclorac was applied and retained in the upper soil horizon (Table 3 and 8). Selective placement and retention of the herbicide might provide added selectivity.

In an attempt to reduce the movement of quinclorac, optimize weed control and protect the crops studies exploring the use of lignin to control the release of quinclorac.

Co-grinding technical grade quinclorac with lignin resulted in a fine, well-mixed powder. Addition of the powder to water resulted in the separation of the pesticide and the lignin. The passive partitioning of technical grade quinclorac from a saturated or supersaturated aqueous solution into the lignin matrix was not visually evident.

The melting point of quinclorac was higher than the lignin fractions. Once liquified the lignin did not dissolve the technical grade quinclorac. On cooling the lignins and the quinclorac remained in distinct phases.

Since quinclorac has a relatively low solubility in organic solvents, attempts were made to partition the pesticide into the lignin. Solubilization of the lignin with tetrahydrofuran, toluene, n-propyl failed to create a single phase. Efforts to use carbon disulfide yielded limited success but were stopped due to concerns or the toxicity of CS_2.

Quinclorac and most lignin fractions are soluble in acetone. The combination of lignin, quinclorac, and acetone yield a single phase solution. The viscosity of the mixture was indirectly related to the proportion of acetone present. Subsequent volatilization of the acetone resulted in a solution of increasing viscosity. The matrix changes initially from a liquid, then tar, and ultimately to a glass-like materials. The viscosity of the final product was temperature dependent. Successful preparation of the material in quantities required for field applications utilizing standard agricultural application equipment (Tee-Jet nozzles, screens, etc.) required grinding and sieving of the material under freezing or near freezing conditions. To avoid clogging the screens in application equipment the matrix was maintained in a cool environment until application. Warming of the formulation resulted in a congealing of the screened lignin-quinclorac formulation. On a laboratory scale increased stability was achieved by the more extensive removal of acetone. The lignin-quinclorac matrix has a density greater than one and requires constant agitation to maintain a suspension in an aqueous carrier. The effectiveness of the formulation in reducing the movement of the quinclorac in soil was tested in a soil columns (Table 9)

The quinclorac in the commercial formulation was more susceptible to leaching than metolachlor (Table 9). The upper most 3-cm section of soil treated with the lignin-quinclorac formulation contained the largest concentration of quinclorac. Barnyardgrass was similar to the controls in upper most 6 cm of soil in the columns treated with commercial formulation of quinclorac. The majority of the quinclorac applied with the commercial formulation was found in the 9 through 21 cm-area of the column. Notably less quinclorac was available to move through the columns treated with the lignin-quinclorac formulation. The foliar uptake of ^{14}C quinclorac in barnyardgrass, corn, morningglory, and soybeans varied from 0.4 to 0.9 percent of the total recovered isotope (Tables 10 - 13). Recoveries ranged from 86 to 100 percent with the lowest recoveries coming from the weed species. As expected the level of isotope found in the food source of the young seedlings (cotyledons or seeds) was negligible. With the exception of corn the average DPM g^{-1} value in new leaves was greater than the other organs. ^{14}C-material was identified in roots of all species. Movement of the ^{14}C-quinclorac from the treated areas to the leaf tips of the dicots was relatively large when compared to the levels found in leaf tips of the grasses.

The herbicidal properties of quinclorac prevented the emergence of 100 percent of the barnyardgrass and 83 percent of the soybeans when quinclorac was placed above the seeds. Emergence was 83 percent for soybeans and better than 90 percent for the barnyardgrass for the below seed applications of quinclorac. A marked increase in the level of ^{14}C was found in the shoots of morningglory and corn relative to the levels in the roots in plants grown in an above seed application of quinclorac.

The ^{14}C levels in the shoots of the barnyardgrass grown with quinclorac applied below the seeds were higher than the level in the roots. This occurred because of the extensive barnyardgrass root system that developed near the soil surface. The roots that penetrated the activated carbon layer did not continue to grow in the presence of the treated soil. A the same time the contact was significant enough to allow the take up and translocation of observable levels to the shoots. Similar root to shoot distribution of the isotope was observed in the other species.

The selective placement and retention of quinclorac in the soil above the seeds of corn, soybean, wheat and rye resulted in the selective control of both morningglory and barnyardgrass. Uptake and translocation of ^{14}C quinclorac occurred from below and above seed soil applications as well as from foliar application. The growth of barnyardgrass and morningglory shoots through the treated soil resulted in greater injury when compared to the below seed soil applications of quinclorac. Foliar applications of quinclorac on corn and wheat did not reduce growth when the spray was excluded from the root zone. Once again both weed species were either killed or the growth retarded due to post-emergence applications. The roots of all species tested were adversely affected when the herbicide was available for root uptake. The effect of placement on the phytotoxic properties of quinclorac and differential species responses opens the possibility for exploiting the selective properties of the pesticides. The lignin formulation of quinclorac retained a measurable quantity of the herbicide in the upper horizon, whereas the dry flowable formulation was completely leached to the lower zones. The further development a controlled release formulation of quinclorac may provide a product suitable for Midwestern crops.

Table 1. Visual evaluation of the phytotoxic effects of rate and site of placement of quinclorac on barnyardgrass.

Treatment site	Quinclorac rate	Control[1]
	(kg/ha)	(%)
Above seed	1.4	99 A[2]
Above seed	0.6	99 A
Below seed	1.4	82 B
Foliage	1.4	71 C
Foliage	0.6	65 CD
Above seed	0.1	56 D
Foliage	0.1	31 E
Below seed	0.6	10 F
Below seed	0.1	0 F

[1] Control of barnyardgrass was evaluated 16 days after the soil applications and 8 days after the postemergence applications.

[2] Means followed by the same letter are not significantly different from each other by the Duncan's Multiple Range Test at the 1% level of significance.

Activated carbon, peat or vermiculite was not used.

Table 2 Selective placement of quinclorac on wheat and rye seedling emergence and shoot growth.

Treatment	Shoot weight[1] wheat	rye	Shoot length wheat	rye	Emerged seedling wheat	rye
	(g)/plant		(cm)/plant		number/plot	
BASF 514						
Post	.29 A	2.3 A	23 A	20.3A	10 A	9 A
Check	.28 A	2.1 A	23 A	19 AB	10 A	9 A
Below	.28 A	1.9 A	21 A	18 B	9 A	8 A
Above	.24 A	1.8 A	18 B	17 B	6 B	7 A

1. Means followed by the same letter are not significantly different from each other by the Duncan's Multiple Range Test at the 1% level of significance.

Table 3. Placement of quinclorac and irrigation on barnyardgrass growth.

Quinclorac Treated zone	Watering	Shoot weight	Shoot length
		--------% of control[1]--------	
Postemergence	sprinkler	1.00 D	3.00 D
Above seed	"	25.75 BC	27.25 C
Below seed	"	44.50 B	68.25 B
Postemergence	sub	14.00 CD	28.25 C
Above seed	"	0.00 D	0.00 D
Below seed	"	112.50 A	114.50 A

Evaluated as a percent of the nontreated control.

1. Means followed by the same letter are not significantly different from each other by the Duncan's Multiple Range Test as the 5% level of significance.

Table 4. Placement of quinclorac and the effect of surface vs. sprinkler irrigation on wheat growth.

Quinclorac Treated Zone	Watering	Shoot Length
		% of control
Postemergence	sprinkler	87[1]B[2]
Above seed	"	100 A
Below seed	"	87 B
Postemergence	sub	100 A
Above seed	"	100 A
Below seed	"	100 A

1. Evaluated as a percent of the nontreated control.

2. Means followed by the same letter are not significantly different from each other by the Duncan's Multiple Range Test at the 5% level of significance.

Table 5. Placement of quinclorac and the effect of surface vs. sprinkler irrigation on rye growth.

Quinclorac Treated Zone	Watering	Shoot Length
		% of control
Postemergence	sprinkler	63[1]E[2]
Above seed	"	112 A
Below seed	"	80 D
Postemergence	sub	90 C
Above seed	"	100 B
Below seed	"	105 B

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1. Evaluated as a percent of the nontreated control.

2. Means followed by the same letter are not significantly different from each other by the Duncan's Multiple Range Test at the 5% level of significance.

Table 6. Placement of quinclorac and the effect of surface vs. sprinkler irrigation on corn growth.

Quinclorac Treated zone	Watering	Root weight	Root length	Shoot weight	Shoot length
		------------% of control[1]------------			
Postemergence	sprinkler	84 C[2]	59 D	62 C	68 C
Above seed	"	98 AB	98 B	94 AB	103 A
Below seed	"	26 D	78 C	67 CA	80 B
Postemergence	sub	92 BC	98 B	74 BC	100 A
Above seed	"	101 A	122 A	104 A	99 A
Below seed	"	99 AB	87 BC	109 A	102 A

1. Evaluated as a percent of the nontreated control.

2. Means followed by the same letter are not significantly different from each other by the Duncan's Multiple Range Test as the 5% level of significance.

Table 7. Placement of quinclorac and the effect of surface vs. sprinkler irrigation on soybean growth.

Quinclorac Treated zone	Watering	Root weight	Root length	Shoot weight	Shoot length
		------------% of control[1]------------			
Postemergence	sprinkler	89 A[2]	83 B	49 C	63 C
Above seed	"	110 A	100 A	101 A	100 A
Below seed	"	49 B	34 C	41 C	78 B
Postemergence	sub	110 A	83 B	64 B	72 BC
Above seed	"	107 A	99 A	103 A	100 A
Below seed	"	103 A	97 A	99 A	105 A

1. Evaluated as a percent of the nontreated control.

2. Means followed by the same letter are not significantly different from each other by the Duncan's Multiple Range Test as the 5% level of significance.

Table 8. Placement of BAS 514 and the effect of surface vs. sprinkler irrigation on morningglory growth.

Quinclorac Treated zone	Watering	Root weight	Root length	Shoot weight	Shoot length
		------------% of control[1]------------			
Postemergence	sprinkler	37 D[2]	55 CD	23 C	26 D
Above seed	"	110 A	91 AB	95 A	88 A
Below seed	"	87 BC	41 D	54 B	52 BC
Postemergence	sub	72 C	72 BC	32 C	33 CD
Above seed	"	92 ABC	87 AB	66 B	66 B
Below seed	"	95 AB	98 A	98 A	103 A

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1. Evaluated as a percent of the nontreated control.

2. Means followed by the same letter are not significantly different from each other by the Duncan's Multiple Range Test as the 5% level of significance.

Table 9. Leaching properties of quinclorac, metolachlor, and lignin-quiclorac in a Spinks loamy sand soil.

Depth	Shoot Length		
	Quiclorac	Lignin-Quinclorac	Metolachlor
(cm)	(% of control)		
0-3	91 A-D[1]	38 H	5
3-6	92 A-D	93 A-D	3
6-9	82 C-F	81 C-F	11
9-12	67 EFG	82 C-F	30
12-15	60 G	82 C-F	127
15-18	65 FG	85 B-D	112
18-21	77 D-G	87 A-D	124
21-24	103 AB	98 ABC	116
24-27	101 AB	105 A	107
27-30	86 A-D	103 AB	82

LSD = 16

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[1] Means followed by the same letter are not significantly different from each other by the Duncan's Multiple Range Test at the 5% level of significance.

