

Kraft Lignin Adsorption of Metribuzin as a Controlled-Release Function Evaluation

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Metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4*H*)-one] adsorption by the nonsulfonated kraft lignins PC940A, PC940C, and Indulin AG was evaluated to determine if adsorption could explain the presence or absence of a controlled-release function. Indulin AG, a commercial grade lignin, adsorbed more than twice as much [¹⁴C]metribuzin in 6 h as did PC940C, an oxidized experimental lignin; however, by 24 h, PC940C had adsorbed approximately 80% as much [¹⁴C]metribuzin as did Indulin AG. PC940A, an experimental chemically modified, high-surface-area lignin, adsorbed the largest amount of [¹⁴C]metribuzin and established equilibrium in 10 min. In view of an earlier study, which found PC940C to be 3 times more effective than PC940A in reducing the mobility of [¹⁴C]-metribuzin in soil and which found Indulin AG to have no effect, results of the adsorption study lead to two general conclusions. The first is that adsorption analysis should not be the sole criterion for selecting a kraft lignin as a potential controlled-release agent for a soil-applied pesticide. The second is that if a kraft lignin has been found to alter the soil mobility pattern of a pesticide, then adsorption analysis may prove useful in determining how the controlled-release function operates and may prove useful in maximizing the potential of a lignin as a controlled-release agent.

INTRODUCTION

Kraft lignin interactions with many different pesticides have been examined in earlier papers. Kraft lignins were evaluated as controlled-release agents for 2,4-D [(2,4-dichlorophenoxy)acetic acid], ethoprop [phosphorodithioic acid *O*-ethyl *S,S*-dipropyl ester], and pentachloronitrobenzene (DelliColli, 1977, 1980) and for metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4*H*)-one], alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide], and chloramben [3-amino-2,5-dichlorobenzoic acid] (Riggle and Penner, 1988). Kraft lignin was shown to adsorb atrazine [6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine] (Dunigan and MacIntosh, 1971), carbendazim (1*H*-benzimidazol-2-ylcarbamic acid methyl ester), triadimefon [1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanone], and fenarimol [α -(2-chlorophenyl)- β -(4-chlorophenyl)-5-pyrimidinemethanol] (Barak et al., 1983). Kraft lignin is known to contain hydroxyl, carboxyl, keto, and phenoxy groups (Glasser et al., 1983). These functional groups can potentially adsorb different types of pesticides by either hydrogen-bonding, ionic-bonding, and/or van der Waals forces. Kraft lignin is composed of a series of cross-linked polymers that are spheroidal in shape and which may function as micelles (Goring, 1971). These micelles are believed to attract to one another by secondary bonding to form larger macromolecules (Goring, 1971). If a pesticide were attached to these micelles and in turn these micelles formed stable macromolecules, then it is possible that these macromolecules could function as controlled-release agents by serving as diffusion barriers for the entrapped pesticide. Using soil thin-layer chromatography (STLC), Riggle and Penner (1987) found that the experimental kraft lignins PC940A and PC940C, when combined with [¹⁴C]metribuzin, reduced the mobility of [¹⁴C]metribuzin in soil while the commercial kraft lignin Indulin AG had no effect. In addition, PC940C was found to reduce the mobility of [¹⁴C]metribuzin in soil columns

(Riggle and Penner, 1988) and to reduce metribuzin-related phytotoxicity for both greenhouse- and field-grown soybeans [*Glycine max* (L.) Merr.] while having no adverse effect on metribuzin-related weed control (Riggle and Penner, 1989). The purpose of this study was to examine [¹⁴C]metribuzin adsorption from an aqueous solution by the kraft lignins PC940A, PC940C, and Indulin AG to determine if adsorption patterns can explain the presence or absence of a controlled-release function.

MATERIALS AND METHODS

Kraft Lignins. Pine kraft lignins PC940A, PC940C, and Indulin AG were provided by Westvaco, Polychemicals Department, Charleston Heights, SC. Indulin AG is a commercial nonsulfonated pure kraft lignin, PC940A is a chemically modified nonsulfonated high-surface-area lignin that was derived from Indulin AG, and PC940C is an oxidized nonsulfonated kraft lignin that was also derived from Indulin AG. Lignins used were dark brown, dry powdered, grainy materials and were stored at room temperature in airtight plastic bottles.

