

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 contaminants 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 bipyridiliums 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-

¹⁴C-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 ¹⁴C 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 State 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 <u>irrigation</u>
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% H²O 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 H²O 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 Na₂SO₄. 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 H₂O. 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:

<u>Lignin fraction</u>	<u>Coded as</u>
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 Perkin 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 measured in the tons per acre versus 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 than 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 encase the pesticide. Many of the lignin fractions demonstrated a tendency to dissolve in acetone. On drying the lignin becomes 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 through 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 than the other treatments but not at 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 controlled 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 must be higher for comparable control. The success of release of dichlorvos (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 where 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 with 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 explain 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 formulation and the 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.

Time (hr)	-- with Lignin --	-- without Lignin --
	----- 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 H₂O in the sequence described: 30 ml of ¹⁴C-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 ¹⁴C-metolachlor form various lignin fractions.

<u>Lignin Fraction</u>	----- Eluent Fraction (ml) -----				
	0-2	2-4	4-6	6-8	Acetone
	<u>Percentage of ¹⁴C-Metolachlor Released</u>				
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.

<u>Lignin Fraction</u>	0-2	----- Eluent Fraction (ml) -----			Acetone
		2-4	4-6	6-8	
<u>Percentage of ¹⁴C-Metolachlor Released</u>					
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.

<u>Lignin</u>	<u>Percentage of ^{14}C-Metolachlor Recovered</u>				
	0-2	----- Eluent Fraction (ml) -----			Acetone
		2-4	4-6	6-8	
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 (cm)	Metolachlor	Lignin:Metolachlor
	Shoot Length -----(% 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

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			(cm)
	Water leached through columns			Water leached through columns			
	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 -metolachlor.

Ratio Formulation	----- Eluent Fraction (ml) -----				
	0-2	2-4	4-6	6-8	Acetone
	<u>Percentage of ^{14}C-Metolachlor Recovered</u>				
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)

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 (cm)	Dual	Lignin: Metolachlor (2:1)	Lignin: Metolachlor (3:1)
		Shoot Length -----(% 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

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 ¹⁴C-metolachlor.

(mesh size) Formulation	----- Eluent Fraction (ml) -----				
	0-2	2-4	4-6	6-8	Acetone
	<u>Percentage of ¹⁴C-Metolachlor Recovered</u>				
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 ¹⁴C-metolachlor released with each aliquot.

Table 9. Water bath test effect of time and particle size on the release of metolachlor¹.

Time (hr)	-----Particle size (mesh)-----				
	<40 ²	40	60	80	Mix
	-----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 ¹⁴C-metolachlor from lignin (BEC).

<u>Formulation</u>	--- Eluant Fraction (ml) ---				
	----- H ₂ O -----				- Acetone -
	0-2	2-4	4-6	6-8	8-10
	<u>Percentage of ¹⁴C-Metolachlor Recovered</u>				
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 Hydroxyethyl Cellulose.

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

3. The final aliquot is released with acetone.

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

<u>Formulation</u>	----- time (hours) -----					
	1	2	4	8	24	72
	<u>DPMs Recorded From a 0.5ml Aliquot</u>					
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 Hydroxyethyl Cellulose.

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

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

<u>Formulation</u>	----- time (hours) -----				Acetone
	0	24	48	144	
	<u>Percentage of ¹⁴C-Metolachlor Recovered</u>				
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

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.