Table 10. Distribution of foliar applied ^{14}C-labeled quinclorac in morningglory.

Tip	Rinse	Treated area	Cotyledons	New leaf	Stem	Root
(DPM g^{-1})						
785	110347	5789	13	57	183	48
1095	119275	5268	17	274	23	150
2108	145465	6829	65	158	76	37
2911	136412	5828	13	219	7	58
(average DPM g^{-1})						
1725	127875	5929	27	177	72	73
(standard deviation)						
972	15953	652	25	93	80	52

Recovery 86.2%

Table 11. Distribution of foliar applied ^{14}C-quinclorac in soybeans.

Tip	Rinse	Treated Area	Cotyledons	New Leaf	Stem	Root	Unilofiate Leaf
(DPM g^{-1})							
1474	144619	19514	39	117	41	222	127
578	155387	8987	25	159	28	42	9
241	148166	14574	11	120	32	94	52
1619	164979	8247	113	177	62	108	58
(average DPM g^{-1})							
978	153288	12831	47	143	41	117	62
(standard deviation)							
673	8990	5275	45	30	15	76	49

Recovery 100.3%

Table 12. Distribution foliar applied ^{14}C-quinclorac in corn seedlings.

Tip	Rinse	Treated Area	Below Treated Area	Older Leaves	New Leaves	Roots
(DPM g^{-1})						
30	156689	3736	138	605	255	614
10	143369	2322	1187	584	200	479
16	149574	695	224	139	120	296
3	152046	2128	65	86	20	657
(average DPM g^{-1})						
15	150420	2220	403	354	149	512
(standard deviation)						
11	5549	1244	526	279	102	162

Recovery 99.3%

Table 13. Distribution of foliar applied ^{14}C-quinclorac in barnyardgrass seedlings.

Tip of Treated Leaves	Treated Area	Rinse	Below Treated Area	Older Leaves	Newer Leaves	Roots
(DPM g^{-1})						
17	3084	162724	68	22	219	25
16	38307	31569	118	12	641	178
8	5728	142610	90	9	195	46
21	2400	143491	151	13	342	22
(average DPM g^{-1})						
16	3,762	120099	107	14	349	68
(standard deviation)						
5	1436	59745	36	6	204	74

Recovery 100.7%

Table 14. Distribution of soil applied ^{14}C-quinclorac in morningglory.

Below seed applications		Above seed applications	
root	shoot	root	shoot
(DPM g^{-1})			
18005	264	1187	7821
5372	23	1623	16829
8070	89	1039	24730
(average DPM g^{-1})			
10482	125	1283	16460
(standard deviation)			
6653	125	304	8461

Recovery: Below seed 1.2% Above seed 2.0%

Table 15. Distribution ^{14}C-quinclorac in soybeans when applied below seed.

	Root	Shoot	Seed Cotyledons
(DPM g^{-1})			
1	59629	178	--[1]
2	1972	2903	80
3	49773	3580	72
4	4804	3267	--
5[2]			
6	54074	7596	165
(average DPM g^{-1})			
	28795	3505	106
(standard deviation)			
	29692	2657	52

Recovery 4.9%

1. The cotyledons of a number of seedlings were damaged or broken free of the seedling during emergence.

2. The fifth seedling failed to emerge.

Table 16. Distribution below seed applications of ^{14}C-quinclorac in corn seedlings.

Root	Shoot	Seed Cotyledons
(DPM g^{-1})		
28170	6136	1453
13979	247	190
7286	318	79
31894	3182	981
59059	5320	867
19159	337	265
(average DPM g^{-1})		
26591	2590	639
(standard deviation)		
18285	2687	545

Recovery 3.4%

Table 17. Distribution of ^{14}C-quinclorac in corn seedlings when soil applied above the seed.

Root	Shoot	Seed Cotyledons
	(DPM/g)	
423	10392	32
382	11165	65
420	19737	75
222	9749	101
646	6897	59
749	32244	97
	(average DPM g^{-1})	
474	15031	72
	(standard deviation)	
191	9476	26

Recovery 1.8%

Table 18. Barnyardgrass ^{14}C-quinclorac placed below the seed.

Sample	Root tissue	Shoot tissue
	(DPM g^{-1})	
1	166	425
2	120	788
3	260	212
4	81	162
5	141	695
6	287	475
	(average DPM g^{-1})	
	176	460
	(standard deviation)	
	81	250

Recovery 0.5%

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CHAPTER FOUR

CONTROLLED RELEASE PROPERTIES OF LIGNIN FOR METOLACHLOR

ABSTRACT

The efficacy of lignin as a controlled release matrix for retarding soil movement of metolachlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide) was evaluated. A solution of technical grade metolachlor, lignin and acetone was blended into a homogenous solution. The acetone was allowed to dry leaving a matrix of lignin and metolachlor. Ratios of 3:1 and 2:1, lignin to metolachlor, were applied to a Spinks loamy sand columns and sprinkler irrigated to simulate rainfall. Applications of 100 ml (0.65 cm), 200 ml (1.3 cm) and 400 ml (2.6 cm) of water resulted in measurable amounts of metolachlor moving to the 12, 21 and 24 cm below the surface. Metolachlor movement below the 0 to 3 cm was unmeasurable in the lignin-metolachlor formulation. The lignin-metolachlor formulation provided equal or superior control to the commercial emulsifiable concentrate of barnyardgrass (*Echinochloa crusgali*) in the top 0 to 3 cm of the column. The results of the greenhouse studies were confirmed in the laboratory. Laboratory studies also confirmed that a significant concentration of the metolachlor was not being released. The addition of swelling gels to the lignin-metolachlor matrix improved the release rate but failed to improve the degree of control provided by the commercial emulsifiable concentrate formulation in the field studies. Reduced movement of metolachlor through the soil horizon was not confirmed in the field study. Development of an effective controlled release formulation of lignin-metolachlor will require an enhanced rate of release. The greater availability of the herbicide in the commercial formulation provided superior weed control over a single season. At the present release rates the lignin-metolachlor formulation may provide extended weed control in forestry or orchard conditions but only at higher rates.

Additional index words: metolachlor, barnyardgrass, controlled release, lignin, leaching.

INTRODUCTION

Questions raised regarding the human health and environmental impact of low level chronic exposure to pesticides originate from the private, public and academic sectors (1, 15, 16, 20, 23). It is not difficult to find publications from state or Federal governments that appear to advocate both of the extreme positions regarding safety of pesticides (9, 15, 17, 18, 26). The scientific community is no less divided over the issue (21, 22, 28). The inability of the experts to condense complex issues into easily presented and understood statements often leaves the press and the society confused (13). This inability to communicate risk relationships has contributed to the 1984 EDB cake mix issue, the 1985 watermelon crises, the 1989 diamidazide (butanedioic acid mono-(2,2-dimethylhydrazide) apple boycott and other economically devastating events.

The attention given this issue has forced agricultural researchers and growers to reevaluate their research and growing objectives. Journals and publications similar to the Journal of Sustainable Agriculture and New Farm give some indication of the growing acceptance of change and in some situations concession to change. The Nations Academy of Sciences publication Alternatives to Agriculture gave added credibility to the movement (1).

The changes are often forced as a result regulatory implementation of legislation. Few regulatory policies hold the potential for impacting agriculture to the degree that the Pesticides and Ground-Water Strategy proposed by the US EPA does (19).

Pesticides have been found in the ground-water of every major agricultural state in the United States (29). All of the findings have been at levels below the health advisory levels and limited to isolated wells. Pesticide residue contamination is not limited to ground-waters. Residue levels peak in Midwestern surface waters during periods of high use. The findings, though considered by some to be more a tribute to current analytical capabilities rather than toxicologically significant, have drawn into questions various farming methodologies.

Off-site movement of pesticides and subsequent contamination of waters need not be the prerequisite for banning a given pesticide. The use of contour farming can reduce run-off. Adjuvants designed to increase the surface tension of aqueous solutions can be used to reduce aerosol formation. Reducing or removing the smallest droplets will result less drift. Adjuvant or altered formulations can be developed to produce desired controlled release properties.

The EPA survey found DCPA (dimethyl 2,3,5,6-tetrachloro-1,4-benzenedicarboxylate) and its primary metabolites to be the most common well water contaminate (29). Another herbicide, atrazine was also among the most commonly found. Surprisingly, many of these contaminates have a very low water solubilities and high octanol water partitioning coefficients (K_{oc}). Not so surprising, the pesticides have relatively long half lives. Formulation alterations of existing efficacious pesticides may currently be the most cost effective but altered formulations be the only viable means of complying with all of the regulatory requirements. Controlling the delivery of a pesticide also holds promise as a possible means of improving on performance.

Successful development of controlled release formulations in agricultural chemicals is dependent the cost, supply, quality and consistency of the raw materials (8, 12). Much of the early developmental work in controlled release of bio-active chemicals occurred in pesticide field (4, 5). More recently the development of most new controlled release technologies has occurred in the area of drug delivery by the pharmaceutical industry (11). The consistency of the physical environment, the relatively low volume of material used and potential of passing on the cost all contribute to the shift in controlled release research moving to the pharmaceutical field. Economic constraints limit the utilization of many of the gains achieved in controlled release of pharmaceuticals.

Lignin, the by-product of the wood pulping process is a low cost material in ample supply, that can be consistently delivered within specified quality guidelines (7). Lignin and humic acid have relatively similar chemical properties (27). In theory, lignin should possess sorptive properties similar to humic acid.

Pesticides have been noted to interact with the inorganic and organic constituents of the soil. Covalent bonding of many pesticides to soil organic matter often results from microbial activity. The strong ionic binding of the bipyridilums occurs due to the strong negative charges on the clay surface. Soil Ph impacts binding to both inorganic and organic fractions of the soil and markedly effect the residual levels of many chemicals (6, 27). The van Der Waals forces acting between pesticides and various soil constituents represents one of the weakest molecular interactions but is prevalent in all interactions. The partitioning of non-ionics into soil organic matter represents one of the weaker molecular interactions. Despite the weak character of the interaction partitioning may represent the most significant soil pesticide interaction with respect restricting to movement, efficacy and persistence (14, 27).

Braverman demonstrated that metolachlor was mobile in soils but that the sorptive properties of the soil with regard to metolachlor were positively correlated to soil organic matter levels (3). He further demonstrated that the soil half life of metolachlor is significantly increased by eliminating leaching of the pesticide.

Studies reviewing the impact of residual wheat straw, a third to a sixth the normal levels, left on the soil surface prevented over 50% of the applied metolachlor from reaching the soil surface (2). The wheat straw retained more of the metolachlor than the alachlor (2-chloro-2',6'-diethyl-N-methoxymethyl acetanilide). The reduced efficacy of the herbicide as a result of surface straw residues has serious implications for metolachlor as a weed control material in no-tillage systems.