Metribuzin Solutions. A metribuzin stock solution was made to the equivalent of 5.69 mM (1200 mg/L) using technical grade material and distilled water. This concentration represents the maximum water solubility of metribuzin under standard room conditions (Merck Index, 1989).

Radiolabeled [¹⁴C]metribuzin, labeled at the carbonyl group with a specific activity of 21.9 mCi/mmol, was prepared in methanol to the equivalent of 9.12 mM. Purity of [¹⁴C]metribuzin was confirmed by thin-layer chromatography using silica gel plate and developing with methanol and water (50:50 v/v). The plate was scanned with a Berthold 2D-TLC scanner LB276 using methane as the ionizing gas.

Adsorption Measurements. Adsorption measurements were made as follows. A sample of lignin (250 mg) was combined with metribuzin stock solution (2.5 mL) and [¹⁴C]metribuzin solution (3 μ L) in a 50-mL glass centrifuge tube. The ratio of lignin to combined metribuzin stock solutions was the same as used in an earlier STLC study (Riggle and Penner, 1987). The control consisted of the two combined metribuzin stock solutions, which were combined at the same ratio as used for the lignin tests but with no added lignin. Holding times consisted of 10 and 40 min and 1, 6, and 24 h. Each holding time was replicated four times. Tubes were shaken by a wrist-action shaker at 200 reciprocations/min, removed from the shaker, and centrifuged at 200g for 2 min.

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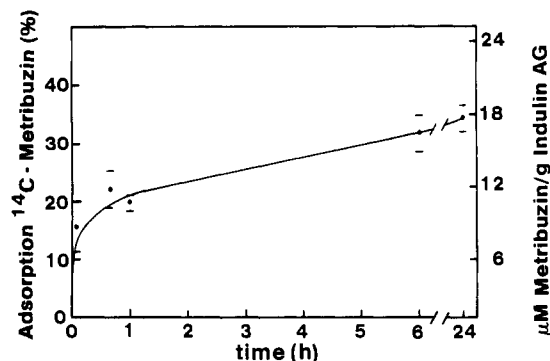


Figure 1. Indulin AG adsorption of [^{14}C]metribuzin from an aqueous solution as measured over 24 h. The linear equation for 0–1 h was $Y = 6.76 + 0.28X$ ($r = 0.77$) and for 1–24 h was $Y = 23.2 + 0.01X$ ($r = 0.78$).

Radioactivity in the resulting supernatant was determined by removing 100- μL subsamples, which were then placed in vials containing 10 mL of liquid scintillation counting fluid. Radioactivity levels were determined by liquid scintillation spectrometry using a Beckman liquid scintillation spectrometer. A reduction in radioactivity of the supernatant as compared to the control was attributed to [^{14}C]metribuzin adsorption by the lignin.

Adsorption Determinations. Adsorption data are presented as both a percentage of ^{14}C activity and as micromoles (unlabeled) of metribuzin per gram of lignin remaining in the container after the solution was removed. Percentage of the total value was determined by calculating radioactivity remaining in the supernatant compared to the total applied. The difference between the original total applied and the amount remaining in the supernatant was determined to be the amount adsorbed by the lignin. This was then calculated as micromoles per gram of lignin. It was assumed that there was no discrimination in adsorption between the labeled and nonlabeled metribuzin for all of the tested lignins. Linear equations for adsorption were determined as well as the coefficients of variation. Standard errors were determined and are depicted by brackets above and below the data points in the figures.

RESULTS AND DISCUSSION

Distilled water, 99.88% of total solvent, was used to analyze the interaction between metribuzin and lignins without the aid of an organic solvent. While organic solvents, such as dimethylformamide or acetone, would have allowed for higher metribuzin concentrations in solution, these solvents, if used in concentrated amounts, most likely would have altered both the physical and the chemical properties of the lignins. While methanol was the solvent for the [^{14}C]metribuzin solution, the final amount of methanol used in the lignin metribuzin preparations was less than 0.12% of the total volume. The solvent ratio of distilled water to methanol was similar to that used in an earlier study, which evaluated the desorption of metribuzin from the three lignins (Riggle and Penner, 1987).