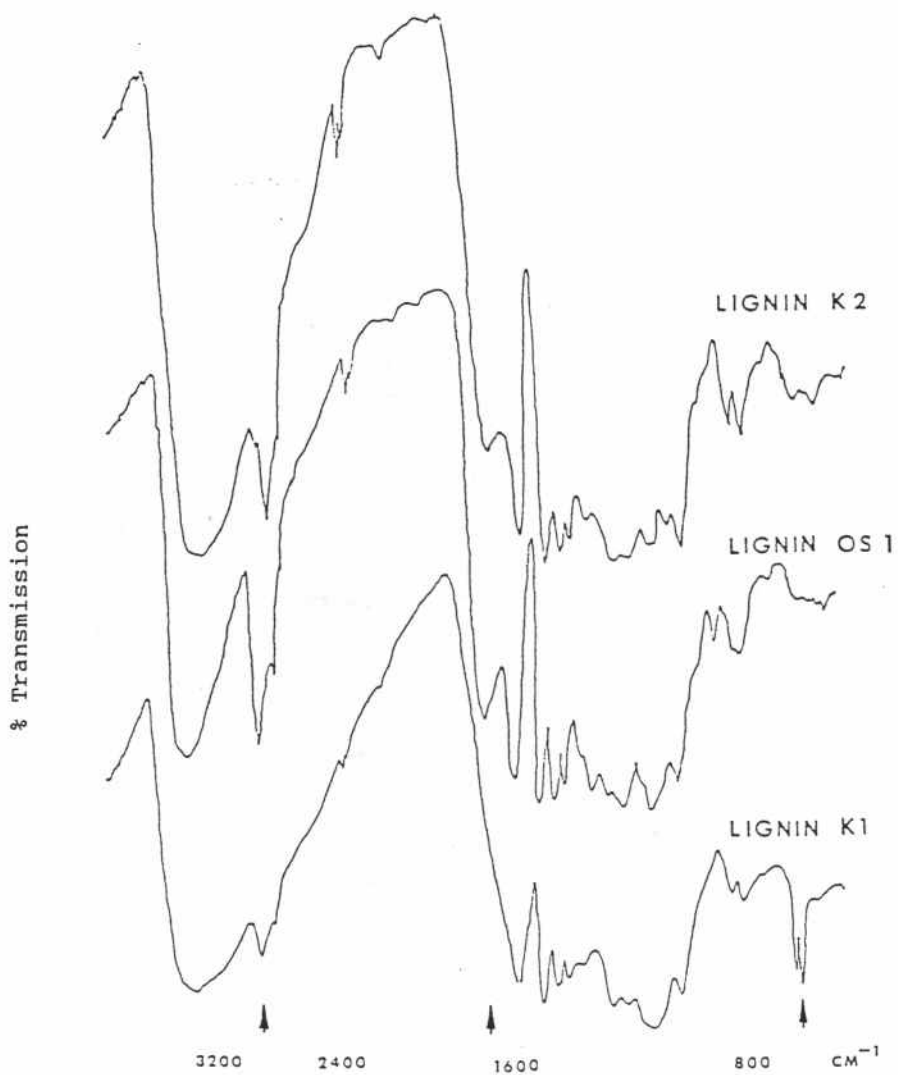


Figure 1. The infrared spectra of the lignin fractions:
K₁ - PC922W, K₂ - 5528-60E, and OS₁ - BEC Spbil 807.

Figure 1. Infrared spectra of lignin fractions K₁, K₂ and OS₁.