The chloroacetamides of which metolachlor is a member are limited to controlling young seedling. Correct soil placement and timing are essential for obtaining weed control (10). To address the problem of lost efficacy resulting from increased surface plant residues the manufacture altered the formulation. The new formulation was a microencapsulated controlled release emulsifiable concentrate. Studies were conducted to compare the efficacy of the micro-encapsulated metolachlor to the emulsifiable concentrate on no-till and in incorporated plots (30). The new formulation provided superior control in no-till situations. Performance in the incorporate plots was rated comparably between the two treatments. Release of the pesticide appears to be accelerated by wetting dry cycles, with release accelerated on drying.

Riggle demonstrated the feasibility of lignin as a controlled release material for alachlor (24, 25). He found that various lignin fractions provided controlled release properties a finding not dissimilar to findings of Garbarini that the nature of the soil organic matter significantly impacts the sorption properties of a soil.

Utilizing the natural sorptive properties of lignin for metolachlor a series of studies were conducted to assess the potential of developing a control release matrix of lignin-metolachlor. The objective was to increase delivery of the pesticide to the weeds by reducing off-site movement of the herbicide with a monolithic lignin controlled release matrix.

MATERIALS AND METHODS

Preparation of ^{14}C materials. All metolachlor tracer studies and ^{14}C-metolachlor-lignin formulations were prepared from a methanol stock solution. A 10 ml-methanol stock solution was prepared by adding 1 mg of a ^{14}C metolachlor (ring labeled ^{14}C-CGA-24705, radiochemical purity determined to be 97.4% on 12/11/86 by CIBA-GEIGY) with a specific activity of 49.4 uCi mg^{-1}. The purity of the ^{14}C-metolachlor was verified by silica thin layer chromatography utilizing a hexane:chloroform: ethylacetate mobile phase. A single spot (rf 0.25) was identified which corresponded to the technical grade metolachlor. A 10 ul-aliquot of the ^{14}C metolachlor methanol stock solution contained an average of 89,737 DPM with a standard deviation of 1,488 DPMs.

Chloramben lignin formulations were formed in the same manner as the lignin metolachlor formulation. The only deviation being the substitution of chloramben for metolachlor. All chloramben tracer studies are prepared from a stock solution. The lignin herbicide formulations were prepared in micro disposable tissue grinders. The lignin metolachlor matrix was prepared by adding 10 ul of the ^{14}C metolachlor stock solution. The concentration of ^{14}C-metolachlor was a small fraction of the total metolachlor and thus not factored into the lignin metolachlor ratio. The ratio of lignin to metolachlor was determined by the concentration of non-

^{14}C-technical grade metolachlor added with the labeled pesticide. A 3:1 ratio of lignin to metolachlor was made by adding 1 ml of an acetone solution containing 10,000 ppm cold technical grade metolachlor (10 ul of technical metolachlor), 10 ul of ^{14}C metolachlor stock solution, 30 mg of lignin and 100 ul of acetone. To increase or decrease the ratio, the concentration of lignin was altered: 6:1 utilized 60 mg of lignin, a 1:1 formulation utilized 10 mg of lignin. Acetone additions were increased or decreased until the lignin was completely dissolved.

Lignins that demonstrated little or no metolachlor retention properties in the micro sand column test also proved to have limited solubility in acetone. These lignins proved to be the most difficult formulation to prepare.

The mixed solution was air dried while in the disposable micro tissue grinder. An over night drying period adequately removed the acetone. After drying, the base of the tissue grinder was submerged in an acetone dry ice bath. The cooled mixture was then ground to a fine powder. The lignin-metolachlor formulation used in the field was sieved to remove larger particles. Where sieving was required in the laboratory studies it was noted. The 1:1 formulations of lignin to metolachlor were viscous at room temperature and in the dry ice acetone bath. This formulation was scraped free from the walls of the tissue grinder while in the dry ice bath and ground using 20 g of sand. All formulations tested in the micro sand columns or water baths were placed directly into a scintillation vial containing 20 g of a fine sand or into an empty scintillation vial for future use.

Separation of the lignin metolachlor formulations was done using various sieves (40, 60 and 80 mesh). All materials which passed through the 80 mesh screen were defined as 80 mesh. The formulated material passing through the 40 but not the 60 mesh was referred to as 40 mesh material. Sixty mesh material was prepared in a similar manner. All material not passing through the 40 mesh screens was referred to as greater than 40 mesh. The following is breakdown of the measurements of the various mesh sizes:

mesh size	radius	area	volume	normalized
----------	--um--	--um^2--	--um^3--	--1000^{-3}--
80	90	10,179	171,767	59.26
60	125	196,350	4,601,942	42.67
40	213	567,450	22,609,340	25.10

surface area comparisons 80:60:40 = 2.4:1.7:1.0

volume comparisons 80:60:40 = 1:26:131

Samples identified by a code other the lignin fraction were prepared in a similar manner. A test measuring the sorptive or absorptive properties of talc was preformed by substituting talc for the lignin. A test of the sands sorptive or absorptive properties of the sand was referred to as the technical sand sample. The ^{14}C-metolachlor stock solution and the technical metolachlor was used and added directly to the fine sand. Non-kraft lignin or the lignin derived by the organo-solvent method was treated similar to the kraft lignin.

To alter the release properties of the lignin-metolachlor formulations various lignin alterations and additives are added to the formulations. The formulation labeled BEC W/SEPH was a formulation composed of; 10 ul of the ^{14}C metolachlor stock solution, 10 ul of technical grade metolachlor, 30 mg of a lignin sephadex G 10 and 100 ul of acetone. Sephadex was added to the lignin (BEC) at a 1 to 10 ratio prior to the introduction of any metolachlor.

The formulations labeled as Gel A through F are mixtures of lignin fraction BEC and various swelling materials. The swelling materials are ground and added to the lignin at a 5:1 ratio (lignin to swelling material). The lignin-swelling materials were then mixed with the metolachlor as described above to yield a 3 to 1 ratio of lignin-swell material to metolachlor.

All sands used in the studies were washed with water followed by a methanol rinse. The sands were then allowed to dry prior to use. Micro columns were prepared by placing a small amount of glass wool at the base of a Pasteur pipet. The sand formulation mixture was then added to the pipet and capped with additional piece of glass wool.

Sorption / Absorption Studies. Twenty ml of room temperature water was added to a small Erlenmeyer flask followed by 30 ul of the ^{14}C-metolachlor stock solution, 30 ul of technical grade metolachlor and 90 mg of a kraft lignin (BEC). The solution was agitated and at designated times a 0.5 ml aliquot of solution was removed. Prior to removal the shaker was stopped and the solution was allowed to settle. Visual examination was used to assure that no lignin was extracted with the aliquot. To a second series of flasks the stock solution and technical metolachlor were added without adding the lignins. Samples were taken from this solution in a like manner.

Sand micro column studies. The materials used in these studies were described above. The micro sand column studies were divided into two types depending on the frequency that water was added to the column. Studies referred to as continuous were conducted by adding 8 ml of distilled water in 2 ml aliquots, one immediately following another. A 2 ml aliquot of water was added to the top of the pipet and allowed to freely flow through the column into a scintillation vial. After the last 2 ml aliquot, 2 ml acetone was added in 1 ml aliquots. The timed studies were conducted by adding 8 ml of water in succession. At designated times (e.g. 0, 24 48 and 144 h) a new series of 2 ml aliquots is added until 8 ml of water is collected. After collection of the last 2 ml aliquot of the last 8 ml fraction acetone was once again added (2 ml in 1 ml aliquots). A scintillation cocktail was added to the 2 ml aliquots after completion of the study.

Water bath release studies. The water bath studies were performed either to identify the release properties of various lignin fractions or the effect of incorporating different materials into the lignin. Various lignin metolachlor formulations were added to a 125 ml Erlenmeyer containing 20 ml of distilled water at room temperature. A 0.5 ml aliquot of the solution was removed at designated times.

Soil column studies. A spinks loamy sand soil (83% sand, 3% silt, 15% clay, pH 7.4 with organic matter level of 0.8 %) was screened to remove material larger than 2 mm and then placed in 30 cm columns with 7 cm diameter. Metolachlor formulated in one of three forms was applied to the surface of the columns at 2.24 kg ha^{-1}. The formulations used were an emulsifiable concentrate or as a dry flowable in a lignin matrix at 2 or 3 to 1 ratios, lignin to metolachlor. Applications were made using water as the carrier applied at 375 L ha^{-1} by a belt sprayer with a pressure of 10.25 kg cm^{-1} and a TeeJet SS8002E flat fan nozzle. The treated columns were then sprinkler irrigated with 100, 200 or 400 ml (2.6, 5.2 and 7.8 cm respectively) of water applied at 5 ml min^{-1}. Forty-eight hours after watering the soil from each 3-cm increment (0-3, 3-6, etc.)

was removed, mixed and placed over 20 barnyardgrass seeds. The herbicidal effects were evaluated when leaves of the controls were 10 cm tall. Evaluations consisted of measuring individual shoot lengths and averaging the shoot lengths for each pot. An ANOVA was run on the averages and differences between treatment means were determined using a Duncan's Multiple Range test at the 5% level of significance.

Field studies. Field studies were conducted on the Michigan States University farm located in East Lansing, Michigan. The treatments were replicated 6 times on 3 by 9 meters plots. The Capac soil had the following properties:

> at 0 to 15 cm, pH 6.6, organic matter (OM) 2.2%, a sandy loam soil 69% sand 18% silt and 13% clay and a cation exchange capacity (CEC) of 13.3 me/100g;
>
> at 15 to 30 cm, the pH is 6.8, the OM is at 1.3%, a sandy loam soil 63 sand, 18 silt, 19 clay and CEC 11 me 100 g^{-1}; and at
>
> 30 to 45 cm the pH 6.4, OM 1.4%, sandy clay loam 57% sand, 22% silt, 21% clay and CEC 11 me 100 g^{-1}.

Applications were made on June 29, 1987. The field study included four treatments: the non-treated control, BEC-super-slurp-metolachlor, BEC-metolachlor and Dual. The applications were made with the following equipment: a hand boom with four 8008ss nozzles, with 52 gallons of carrier applied per acre and 2.0 lbs ai a^{-1}.

Efficacy was evaluated by visually evaluating the growth of barnyardgrass planted on one half of each plot at two times: July 18 and August 4. The July 18 planting was evaluated on the 4th of August. The August 4th planting was evaluated on the 11th of August.

The site was established with overhead irrigation system. The rainfall events were recorded:

Date	Cm of rainfall or irrigation	
June 30	0.7	rainfall
July 1	0.1	rainfall
July 2	8.9	irrigation
July 5	0.4	rainfall
July 10	2.2	rainfall
July 11	0.4	rainfall

On June 30th 0.66 cm of rain fell one day after the herbicide application. A total of 8.9 cm of water was applied 3 days after application by overhead irrigation.

