CHEMICAL PROPERTIES INFLUENCING RATE OF RELEASE
OF STARCH ENCAPSULATED HERBICIDES:
IMPLICATIONS FOR MODIFYING ENVIRONMENTAL FATE

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ABSTRACT

Starch encapsulation is a controlled release technology which may reduce a chemical's environmental contamination potential. Effectiveness of starch encapsulation in modifying environmental fate is not uniform for all herbicides. We quantified the time required for complete release of herbicides encapsulated in unmodified cornstarch (amylepectin:amylose ratio approximately 3:1) by an extrusion process. These herbicides exhibited a range of chemical properties. Time required for complete release of herbicides, encapsulated using this technology, was strongly correlated with water solubility of the encapsulated chemical. As water solubility of the encapsulated chemical decreased, time required for complete release increased exponentially. Results of field scale experiments suggests that starch encapsulation influences the environmental fate of an encapsulated herbicide when the time required for complete release is from 14 to 21 days. Results suggest that starch encapsulation will provide a satisfactory rate of release for herbicides that have water solubilities of 20 to 300 mg L⁻¹.

INTRODUCTION

Detection of agriculturally applied herbicides in precipitation (Buser, 1990; Goolsby et al., 1993; Nations and Hallberg, 1992; Trevisan et al., 1993), surface water (Goolsby and Battaglin, 1993; Thurman et al., 1991, 1992), and groundwater (Hallberg, 1989) has lead to an increase in awareness of the potential for environmental contamination by these chemicals. This increased awareness has resulted in an increase in efforts to develop formulation modifications or management practices that will reduce the potential for environmental contamination by agricultural herbicides. One formulation modification that is receiving increased attention is a controlled release technology involving the encapsulation of the herbicide in a cornstarch matrix using an extrusion process (Carr et al., 1991). Much of the research conducted with starch encapsulated herbicides has been done under greenhouse or
laboratory conditions with relatively few field experiments. The lack of field experimentation is likely the result of the expense associated with such research. To increase the efficiency with which research resources are utilized, a better understanding of how starch encapsulation influences herbicide behavior would be useful.

Starch encapsulation is a controlled release technology. The objective of controlled release is to deliver a sufficient concentration of herbicide to control weeds over some time period (Schreiber et al., 1987). Controlled release accomplishes this by reducing the susceptibility of the herbicide to losses by leaching, volatilization, and degradation. Controlled release should, therefore, also reduce the potential for environmental contamination by herbicides (Schreiber et al., 1987). Release of a starch encapsulated compound is governed mainly by a diffusion process. When starch granules are applied to the soil they imbibe water, swell, and the encapsulated compound diffuses out of the starch matrix. A number of factors influence the rate at which the release process proceeds: starch granule characteristics (i.e. size of granules, type of starch) (Wing et al., 1987, 1988), characteristics of the encapsulated chemical (Baur, 1980), and environmental factors (Wienhold and Gish, 1992).

Here we report on release kinetics of a number of starch encapsulated herbicides measured under several release conditions and relate release kinetics to known chemical properties of the encapsulated herbicides. We then review the results from those field experiments comparing the environmental fate of starch encapsulated herbicides to that of commercially formulated herbicides. We use the results of these studies to determine if the magnitude of the effect of starch encapsulation on modifying environmental fate could be explained using the relationship between release kinetics and chemical properties of the encapsulated herbicide.

**MATERIALS AND METHODS**

**Rate of herbicide release from starch granules**

Herbicides used in this study were alachlor [2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide], atrazine [2-chloro-4-ethylamino-6-isopropylamino-s-triazine], EPTC [S-ethyl dipropylthiouracilate], metolachlor [2-chloro-N-(2-ethyl-6-methyl)phenyl)-N-(2-methoxy-1-methylethy)acetamide, and metribuzin [4-amino-6-(1,1-dimethylthyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one]. Herbicides were encapsulated in unmodified cornstarch (amylopectin:amylose ratio approximately 3:1) using an extrusion process (Carr et al., 1991) (Table 1). Two size classes of starch granules were used; the large granules were 0.85 to 1.4 mm in diameter and the small granules were 0.425 to 0.85 mm in diameter. Starch encapsulated herbicides were produced at the Northern Regional Research Center, Agricultural Research Service, U. S. Department of Agriculture, in Peoria, IL. Herbicide standards were provided by the Pesticide Reference Standards Laboratory, U. S. Environmental Protection Agency, in Beltsville, MD.