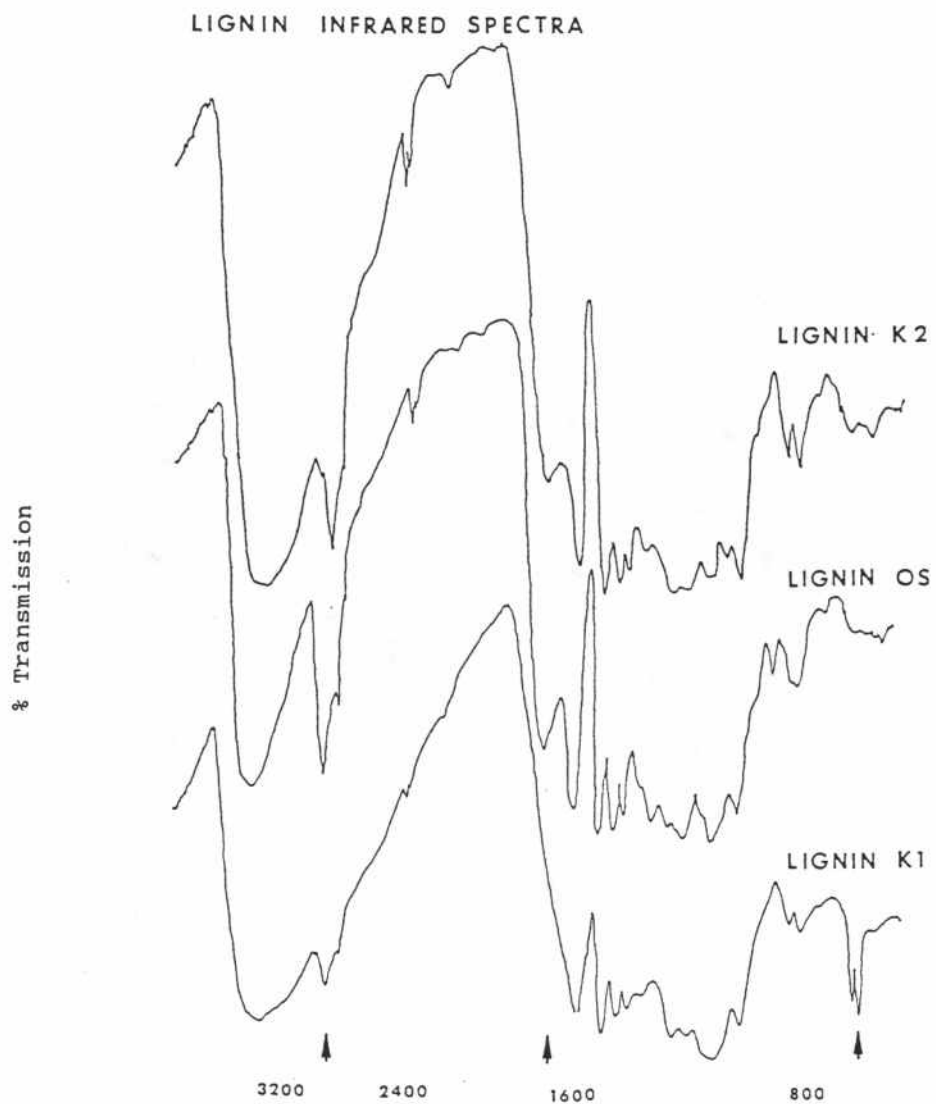


Figure 2. The infrared spectra of the lignin fractions:

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 .

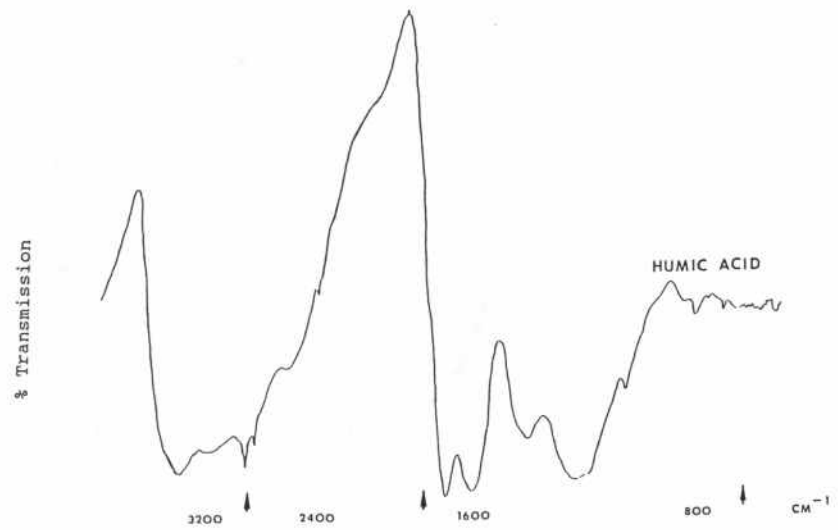


Figure 3. Infrared scan of humic acid (Aldrich).