Gas chromatography studies. A soil auger with a 2.5 cm diameter was used to collect soils on August 14th. Twenty separate cores were taken from each plot. Each core was divided into three sections: 0-15 cm, 15-30 cm and 30-45 cm. Soils were collected in plastic containers and frozen at less than -40°C) until analyzed. Prior to freezing three non-treated control samples were spiked with 0.2, 1.0 and 2.0 ppm of metolachlor. During analyses the metolachlor was recovered at 150, 77 and 95% of the original spiked values, respectively.

Soils were removed from the freezer and brought to room temperature. A 50 g sub-sample was dried at 105°C over night and weighed again to determine the water content. A 45 g sub-sample of soil was removed for the analysis of metolachlor. One hundred ml of a MeOH solution containing 10% H^2O was added and the soil solutions were placed on a reciprocal arm shaker for 2 h. The solution was then removed and vacuum filtered with a Whatman #2 filter paper. One hundred ml of H^2O and 10 ml of a saturated NaCl solution were added to the filtered extract. The pesticide was extracted with three 50 ml portions of hexanes. The 150 ml of the hexanes were dried with Na_2SO_4. The dried hexanes were then decanted into a round bottom flask. The flask was placed in a 40°C water bath and attached to a rotary evaporator. The hexanes were then evaporated to dryness. The residues were dissolved in two 5 ml aliquots of hexane.

The two 5 ml aliquots were cleaned on a column containing 12.5 grams of basic alumina. The alumina was oven dried and then deactivated with 16% distilled H_2O. The alumina column was pre-eluted with 30 ml of hexane. The sample was then added to the column top and eluted with 100 ml of hexane, which was discarded. The column was eluted next with 100 ml of an 8% ethyl ether in hexane solution. The 8% ethyl ether in hexane solution was taken to dryness on the rotary evaporator and dissolved in 10 ml of hexane.

The hexane was then analyzed for metolachlor by gas chromatography using a $_{63}Ni$ electron capture detector. Instrument conditions were as follows: column 216°C, injector 250°C, detector 290°C, mobile phase N_2 at 30 ml/min. The reported lower detection level for the method in this soil was 5 ppb (w/w). Positive identification was verified on selected samples by using a Ner Mag R10-10C quadrapole mass spectrometer operating in the electron impact mode (70 ev).

Lignin fraction screening. Infrared spectra of the following lignin fractions are presented in Figures 1 thru 3:

Lignin fraction	Coded as
5528-60E	Lignin K_2
RLX 5528-6B	Lignin K_3
PC922W	Lignin K_1
BEC Spbil 807	Lignin OS_1
BEC Spbil 826	Lignin OS_2
PC959B	Lignin K_4
Aldrich humic acid	Humic acid

Spectra were obtained using a Perkin Elmer 1710 Infrared Fourier Transform Spectrometer. A three mg lignin sample was added to 400 mg of KBr and the pellet was formed by applying 2,000 psi of pressure under vacuum. Lignins and humic acid were oven dried prior to pressing for 48 h at 105°C. After pressing the mixture was dried at 105°C for 48 h, then pressed into a KBr pellet. A Perken Elmer 1710 infrared Fourier transformed spectrometer was used to scan the sample.

RESULTS AND DISCUSSION

Though the absorption or sorption of many herbicides by soil organic matter has been well documented, the proportion of organic matter is measures in the tons per acre verse the pesticides which are measured in pounds or ounces. Due to transportation cost a commercially viable pesticide formulation would require that the absorption/sorption properties would have to manifest themselves at relatively close ratios. The data in table one demonstrates that the sorptive/absorptive properties of this Kraft lignin fraction (BEC) are not measurable over a 4 day period. Rather it appears that the metolachlor in the presence of lignin reaches an equilibrium more rapidly then without the lignin. Various lignin fractions are currently utilized as suspending agents in a number of pesticide formulations. These results indicate that finest particles may assist in suspending the metolachlor but that the larger lignin particles are not effectively absorbing/sorbing the pesticide.

Since the lignin failed to absorb\adsorb the metolachlor attempts were made to physically encased the pesticide. Many of the lignin fractions demonstrated a tendency to dissolve in acetone. On drying the lignin become hard and brittle. When metolachlor is added to the acetone lignin solution the pesticide becomes encased in what is referred to as a monolithic lignin matrix. Evaluation of available lignins showed that the lignin fractions either hold the herbicide relatively firmly or release it readily (Table 2 and 3). The tech-sand (technical metolachlor applied to sand) and the talc-sand (metolachlor applied to a talc) were used as controls the provided only weak surface adsorption. The lignin fractions that release metolachlor readily were the least soluble in acetone. The lack of solubility appears to result in the metolachlor coating rather than being incorporated into the matrix. They released metolachlor in a pattern similar to the tech-sand and talc-sand treatments.

As a result of these studies the lignins are grouped either as rapidly releasing materials or slow release material. The rapid release materials offered no apparent benefit in controlled release of metolachlor. The slow release materials retained a considerable concentration of the herbicide, normally on the order of 70%. Since the majority of the lignins provided strong retention the emphasis shifted to finding fractions that would provide a high but consistent release rate after the initial 2 ml of water was added. Because of the relatively high release rates of the BEC fraction in the 2 through 8 ml fractions this fractions was targeted for further studies (Table 2 and 3).

The metolachlor-BEC matrix was next tested in a greenhouse study designed to compare the leaching of the herbicide from different formulations through a soil column (Table 5). The lignin-metolachlor formulation yielded results similar to those of the laboratory studies. Less herbicide moved into the lower soil layers when formulated with lignin.

A more rigorous test utilizing 100, 200 and 400 ml of water was used next (Table 6). The migration of metolachlor in the columns treated with the emulsifiable concentrate and leached with 200 and 400 ml was significant. Measurable effects were observed as deep as 21 cm and 24 cm in columns leached with 200 ml and 400 ml of water, respectively. In contrast the lignin formulations produced small to negligible levels of control beyond the 0 to 3 cm layer. In addition, the level of control found in the top 0 to 3 cm of the lignin formulation was equal to or superior to the commercially available emulsifiable concentration formulation.

The reduced control observed in the lignin formulation in the 200 and 400 ml leaching studies though not significantly different from the 100 ml columns supported the findings of the sand micro column studies. In the sand micro column studies anywhere from 60 to 73 percent of the metolachlor was retained in the matrix until released with acetone. Both studies indicated that the metolachlor was retained but not available for weed control during the assay.

Next a series of test explored the effect of altering the ratio of lignin to metolachlor (Table 7 and 9). Increasing the relative level of lignin to metolachlor decreased the initial release of the herbicide. As the concentration of lignin was lowered to an equal concentration with the metolachlor the formulation became more viscous. Working the 1:1 formulation was considerably more difficult. The formulation could not be ground into a fine powder.

A ratio study with chloramben (crystalline form at room temperature) and metolachlor (viscous liquid at room temperature) was conducted to determine if the release rates were attributable to the physical properties of the herbicides (Table 7). The 1:1 lignin to chloramben formulation is much easier to grind into a fine powder. In both studies the initial release of the 1 to 1 ratio were markedly increased over the other ratios. The retention of the herbicides at higher ratios was similar. The lack of difference implies that the lignin is determining the release rate. The similar release rates also imply that a number of herbicides may respond in a similar manner.

To determine effect of altering the lignin to metolachlor ratio a greenhouse study was run observing the effect of a 2 to 1 and a 3 to 1 formulation of BEC to metolachlor (Table 9). Though no notable differences existed between the 2:1 and 3:1 formulations both prevented the movement of the herbicide into the lower soil profile. Each also provided weed control in the 0-3 cm zone of the soil.

The 3:1 lignin metolachlor formulation was ground and divided by size (Table 10 and 11). Material passing through a 40 mesh screen but not a 60 mesh screen, analyzed separate from the material passing through the 60 but not the 80 mesh screen and all material passing trough the 80 mesh screen were designated 80 mesh size. As expected the largest materials yield the lowest initial release rates. No difference existed between the ^{14}C-metolachlor released in the initial 2 ml of water for the 60 and 80 mesh fractions (Table 10). The ^{14}C-metolachlor released in the subsequent 2 ml aliquots was relatively constant for the 60 mesh fraction and higher for the 80 mesh fraction. The percentage of ^{14}C-metolachlor actually increased with each measurement from 2 ml to 8 ml. The percentage of ^{14}C-metolachlor remaining in the lignin after passing 8 ml of water through the column was inversely related to the particle size. At a particle size smaller than 80 mesh the retained metolachlor still averaged greater than 65% of the total present. The 80 mesh lignin-metolachlor reached an equilibrium in less than two hours. The ^{14}C-metolachlor released from all other fractions (<40, 40, 60 and mixed) increased throughout the 96 hour study (Table 11).

When the addition of water is continuous and the measurements made over a short time frame 1 h or less the release of ^{14}C-metolachlor from the lignin matrix is not enhanced by the addition of the swelling materials (Table 12). When the release properties of the lignin-swelling materials are tested over 6 day period percentage of released ^{14}C-metolachlor increases throughout the study (Table 13). In the timed studies using the water bath and micro sand column test materials referred to as Gel A and Gel D appear to increase the release rate to a greater degree than the other 4 swelling materials (Tables 13 and 14). Gel A when mixed with the BEC lignin produces a near 0 order release rate.

The most useful method of distinguishing between lignin fractions that provide a rapid release rate and those that provide a slow release is by observing the solubility of the lignin in acetone. Infrared spectrometry offers an method of better understanding the structural similarities and differences in various lignin fractions. In addition the spectra offer a potentially more quantifiable method of screening the lignin fractions for their potential controlled release properties.

The infrared spectra of the organo-solvent lignins OS 1 and OS 2 have spectra similar to the Kraft lignins K2 and K3 which provide similar metolachlor release properties. The lignin fractions labelled K1 and K4 represent fractions that have low acetone solubility and rapidly release metolachlor in the assays. In general the absorbance of these lignins in the infrared region of the spectra are markedly different from the slow release lignin.

Lignins that release metolachlor slowly: K2, K3, OS1 and OS2 have a high transmission level in the 1525 to 1575 cm^{-1} region of the spectra. The slow release lignins have a region has a low transmission level near 2665 cm^{-1}. The lignins that release the metolachlor rapidly K1 and K4 have a relatively lower transmission level at the 665 and 640 cm^{-1}. At least three regions of the infrared spectra provide distinctively different responses between lignins that appear to be consistent with the metolachlor release characteristics of the lignin. The Kraft lignins that release the metolachlor most rapidly K1 and K4 have been altered by cross-linking agents. The similarities between the organo-solvent lignins and the Kraft lignins may imply the less altered the lignin the greater the polymers potential as a controlled release material.

The spectra of the Aldrich humic acid a relatively nondescript spectra with few similarities to the Kraft or organo-solvent pulped lignins. The absorbance bands are board bands in virtually all region of the spectra and provide little evidence regarding the relationship of the lignins with naturally occurring humic.