Rate of release of the herbicides from the starch matrix was quantified by placing starch granules containing 0.5 mg active ingredient in a glass jar containing 25 ml of solution of known water potential. Water potential was adjusted by adding sufficient polyethylene glycol to deionized water to achieve water potentials of 0 and -1.0 MPa. Polyethylene glycol is a macromolecule that is readily soluble in water and has been used to simulate soil matric potential (Michel and Kaufmann, 1973). As water potential declines, more of the water is bound to the
polyethylene glycol macromolecule and water availability is reduced. The high level of water availability (0.0 MPa) used corresponds to a wet soil while the low level of water availability (-1.0 MPa) corresponds to a fairly dry soil. These two levels of water availability were chosen to encompass the range of water availabilities influencing starch granules in the field following a rainfall event and subsequent drydown. Samples were left undisturbed until sampled for solution herbicide concentration. The experiment was conducted for both size classes of starch granules and was replicated five times. Solution concentrations were determined after 1 and 6 hours and 1, 3, 5, 14, and 28 days. Solution concentration was determined by passing the sample through glass fiber filter paper to remove the starch granules and isolating the herbicides by solid-phase extraction (Nash, 1990). Recoveries of spiked samples using this extraction procedure were 111% for EPTC, 104% for atrazine, 108% for metribuzin, 104% for alachlor, and 80% for metolachlor. Herbicide concentrations were quantified using a gas chromatograph equipped with a nitrogen-phosphorus detector. Operating conditions of the gas chromatograph were: 30m by 0.32mm silica capillary column coated with 0.26 μm SPB-5; injector temperature of 200°C, oven temperature of 150°C and detector temperature of 220°C; He carrier gas at 2.5 ml min⁻¹. Prometryn [2,4-bis(isopropylamino)-6-(methylthio)-s-triazine] was used as an internal standard. Solution concentration was expressed as a percentage of chemical added to the jars.

Table 1. Percentage active ingredient in the two size classes of starch granules used to assess release kinetics of encapsulated herbicides.

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Large granules</th>
<th>Small granules</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% active ingredient</td>
<td></td>
</tr>
<tr>
<td>Alachlor</td>
<td>10.1</td>
<td>12.4</td>
</tr>
<tr>
<td>Atrazine</td>
<td>11.0</td>
<td>11.3</td>
</tr>
<tr>
<td>EPTC</td>
<td>15.3</td>
<td>14.3</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>8.9</td>
<td>8.5</td>
</tr>
<tr>
<td>Metribuzin</td>
<td>3.3</td>
<td>3.3</td>
</tr>
</tbody>
</table>

*1.4 to 0.85 mm in diameter.
*0.85 to 0.425 mm in diameter.
Data analysis

The rate constant for herbicide release from the starch matrix was determined by fitting the percentage release data to

\[
\% \text{ Release} = 100 \cdot (1 - \exp^{-kt})
\]

where \( k \) is the rate constant (days\(^{-1} \)) and \( t \) is time (days). The length of time necessary for complete release of the herbicides was calculated using these rate constants and solving this equation for \( t \) when the herbicide had been completely released. An analysis was then conducted to determine if the time required for complete release of these herbicides from two size classes of starch granules at two levels of water availability was correlated with chemical properties of these herbicides.

RESULTS AND DISCUSSION

Rate of release

Rates of release differed greatly among the five herbicides (Table 2). Depending on release conditions (granule size class and water availability), the value of \( k \) for the most quickly released herbicide was 20 to 135 times larger than that for the most slowly released herbicide. Release kinetics for all five herbicides were influenced by granule size and water availability. For a given herbicide, release was more rapid (\( k \) was larger) from the small starch granules than from the large starch granules (Table 2). Herbicide encapsulated in the small granules have a shorter diffusion path length than do herbicides encapsulated in the larger granules. Herbicide release from either of the starch granule size classes decreased (\( k \) declined) as water availability declined (Table 2). Many studies evaluating rates of release of starch encapsulated herbicides have been conducted using organic solvents or agitation of the solution. While these methods are useful for comparing different encapsulation techniques or obtaining relative differences in release characteristics among encapsulated herbicides, they are not realistic representations of conditions in the field. Mills and Thurman (in press) used methods similar to those used here to construct a release curve for atrazine encapsulated in starch granules similar to the small granules used in this study. They found that complete release in water (0.0 MPa water availability) required 19 d which is similar to the 16 d required for complete release in this study.