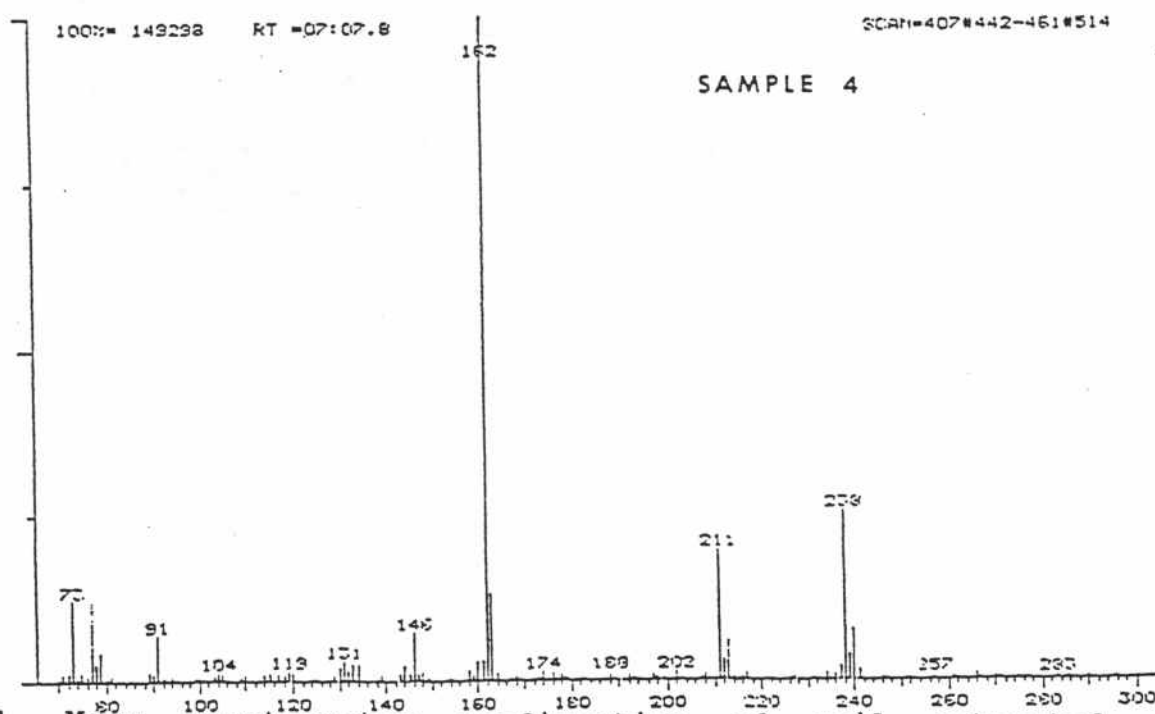
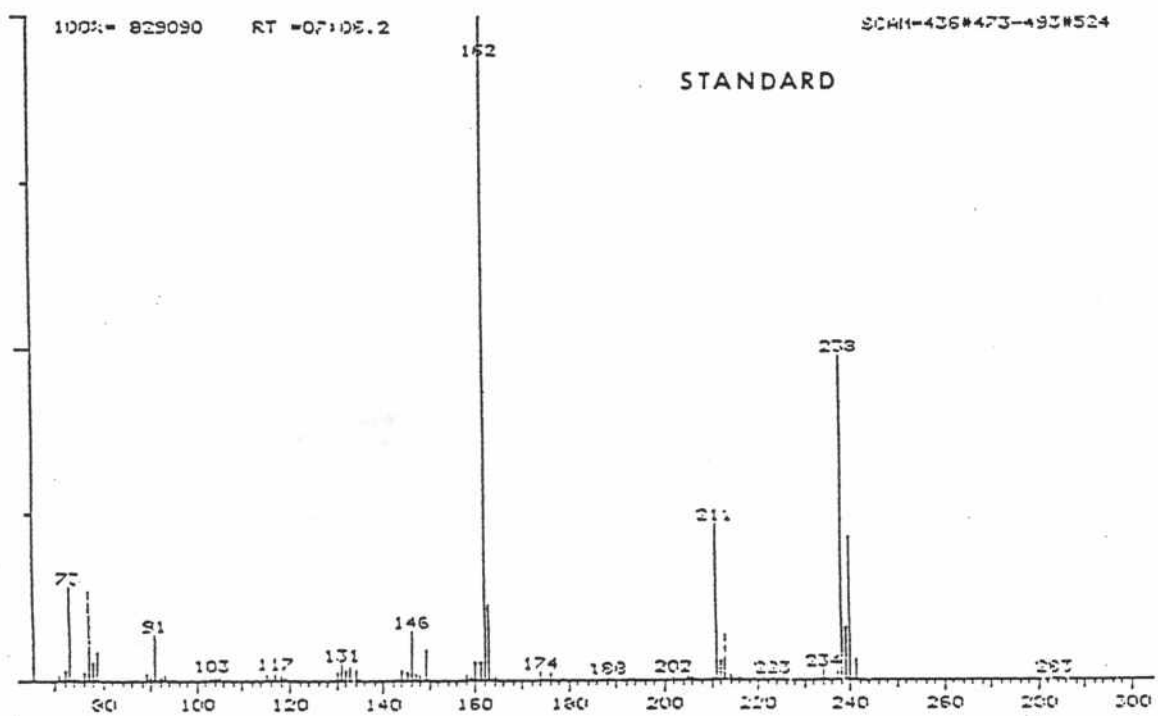


Figure 4. Mass spectrometer confirmation of soil extracted metolachlor.

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