A field study designed to examine the efficacy and the movement of metolachlor through the soil profile as effected by three different formulations: an commercially available emulsifiable concentrate, BEC-gel a-metolachlor and BEC-metolachlor. The better than 90% control provided by the commercial formulation indicates that the neither enough water had been applied to the field or enough time had passed for the active material to lose its efficacy. The poor efficacy of the BEC formulation observed in on the first and second evaluation date supports the findings of earlier studies that indicated that a considerable percentage of the formulation applied never becomes available for weed control. The BEC-gel A-metolachlor formulation provided superior performance over the BEC-metolachlor formulation but failed to obtain the level provided by the commercial formulation.

The soil residue studies indicated that the average concentration of metolachlor found in the top 15 cm of soil in the BEC-metolachlor treated plots is greater then the other treatments but not a significant levels. The BEC-metolachlor treatment does cause significantly greater residue levels in the 15 to 30 and 30 to 45 cm levels. The metolachlor levels found in the 30-45 cm level of the BEC-gel A-metolachlor formulation are lower than the BEC-metolachlor levels but greater than the residues left by the commercial formulation.

The use of the term controlled release for the acetone formulated lignin metolachlor formulations is something of a misnomer. Without some type of assistance the release of metolachlor is either negligible or nearly complete depending on the fraction being examined. The occurrence of flushes of germinating seeds occurring in response to rainfall events is well documented. The incorporation of a material that swells in the presence of water holds promise as a control release in material that is triggered by a common event to the germination of the weed seedlings. The studies confirm that the concentration of active ingredient in the controlled release most be higher for comparable control. The success of release of dichlovos (dimethyl-2,2-dichlorovinyl phosphate from polyvinyl (Shell No-Pest Strip) is based on less than 30% of the active ingredient being released.

Until additional field studies are conducted initial weed control will prove less desirable than commercial formulations were 100% of the active ingredient is available on application. The utilization of virtually all of the active material is desirable and can be optimized by enhancing the release of the pesticide to coincide events that weed seed germination.

The occurrence of increased metolachlor levels in the lower soil profiles of the lignin-metolachlor treated plots raises some concern. The movement of lipophilic compounds into the lower soil profile has been theorized to occur as a result of a partitioning of the very lipophilic chemical into a more water soluble humic or fulvic acid and then moving through the soil profile in tandem. This theory may help explained the occurrence of greater metolachlor levels in the lower soil profile. The lignin formulations may be providing a vehicle for the transport of the metolachlor into lower soil profiles.

A careful study of the movement of the lignin-metolachlor movement of the pesticide weighted against the potential gains from improved efficacy should be made. Improving the delivery of a given pesticide to a target organism has considerable merit. The use of lignins as a cost effective base material has been demonstrated to have some possibilities.

Table 1. Sorption of metolachlor from an aqueous media into a kraft lignin (BEC) matrix.

	-- with Lignin --	-- without Lignin --
Time (hr)	DPMs/0.5ml	
1	639 (40)[1]	318 (75)
2	618 (54)	398 (48)
4	623 (31)	528 (24)
8	670 (25)	621 (14)
24	718 (43)	748 (21)
96	745 (34)	745 (34)

[1] Each of the following are added to a series of four 125 erlenmeyer flasks containing 20 ml distilled H_2O in the sequence described: 30 ml of ^{14}C-metolachlor stock solution, 30 ml of cold tech metolachlor, 90 mg of BEC. Aliquots are centrifuged then added to a scintillation cocktail and analyzed.

Table 2. Rate of release of ^{14}C-metolachlor form various lignin fractions.

		------ Eluent Fraction (ml) ------			
	0-2	2-4	4-6	6-8	Acetone
Lignin Fraction		Percentage of ^{14}C-Metolachlor Released			
PC 922L	42.6	12.0	5.0	4.0	30.4
PC 922W	65.8	17.8	4.3	2.4	11.1
PC 949	6.5	1.0	0.5	0.2	92.4
PC 950	22.1	2.3	1.3	0.7	74.0
PC 951B	19.4	1.2	0.6	0.3	78.8
PC 951A	3.4	1.6	0.6	0.6	95.3
PC 953	70.9	8.7	3.8	2.5	14.3
PC 953	41.6	4.1	4.0	2.1	48.4
PC 954	22.3	3.7	2.1	1.5	66.7
PC 955	24.6	3.4	2.0	0.9	69.3
PC 955A	49.0	5.9	2.5	1.9	40.9
PC 955B	7.6	1.6	0.6	0.5	90.0
PC 955B	3.9	1.6	0.7	0.3	94.6
PC 955C	3.0	3.3	1.7	1.0	88.4
PC 959	64.6	29.3	1.2	0.8	5.1
PC 959B	80.4	7.0	7.0	2.1	3.8
5528-60 B	4.6	1.2	0.6	0.5	94.0
5528-60 C	5.2	0.8	0.4	0.3	62.0
5528-60 D	3.0	0.9	0.2	0.3	95.8
5528-60 E	2.5	0.8	0.2	0.1	96.6

Table 2 continued.

Lignin Fraction	0-2	2-4	4-6	6-8	Acetone
	------ Eluent Fraction (ml) ------				
	Percentage of ^{14}C-Metolachlor Released				
5528-61 C	4.3	1.1	0.5	0.4	94.3
5531 75 A	20.3	1.8	1.2	0.9	75.9
5531 75 B	46.6	9.7	2.6	2.0	39.3
5531 75 B	44.4	18.0	3.8	3.4	30.7
5531 75 C	22.1	6.8	3.9	2.5	49.9
5531 75 D	57.2	11.7	3.2	1.6	26.2
REAX	27.9	3.1	1.6	1.3	66.5
RLX 5528 6B	15.8	4.6	2.4	1.4	75.8
BEC	17.9	5.0	3.0	1.8	73.7
OS-lignin	12.0	5.5	2.5	2.0	77.0
BEC W/SEPH	4.4	1.5	0.5	0.4	93.2
Tech Sand	85.8	9.1	1.6	0.8	3.9
Talc Sand	94.4	3.6	0.8	0.4	0.8

Table 3. Effect of various lignin fractions on the rate of release of ^{14}C-metolachlor.

	------ Eluent Fraction (ml) ------				
	0-2	2-4	4-6	6-8	Acetone
Lignin	Percentage of ^{14}C-Metolachlor Recovered				
5531-75B	46.6(3.1)[1]	9.7(7.5)	2.6(0.3)	2.0(0.3)	39.1(5.0)
5531-75A	20.3(1.3)	1.8(0)	1.2(0)	0.9(0.2)	75.6(0.8)
5531-75C	22.1(4.4)	6.8(1.4)	3.6(0.9)	2.5(0.5)	65.2(7.3)
5531-75D	57.2(0.8)	11.7(1.3)	3.2(0.6)	1.6(0.1)	26.4(1.1)
BEC	11.4(4.9)	5.4(3.2)	4.6(1.8)	4.7(1.3)	73.1(7.9)
5528-60E	9.9(8.6)	3.2(2.6)	2.2(1.8)	0.7(0.8)	84.2(12.7)
PC 959B	56.5(18.5)	23.3(8.3)	7.1(6.7)	4.4(4.6)	8.3(5.6)
PC 950W	22.1(1.6)	2.3(0.1)	1.3(0.2)	0.7(0.1)	73.8(1.9)
RLX 5528	15.8(1.1)	4.6(0.1)	2.4(0.1)	1.4(0.1)	75.9(0.6)
5-24-86-A	28.6(2.6)	8.2(0.8)	4.9(0.6)	3.1(0.3)	54.8(3.4)
Technical	76.9(14.3)	16.1(14.7)	3.1(1.3)	2.1(1.0)	3.1(1.3)
Talc	90.1(6.0)	5.5(4.1)	1.6(0.9)	0.9(0.3)	1.8(1.2)

[1] The standard deviation follows the mean of the percentage of ^{14}C-metolachlor released with each aliquot.

Table 4. Leaching properties of an emulsifiable concentrate and controlled release lignin-metolachlor.

Depth	Metolachlor	Lignin:Metolachlor
	Shoot Length	
(cm)	(% of control)[1]	
0-3	0 C	0 C
3-6	0 C	75 B
6-9	75 B	106 A
9-12	91 AB	97 AB
12-15	94 AB	97 AB
15-18	89 AB	97 AB
18-21	101 A	111 A
21-24	108 A	89 AB

LSD = 21

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[1] Means followed by the same letter are not significantly different from each other by the Duncan's Multiple Range Test at the 5% level of significance.

Table 5. Evaluating metolachlor movement as affected by the leaching of 100, 200 and 400 ml of water.

Soil Depth	Emulsifiable Concentrate of Metolachlor			Lignin:Metolachlor		
	Water leached through columns			Water leached through columns		
(cm)	100 ml	200 ml	400 ml	100 ml	200 ml	400 ml
	----(% of control)----			----(% of control)----		
0-3	0 K[1]	81 CDE	36 F-J	1 K	8 IJK	26 H-K
3-6	3 JK	16 H-K	65 EFG	83 CDE	79 CDE	99 B-E
6-9	3 JK	26 H-K	64 EFG	88 CDE	88 CDE	94 B-E
9-12	38 F-I	18 IJK	36 G-J	84 CDE	84 CDE	103 BC
12-15	68 DEF	6 H-K	23 H-K	87 CDE	81 CDE	86 CDE
15-18	86 CDE	17 FGH	21 H-K	83 CDE	95 B-E	106 BC
18-21	94 B-E	46 CDE	20 H-K	87 CDE	87 CDE	104 BC
21-24	92 CDE	88 CDE	41 FGH	107 BC	87 CDE	102 BCD
24-27	107 BCE	91 EFG	95 B-E	90 CDE	92 CDE	126 AB
27-30	145 A	66 F-J	108 BC	87 CDE	97 B-E	103 BC

LSD = 27

[1] Means followed by the same letter are not significantly different from each other by the Duncan's Multiple Range Test at the 5% level of significance.

Table 6. The effect of the ratio of lignin to metolachlor on the release rate of the ^{14}C-metalochlor.

	------ Eluent Fraction (ml) ------				
Ratio	0-2	2-4	4-6	6-8	Acetone
Formulation	Percentage of ^{14}C-Metolachlor Recovered				
Lignin:Metolachlor					
1:1	44.8(10.8)[1]	4.8(1.4)	1.6(0.4)	0.8(0.2)	48.1(12.2)
3:1	20.3(6.8)	6.3(2.3)	3.2(1.7)	2.0(0.8)	66.7(13.0)
6:1	14.8(6.8)	6.1(1.7)	3.6(1.7)	2.7(1.5)	72.6(7.1)
Technical Neat	85.8(5.8)	9.1(3.6)	1.7(0.3)	0.8(0.2)	3.9(0.2)
Lignin:Chloramben					
1:1	56.2(3.0)	14.4(2.8)	5.0(1.7)	3.7(2.6)	20.5(8.0)
3:1	13.3(6.7)	6.0(3.6)	3.3(3.3)	2.7(2.9)	74.5(16.2)
6:1	14.1(5.4)	9.6(6.5)	3.6(1.0)	3.5(2.0)	69.3(13.0)

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1. The standard deviation follows the mean of the percentage of ^{14}C- metolachlor or ^{14}C-chloramben released with each aliquot.