Previously we demonstrated that as water availability declined, swelling of the starch granules was reduced and rate of release of atrazine and alachlor was slowed (Wienhold and Gish, 1992). Here we include several additional herbicides that differ in chemical characteristics. The similarity in the effect of release conditions on release kinetics of the herbicides (i.e. faster release from small granules than from large granules and decrease in rate of release with a decline in water availability), the wide range of release rates exhibited by these herbicides, and the consistent order in rate of release among the herbicides suggests that chemical characteristics of the encapsulated herbicide has a strong influence on rate of release.
Table 2. Rate constants (k) for the release of five herbicides from a starch matrix as a function of starch granule size class and water availability.

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Release conditions*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Large, 0.0 MPa</td>
</tr>
<tr>
<td>Alachlor</td>
<td>$2.213 \pm 0.233^b$</td>
</tr>
<tr>
<td>Atrazine</td>
<td>$0.121 \pm 0.011$</td>
</tr>
<tr>
<td>EPTC</td>
<td>$0.813 \pm 0.195$</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>$1.713 \pm 0.075$</td>
</tr>
<tr>
<td>Metribuzin</td>
<td>$7.870 \pm 0.734$</td>
</tr>
</tbody>
</table>

*Large granules 1.4 to 0.85 mm diameter; small granules 0.85 to 0.425 mm diameter.

Correlation between rate of release and chemical properties

The herbicides used in this study exhibited a wide range of values in selected chemical properties (Table 3). Of these properties only solubility of the chemical in water was correlated with time for complete release of the herbicides under the release conditions used in this study (Table 4). As solubility increased the time required for complete release decreased. Since release was measured in solution it was not a surprise that saturated vapor density was not correlated with time required for complete release (Table 4). To assess whether adsorption affinity of the encapsulated herbicides for the starch matrix influenced the release kinetics, $K_w$ was included in the analysis. The low correlation between $K_w$ and time for complete release suggests that retention within the starch matrix does not appear to significantly effect release kinetics of these herbicides. There was little variation among the herbicides in molecular weight; hence, lack of a correlation between molecular weight and time for complete release seems reasonable. Plotting time for complete release as a function of solubility of the herbicide in water suggests that the relationship between solubility and rate of release is exponential in nature (Fig. 1). As solubility decreases the time required for complete release increases exponentially. Others (Baur, 1982; Mills and Thurman, in press; Wienhold and Gish, 1992) have suggested that solubility of the encapsulated herbicide influences the rate of release but no one has compared release kinetics for a sufficient number of different compounds to discern the nature of the relationship between solubility and rate of release. The relationship between solubility and time for complete release is consistent for all four release conditions used in this study. Solubility influences time for complete release to a greater degree than does granule size class or water availability.
Table 3. Selected chemical properties for the herbicides used in this study.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Solubility mg l⁻¹</th>
<th>Saturated vapor density μg l⁻¹</th>
<th>Kₐ₀ ml g⁻¹</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alachlor</td>
<td>242</td>
<td>0.32</td>
<td>161</td>
<td>269.8</td>
</tr>
<tr>
<td>Atrazine</td>
<td>33</td>
<td>0.008</td>
<td>107</td>
<td>215.7</td>
</tr>
<tr>
<td>EPTC</td>
<td>370</td>
<td>220</td>
<td>280</td>
<td>189.3</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>530</td>
<td>0.2</td>
<td>99</td>
<td>283.8</td>
</tr>
<tr>
<td>Metribuzin</td>
<td>1220</td>
<td>2.0</td>
<td>33</td>
<td>214.3</td>
</tr>
</tbody>
</table>

Table 4. Pearson correlation coefficients for time required for complete release of starch encapsulated herbicides as a function of release conditions and chemical characteristics of the encapsulated herbicide.