The nonsulfonated kraft lignins were not soluble in water and were kept in suspension using the wrist-action shaker. The non-water-soluble characteristic of these nonsulfonated lignins is consistent with earlier reported results (Goring, 1971).

Adsorption test results found all three lignins have distinctly different adsorption patterns (Figures 1–3). For Indulin AG, the initial rate of [^{14}C]metribuzin adsorption in the first 10 min accounted for approximately half of the total adsorbed. Between 10 min and 6 h, the amount of the total [^{14}C]metribuzin adsorbed almost doubled. However, between 6 and 24 h, only a small amount of [^{14}C]metribuzin was adsorbed. For PC940C, the initial amount of [^{14}C]metribuzin adsorbed in the first 10 min accounted

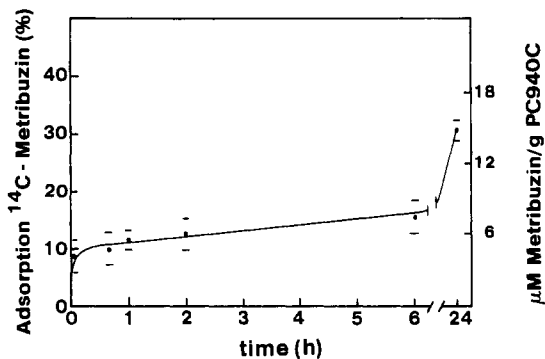


Figure 2. PC940C adsorption of [^{14}C]metribuzin from an aqueous solution as measured over 24 h. The linear equation for the entire 24-h period was $Y = 7.28 + 0.02X$ ($r = 0.93$), which indicated gradual adsorption after the first 10 min.

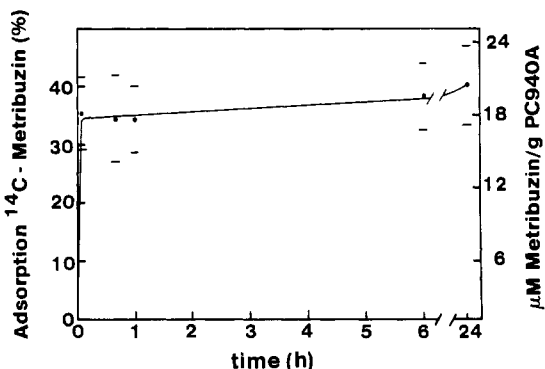


Figure 3. PC940A adsorption of [^{14}C]metribuzin from an aqueous solution as measured over 24 h. The linear equation for 10 min–24 h was $Y = 34.4 + X$ ($r = 0.84$), which indicated little, if any, additional adsorption after 10 min.

for approximately one-third of the total amount adsorbed. Between 10 min and 6 h, the amount of metribuzin adsorbed by PC940C accounted for only a slight increase. However, between 6 and 24 h there was an increase in the amount of adsorbed [^{14}C]metribuzin by PC940C. This increase during the last 18 h accounted for almost half of the adsorbed metribuzin. The adsorption pattern for PC940A was very different from those of the other two lignins. For PC940A, equilibrium was essentially established in the first 10 min of the test.

A comparison of the amounts of adsorbed [^{14}C]metribuzin shows that PC940A adsorbed approximately one-third more [^{14}C]metribuzin in the first 10 min than did PC940C for the entire 24-h period. PC940A adsorbed approximately the same amount of [^{14}C]metribuzin as did Indulin AG.