Table 7. The effect of 2:1 and 3:1 ratios of lignin:metolachlor on the release of metolachlor.

Depth	Dual	Lignin: Metolachlor (2:1)	Lignin: Metolachlor (3:1)
	Shoot Length		
(cm)	----------(% of control)---------		
0-3	0 C[1]	0 C	0 C
3-6	0 C	69 B	77 B
6-9	5 C	102 A	102 A
9-12	107 A	88 AB	104 A
12-15	103 A	91 AB	92 AB

LSD = 21

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[1] Means followed by the same letter are not significantly different from each other by the Duncan's Multiple Range Test at the 5% level of significance.

Table 8. Impact of formulation particle size on the release of ^{14}C-metolachlor.

(mesh size)	------ Eluent Fraction (ml) ------				
	0-2	2-4	4-6	6-8	Acetone
Formulation	Percentage of ^{14}C-Metolachlor Recovered				
40	1.8(1.8)[1]	1.1(0.2)	0.8(0.9)	0.1(0.1)	96.0(0.6)
60	12.4(5.4)	4.4(1.7)	3.3(2.1)	3.2(2.2)	77.9(9.1)
80	12.5(6.4)	5.0(0)	7.0(0.7)	8.5(3.5)	66(12.7)

1. The standard deviation follows the mean of the percentage of ^{14}C-metolachlor released with each aliquot.

Table 9. Water bath test effect of time and particle size on the release of metolachlor[1].

	Particle size (mesh)				
	<40[2]	40	60	80	Mix
Time (hr)	DPMs in a 0.5 ml aliquot				
1	0	5	10	56	46
2	0	13	17	98	27
4	1	11	20	87	38
8	3	20	34	95	47
24	11	30	39	86	55
48	23	40	48	74	61
96	86	65	66	113	86

1. Lignin-metolachlor formulation added to 20.0 ml of water. Release rate determined by DPM's found in 0.5 ml water extract removed and analyzed at the designated times.

2. Mesh size 40 indicate all material failing to pass through a 40 mesh screen, 40 mesh particles passing through a 40 mess screen but not a 60 mesh screen. The mix is a well ground mixture not screened.

Table 10. The effect of swelling materials on the release of ^{14}C-metolachlor from lignin (BEC).

	--- Eluant Fraction (ml) ---				
	------ H_2O ------				- Acetone -
	0-2	2-4	4-6	6-8	8-10
Formulation	Percentage of ^{14}C-Metolachlor Recovered				
BEC[1]	13.3(4.9)[2]	6.2(3.6)	4.8(1.9)	4.6(1.4)	71.4[3](9.4)
Gel A	17.0(6.4)	4.4(1.0)	2.8(0.4)	2.2(0.4)	73.5 (5.7)
Gel B	12.9(2.1)	4.0(0.5)	2.3(0.4)	2.0(0.2)	81.7 (2.9)
Gel C	13.4(3.9)	3.9(0.9)	2.5(0.3)	1.9(0.3)	78.3 (4.7)
Gel D	15.0(5.8)	4.8(0.7)	3.1(0.9)	2.6(0.8)	74.5 (4.4)
Gel E	13.5(5.8)	4.5(1.1)	3.5(0.5)	3.1(0.8)	75.8 (5.3)
Gel F	13.87(6.7)	4.5(2.1)	3.2(1.0)	2.6(0.8)	75.8 (9.0)

1. The following are descriptions of the swelling gels: BEC no gel, gel A - Super Slopper, gel B - Laponite RD, gel C - Re 8797 Carrageenan, gel D - Liqua Gel, gel E - RE 8796, gel F - Natrosal Hydroxyethal Cellulose.

2. The standard deviation follows the mean percentage of ^{14}C-metolachlor released with each aliquot.

3. The final aliquot is released with acetone.

Table 11. The effect of swelling materials on the release of ^{14}C-metolachlor over time.

Formulation	1	2	4	8	24	72
	----- time (hours) -----					
	DPMs Recorded From a 0.5ml Aliquot					
Gel A[1]	45(12)[2]	81(16)	113(27)	153(33)	221(44)	287(48)
Gel B	16(15)	33(30)	52(38)	73(52)	120(74)	168(79)
Gel C	26(6)	56(14)	70(18)	70(15)	83(18)	116(23)
Gel D	110(27)	129(33)	149(34)	192(37)	268(57)	337(157)
Gel E	76(18)	83(19)	92(24)	104(26)	138(7)	147(27)
Gel F	69(14)	75(12)	82(16)	89(16)	96(16)	112(19)

1. The following are descriptions of the swelling materials utilized in this study: Gel A - Super Slopper, Gel B - Laponite RD, Gel C - Re 8797 Carrageenan, Gel D - Liqua Gel, Gel E - RE 8796, Gel F - Natrosal Hydroxyethal Cellulose.

2. The standard deviation follows the mean percentage of ^{14}C-metolachlor released with each aliquot.

Table 12. Water bath test measuring the effect swelling materials on the release of metolachlor.

Formulation	0	24	48	144	Acetone
	----- time (hours) -----				
	Percentage of ^{14}C-Metolachlor Recovered				
BEC	11[1]	6	5	7	71
Gel A	12	14	11	12	52
Gel B	11	11	9	11	58
Gel C	13	8	5	8	65
Gel D	15	15	11	12	47
Gel E	12	8	6	7	66
Gel F	15	14	11	12	49
Technical	94	5	1	0	0
Talc	94	5	1	0	0

---

1. Values reported represent the mean of two replicated studies with a single value generated for each test.

Table 13. Controlled release properties of lignin for metolachlor measured under field conditions.

Treatment	21 DAT	42 DAT
	(percent control)	
Metolachlor	96 A[1]	91 A
BEC-super slurp metolachlor	95 A	77 A
BEC-metolachlor	48 A	29 B
LSD =	27	29

[1] Means followed by the same letter are not significantly different from each other by the Duncan's Multiple Range Test at the 5% level of significance.

Table 14. Field trial results measuring the soil residual levels of metolachlor application.

Treatment	Soil Depth (cm)		
	0 - 15	15-30	30-45
	(ppm w/w)		
Control	0.0 A[1]	0.0 B	0.0 D
Dual	0.26 A	0.02 B	0.01 C
BEC-superslurp metolachlor	0.27 A	0.03 B	0.02 B
BEC-metolachlor	0.38 A	0.09 A	0.03 A

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[1] Means followed by the same letter are not significantly different from each other by the Duncan's Multiple Range Test at the 5% level of significance.

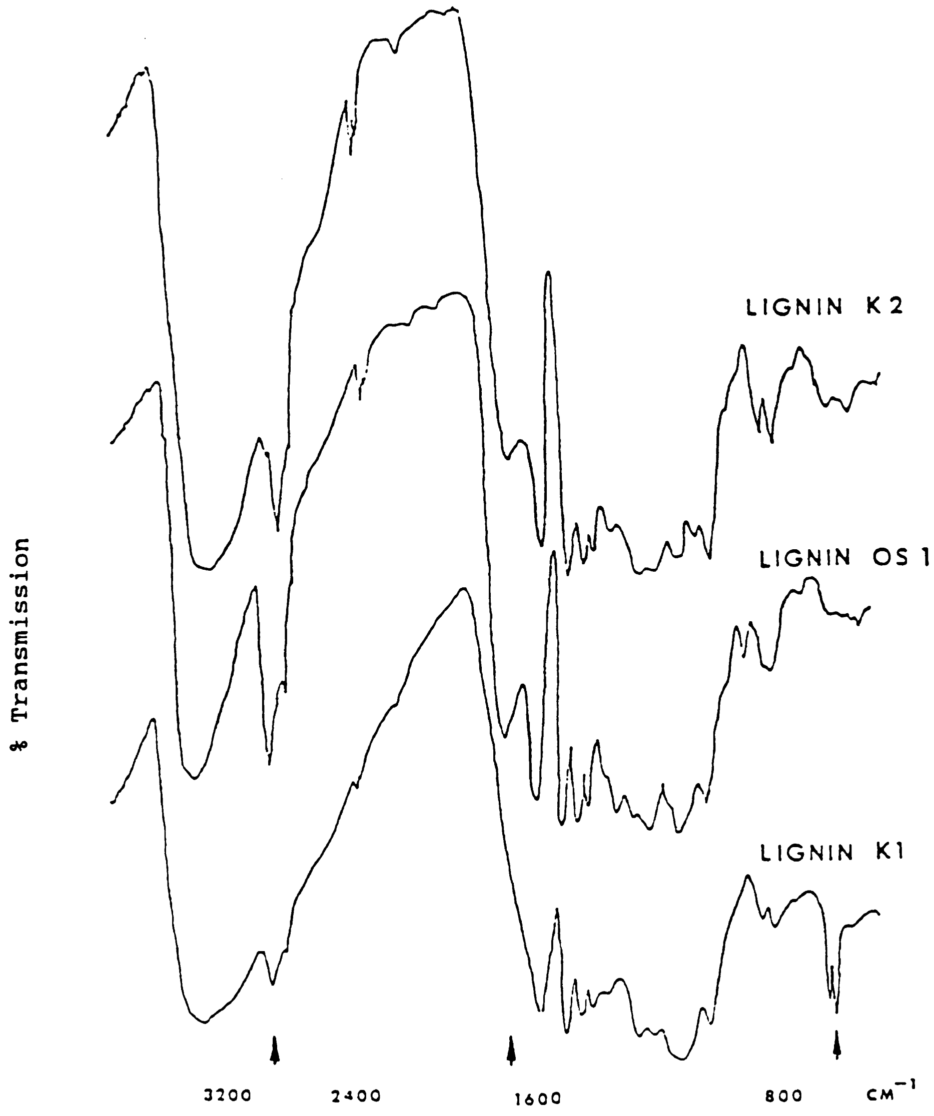

Figure 1. The infrared spectra of the lignin fractions:
K_1 - PC922W, K_2 - 5528-60E, and OS_1 - BEC Spbil 807.

Figure 1. Infrared spectra of lignin fractions K_1, K_2 and OS_1.