<table>
<thead>
<tr>
<th>Chemical property</th>
<th>Release conditions¹</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Large, 0.0 MPa</td>
<td>Large, -1.0 MPa</td>
<td>Small, 0.0 MPa</td>
<td>Small, -1.0 MPa</td>
<td></td>
</tr>
<tr>
<td>Solubility</td>
<td>-0.597*</td>
<td>-0.756**</td>
<td>-0.565*</td>
<td>-0.679**</td>
<td></td>
</tr>
<tr>
<td>Saturated vapor density</td>
<td>-0.122</td>
<td>-0.072</td>
<td>-0.216</td>
<td>-0.173</td>
<td></td>
</tr>
<tr>
<td>K₀</td>
<td>-0.045</td>
<td>0.157</td>
<td>-0.139</td>
<td>-0.006</td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>-0.315</td>
<td>-0.174</td>
<td>-0.281</td>
<td>-0.237</td>
<td></td>
</tr>
</tbody>
</table>

¹Large granules 1.4 to 0.85 mm diameter; small granules 0.85 to 0.425 mm diameter.
²Probability of correlation due to chance alone; *0.01, **0.001.

The effect of granule size on time for complete release can be seen visually by comparing the location of the points for the large granule class in Figs. 1A and 1B to the location of the points for the small granule size class in Figs. 1C and 1D. The time for complete release from the small size class is about one-half that from the large size class. Similarly, the effect of water availability on time required for complete release can be visualized by comparing the location of the points for the high level of water availability in Figs 1A and 1C to their location for low levels of water availability in Fig. 1B and 1D. Lowering water availability doubled the length of time necessary for complete release.
Fig. 1. Time required for complete release (mean ± SE) plotted against herbicide solubility in water. A.) Large starch granules, 0.0 MPa. B.) Large starch granules, -1.0 MPa. C.) Small starch granules, 0.0 MPa. D.) Small starch granules, -1.0 MPa.

Effect of starch encapsulation on herbicide fate

Starch encapsulation is a controlled release technology. The objective of controlled release is to modify the environmental fate of the encapsulated chemical. Desirable modifications include; improved efficacy, reduced worker exposure, increased persistence, and reduced environmental contamination due to volatilization, runoff, and leaching losses. A number of laboratory, greenhouse, and field experiments have been conducted to evaluate the
effect of starch encapsulation on meeting these objectives. Here we will look at studies that have evaluated the
effect of starch encapsulation on environmental fate of two or more herbicides under the same conditions to
determine if rate of release may be a useful parameter for predicting the effect of starch encapsulation on modifying
environmental behavior.

Volatilization

Wienhold and Gish (in press) conducted a field study to determine the effect of formulation and tillage
practice on volatilization losses of atrazine and alachlor. Atrazine and alachlor were applied as either a starch
capsulated formulation or as a commercial formulation to no-till and conventionally tilled fields. After
35 d, cumulative volatilization losses of commercial formulation atrazine were 9% of that applied to the
conventionally tilled field and 4% of that applied to the no-till field. Starch encapsulation reduced atrazine
losses to <2% of that applied to either tillage practice. Starch encapsulation did not affect cumulative volatilization
losses of alachlor from the conventionally tilled field with losses of 14% of that applied for both formulations.
Starch encapsulation reduced volatilization losses of alachlor from the no-till field to 4% of that applied compared
to 9% of that applied as the commercial formulation to no-till fields. In this study, losses of the more slowly
released herbicide (atrazine) were reduced to 25% of those of the commercial formulation. In contrast, starch
encapsulated had little or no effect (depending on tillage practice) on volatilization losses of a herbicide that
exhibited a faster rate of release (alachlor).

Runoff

Mills (1991) compared runoff losses of starch encapsulated atrazine and alachlor from experimental field
plots to runoff losses when the herbicides were applied as a powdered formulation. Herbicides were incorporated
into the 0 to 5 cm soil layer and precipitation (natural rain or irrigation) was applied beginning one day after
herbicide application. The experiment was replicated three times, once in the summer and twice in the fall. Starch
encapsulation reduced total runoff losses of atrazine to 40% of losses of the powdered formulation. In contrast,
runoff losses of alachlor did not differ between the two formulations. Starch encapsulation reduced runoff losses of
the more slowly released atrazine while influencing runoff losses of the more quickly released alachlor.