Results showed that initially [^{14}C]metribuzin was more accessible to the high-surface-area lignin PC940A than to either PC940C or Indulin AG. The PC940A adsorption pattern in the first 10 min suggests that adsorption took place on the surface of the lignin. Rapid adsorption of the [^{14}C]metribuzin in the first 10 min by both PC940C and Indulin AG also suggests that adsorption took place on the surface of these lignins. However, whereas PC940A essentially adsorbed all of its metribuzin in the first hour, PC940C only adsorbed one-third of the total adsorbed [^{14}C]metribuzin in the first 10 min, while Indulin AG adsorbed half of the total adsorbed [^{14}C]metribuzin in the first 10 min. The lower amounts of adsorbed [^{14}C]metribuzin for both PC940C and Indulin AG after the first 10 min suggest that the surface adsorption capacity of these lignins had been reached and that further adsorption was due to a matrix effect.

Just as the adsorption tests demonstrated that all three kraft lignins had different adsorption patterns and could adsorb [¹⁴C]metribuzin, an earlier soil thin-layer plate chromatography study (Riggle and Penner, 1987), which had been designed to evaluate control-release properties, found all three lignins had different desorption patterns. In the chromatography study, both PC940C and PC940A were found to reduce the amount of [¹⁴C]metribuzin that migrated from the point of application when soil thin-layer plates were developed with the water. However, Indulin AG was found to have no effect in reducing the mobility of [¹⁴C]metribuzin when soil thin-layer plates were developed in water.

The differences between the adsorption analysis results and the cited STLC results for PC940C and Indulin AG may be due to differences in the abilities of the micelles of the two kraft lignins to form tightly held macromolecules. Data suggest that PC940C formed a stable structure during the adsorption process that allowed for entrapment of [¹⁴C]metribuzin. Data also suggest that Indulin AG did not form a stable structure that could entrap metribuzin. The entrapment process allowed for a sustained release of metribuzin as measured in the cited STLC experiment. Evidence for entrapment is suggested by Goring (1971). In his review, Goring suggests the possibility that gellike spherical subunits of lignin may undergo micellar formation. Further evidence is provided that suggests that these micelles can form large macromolecules by secondary bonding. This suggests that PC940C micelles first adsorbed metribuzin onto their surfaces and then the micelles formed stable macromolecules, which in turn entrapped the metribuzin. These macromolecules proved to be stable in soil systems when exposed to water since they retained metribuzin. The evidence also suggests that under the same conditions Indulin AG micelles also adsorbed metribuzin onto their surfaces. However, these micelles did not form stable macromolecules, as was demonstrated by the soil thin-layer chromatography study that showed that [¹⁴C]metribuzin was not retained by the lignin when exposed to water. The differences between the two lignins in their ability to form stable macromolecules is most likely dependent upon the manufacturing processes used to generate them. Since PC940C is an oxidized form of Indulin AG, it is possible that PC940C micelles had different reactive functional groups than Indulin AG micelles and that these were responsible for forming more tightly cohesive macromolecules.

PC940A adsorption and desorption (cited STLC results) data suggest that, for this lignin, metribuzin adsorption is not dependent upon the formation of tightly held macromolecules. The results also suggest that PC940A has a higher loading capacity for metribuzin than was achieved using a 1200 mg/L concentration. While there was rapid adsorption of metribuzin by PC940A, there was also an increase in desorption (Riggle and Penner, 1987). This is in contrast to the proposed stable macromolecular formation effect of PC940C that resulted in a slower desorption of [¹⁴C]metribuzin from PC940C. PC940C was found to be almost 3 times more effective than PC940A

in reducing the mobility of [¹⁴C]metribuzin as measured by STLC (Riggle and Penner, 1987). These differences suggest that either PC940A consists of highly adsorptive stable macromolecules that do not reconstitute in shape or that PC940A consists of highly adsorptive micelles that are not capable of forming stable macromolecules.

The results of the adsorption measurements and a comparison of these results to the earlier STLC study lead to two general conclusions. The first is that, for nonsulfonated kraft lignins, adsorption measurements per se are not necessarily good indicators for potential controlled-release agents of soil-applied pesticides. The second is that if a nonsulfonated kraft lignin has been found to alter the soil mobility pattern of a pesticide, then adsorption analysis may be useful in determining the nature of the controlled-release function and may ultimately prove to be useful in maximizing the potential of the lignin as a control-release agent.

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