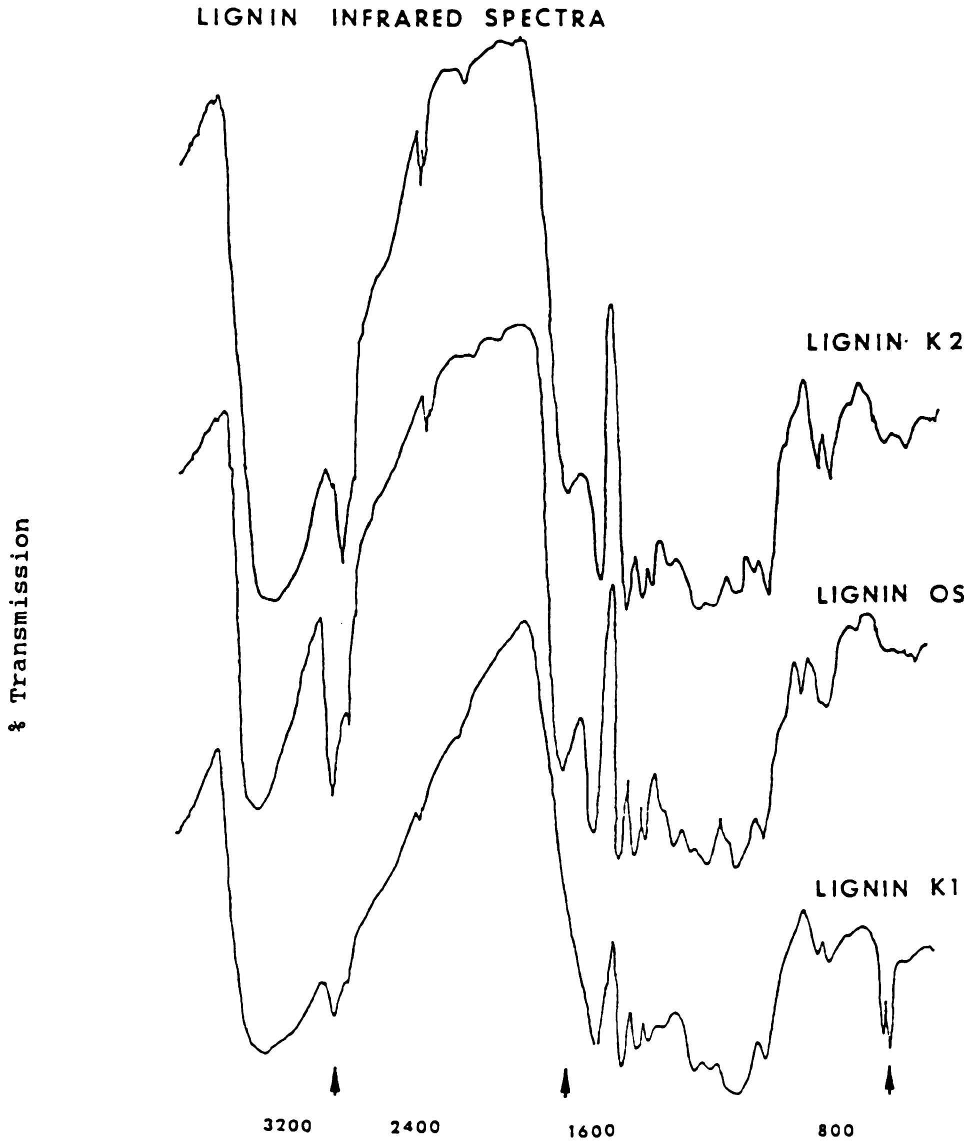

Figure 2. The infrared spectra of the lignin fractions:
K_3 - RLX 5528-60B, and OS_2 - BEC Spbil 826.

Figure 2. Infrared spectra of lignin fractions K_3, K_4 and OS_2.

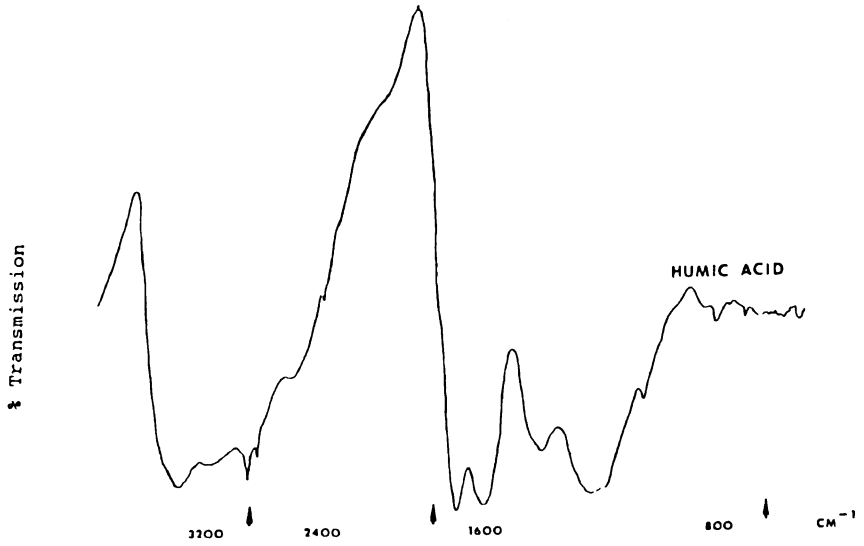

Figure 3. Infrared scan of humic acid (Aldrich).

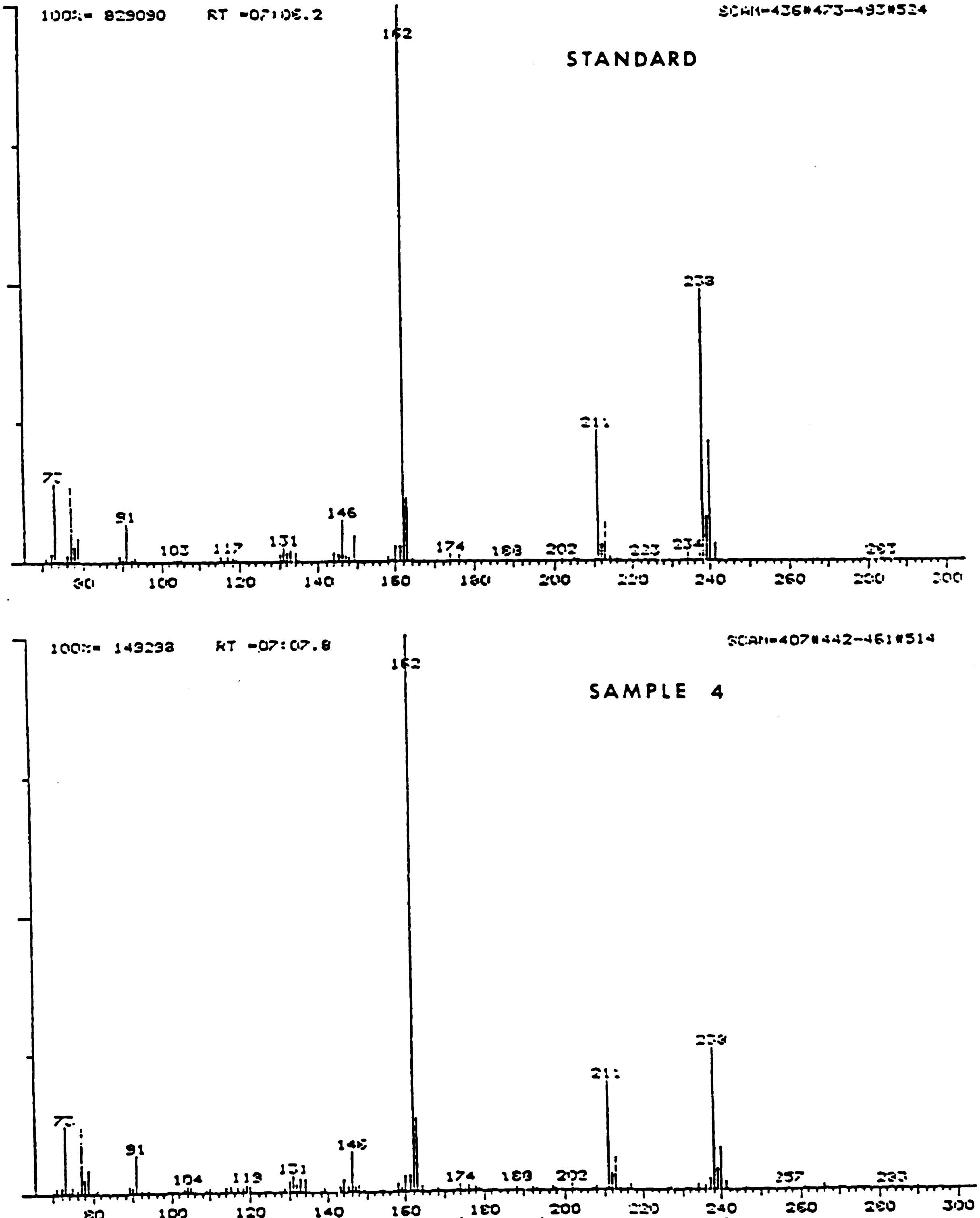

Figure 4. Mass spectrometer confirmation of soil extracted metolachlor.

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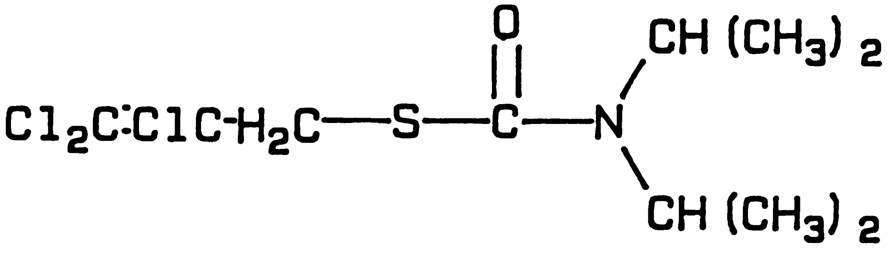
APPENDIX A

TRIALLATE

Physical form: Colourless crystals (technical: oily amber liquid)
Melting point: 29 - 30 C
Boiling point: 117 C at 0.3 mmHg
Vapour pressure: 16 mPa at 25 C
Solubility: 4 mg/l in water at 25 C
Misc: Limited use in small grains for wild oat control.

Figure 1. Triallate structure and physical properties.

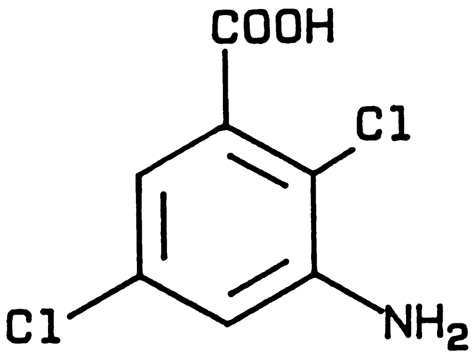


$$Cl_2C{:}ClC\text{-}H_2C-S-\overset{\overset{O}{\|}}{C}-N\begin{matrix}CH(CH_3)_2\\ CH(CH_3)_2\end{matrix}$$

TRIALLATE

CHLORAMBEN

Physical form: Colourless liquid
Boiling point: 100°C at 0.001 mmHg
Vapour pressure: 1.7 mPa at 20°C
Solubility: 530 mg/l in water at 20°C
Misc: Concern regarding ground and surface water contamination.



CHLORAMBEN

Figure 2. Chloramben structure and physical properties.

QUINCLORAC

Physical form: Colorless crystalline, faint odor
Melting point:
Boiling point:
Vapour pressure:
Solubility: 6.2 mg/100 ml in water at 25°C
Misc:

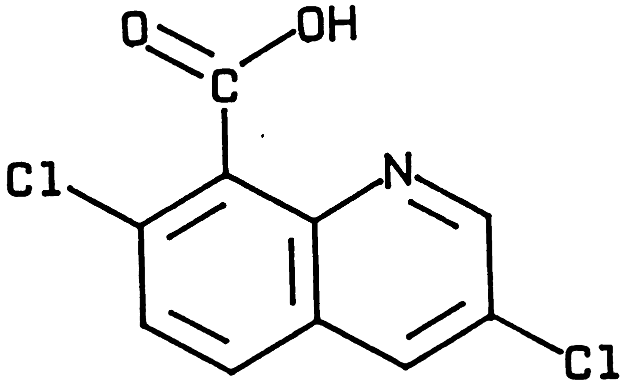


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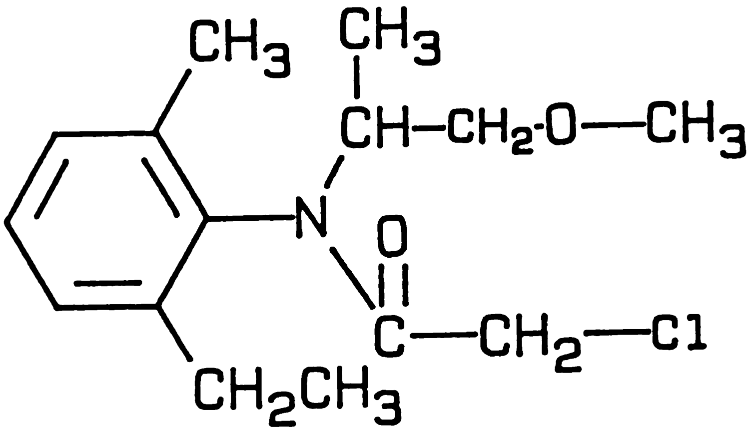
Figure 3. Quinclorac structure and physical properties.

METOLACHLOR

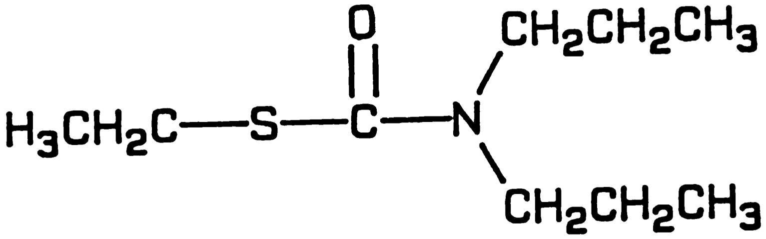


METOLACHLOR

Figure 4. Metolachlor structure and physical properties.

EPTC

Physical form:	Colourless liquid
Boiling point:	127°C at 20 mmHg
Vapour pressure:	4.7 Pa at 25°C
Solubility:	375 mg/l in water at 25°C
Misc:	Subject to rapid microbial breakdown3

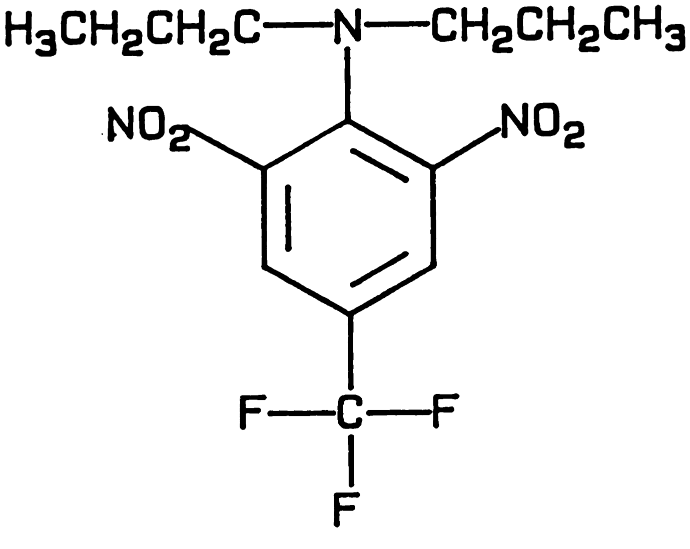


EPTC

Figure 5. EPTC structure and physical properties.

TRIFLURALIN

Physical form:	Yellow-orange crystals
Melting point:	48.5 - 49°C
Boiling point:	139 - 140°C at 4.2 mmHg
Vapour pressure:	4.7 Pa at 25°C
Solubility:	375 mg/l in water at 25°C
Misc:	Decomposition by UV light

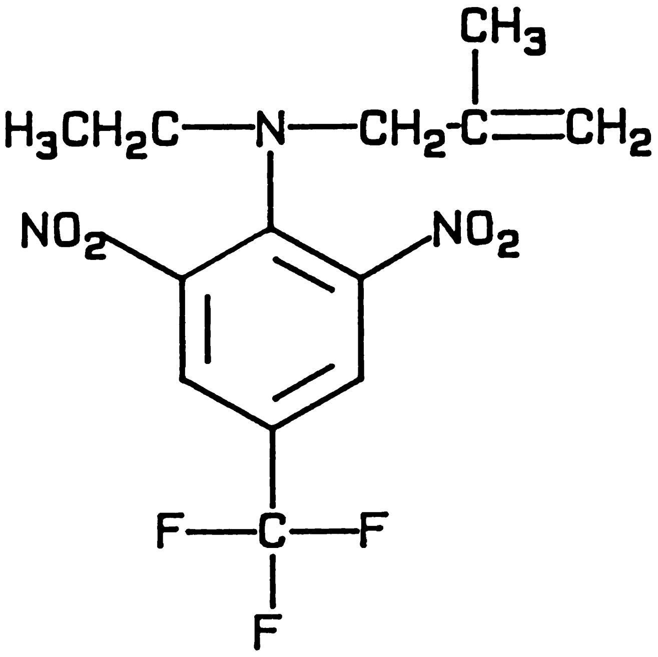


TRIFLURALIN

Figure 6. Trifluralin structure and physical properties.

ETHALFLURALIN

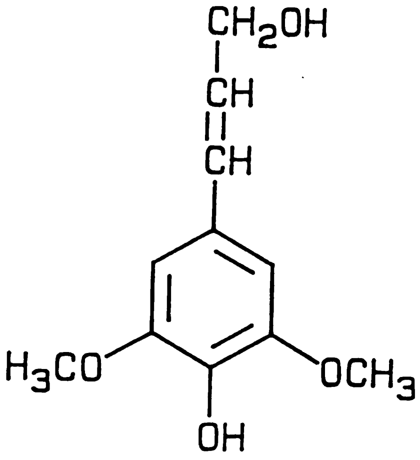
Physical form: Yellow-orange crystals
Melting point: 57 - 59°C
Boiling point: Decomposes at 256°C
Vapour pressure: 0.11 mPa at 25°C
Solubility: 0.2mg/l in water at 25°C
Misc: Decomposition by UV light



ETHALFLURALIN

Figure 7. Ethalfluralin structure and physical properties.

CONITERYL ALCOHOL



SINOPYL ALCOHOL

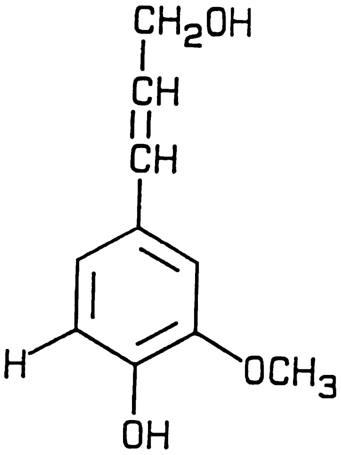


Figure 8. Coniferyl and sinapyl alcohol basic components of lignin.

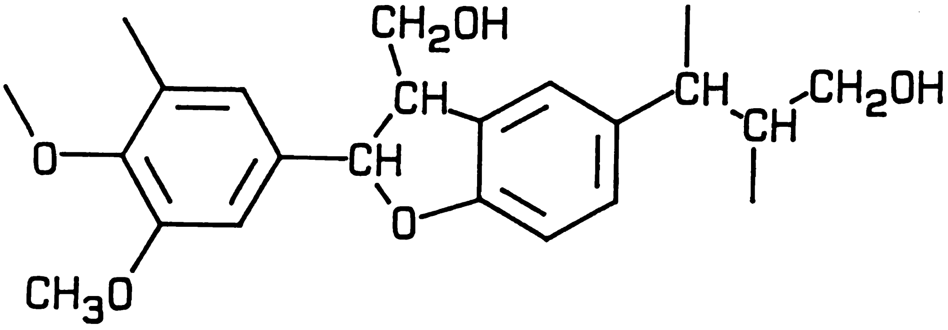


Figure 9. Proposed structure for lignin.

APPENDIX B

#	Description	% Solid
5531-75A	tal lignin pptd from Batch P____ Liquor at pH=2.	29.7
5531-75B	HEXA lignin 10 Moles NH_3, 1 mole HEXA	17.8
5531-75C	Indulin A - spray dried	17.6
5531-75D	Methylocated lignin (3 mole HCHO) plant PC910 2/6/85	20.5
5531-75E	Hardwood lignin (Rx-31) 16.5%	16.5
5531-75F	Peat slurry	7.7
5528-60A	"A" crosslinked with 0.25 moles HCHO	30.8
5528-60B	"A" crosslinked with 0.50 moles HCHO	26.8
5528-60C	"A" crosslinked with 0.75 moles HCHO	14.9
5528-60D	"A" crosslinked with 0.25 moles glut__________	29.1
5528-60E	"A" crosslinked with 0.50 moles glut__________	26.9
5528-61A	"B" oxidized 1.5 days at pH=12, room temperature Co^{++}cat	23.4
5528-61B	"A" oxidized with 10% H_2O_2 at pH=15	19.4
5528-61C	"A" oxidized with NaOcl* at pH=3.5 * 1ml/g lignin, 4-6% active on chlorine	19.5

PC922 L	"C" isolated at pH=2 to pH=12, oxidized at 180 F to chi______ 30 or less	17.7
PC922 LW	PC922L washed to remove soluble lignin and inorganice material	16.0
PC922 H	"C" isolated at pH=6 to pH=12, oxidized at 180 F to chi_______ of 30 or less	13.6
PC922 HW	PC922 H washed to remove soluble lignin and inorganic material	12.3
PC949 W	"C" isolated at pH=6 to pH=12, oxidized at 150 F for 47 hours and pptd at pH=6	10.8
PC949 N	PC949 adjusted to pH=7 after pptd and washed	9.0
PC950 W	"C" isolated at pH=6 to pH=12 oxidized at 150 F for 48 hours, final product pptd at pH=2	6.0
PC950 N	PC950 adjusted to pH=7 after pptn and washed	6.6
PC940 C	Plant A oxizided at pH=12 for 37 days at ambient temperatures	7.0
PC940 D	Spray dried PC940 C (=to 940C)	