Leaching

Field scale mobility of starch encapsulated atrazine and alachlor was compared to that of commercially
formulated atrazine and alachlor under two tillage practices by Gish et al. (in press). Starch encapsulation reduced
the mobility of atrazine but did not modify the mobility of alachlor. Essentially all of the starch encapsulated
atrazine was confined to the root zone of the soil, mostly (50%) in the 0 to 5 cm layer compared to <20% of
commercial formulation atrazine. The commercially formulated herbicides and the more rapidly released starch
encapsulated alachlor are susceptible to preferential transport until they are adsorbed by the soil. In contrast, slowly
released starch encapsulated atrazine is retained within the starch matrix and is less likely susceptible to preferential
transport. As atrazine diffuses out of the granule it is adsorbed or diffuses into the smaller pores of the soil matrix
where transport is very slow. The authors suggested that as rate of release decreases, convection is reduced and
diffusion increases in importance with regard to herbicide transport. Since convection is potentially a much more
rapid transport process than is diffusion, a shift from convection to diffusion should result in decreased mobility of field applied herbicides.

Persistence

When rate of release of a starch encapsulated herbicide is slow enough that losses due to volatilization, runoff, and leaching are decreased, persistence should increase. Gish et al. (in press) found that starch encapsulation did not effect field-scale persistence of the rapidly released alachlor when compared to the commercial formulation. Persistence of the slowly released atrazine was greatly increased with nearly 25% of the chemical remaining in the surface 20 cm compared to <1% of the commercial formulation atrazine a year after application. White and Schreiber (1984) demonstrated that starch encapsulation increased persistence of incorporated trifluralin [a, a, a-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine] sufficiently that the herbicide could be applied the previous fall and weed control the following spring was sufficient to prevent any reduction in soybean yield. Trifluralin has a very low solubility in water (0.3 mg l⁻¹) and should have a very slow rate of release. The increased persistence exhibited by some herbicides when compared to commercial formulations of these herbicides suggests that losses via the available pathways has been reduced. This reduction in the loss of herbicides should allow for lower initial application rates. Increased persistence may also result in carryover of the herbicide to the next growing season resulting in injury to sensitive crops being used in rotation.

Implications for modifying environmental fate

The above examples demonstrate that potential modification of the environmental fate of a herbicide is dependent on the rate of release of the encapsulated chemical. The environmental fate of those herbicides that exhibit slow rates of release were modified greatly when compared to their commercial formulation (Trifluralin persistence was greatly increased; volatilization, runoff and leaching losses of atrazine were reduced to 25% that of the commercial formulation and persistence was greatly increased). If the encapsulated herbicide is released too quickly the environmental fate of the chemical will be similar to that of the commercial formulation (decrease in volatilization loss of alachlor under no-till but not under conventional tillage, and no change in runoff and leaching losses of persistence of alachlor).

Since the effect of starch encapsulation on a slowly released herbicide extends beyond the time period required for complete release it appears that controlled release is facilitating a secondary process that influences herbicide fate. One such process may be adsorption of the herbicide by soil. In general, adsorption equilibria is attained rapidly (2 to 24 h). Clay and Koskinen (1990) found that 88% of the alachlor and 98% of the atrazine adsorbed within 24 h was adsorbed in the first two hours and that little (<2%) adsorption occurred after 48 h. However, the slope for most adsorption isotherms for most herbicides are <1 meaning that as the concentration of herbicide in soil solution increases the mass of herbicide bound by the soil decreases (Koskinen and Harper, 1990). In addition, there is a tendency for adsorption of herbicides to strengthen over time (i.e. more of the herbicide becomes nonextractable). Hence, controlled release may increase adsorption by reducing the soil solution concentration and increasing the length of time for adsorption to occur. At slow rates of release a large percentage of the herbicide mass is retained in the starch matrix at early times where it is not susceptible to loss pathways; the
soil concentration will remain low allowing a larger portion of the herbicide to be adsorbed as it is released, and the herbicide will be more strongly adsorbed by the soil. If the rate of release is too slow soil solution concentration will be too low for adequate weed control. At fast rates of release little herbicide will be retained within the starch matrix; a large mass of the chemical will be susceptible to loss pathways, and the soil solution concentration will be higher reducing the amount of herbicide that will be adsorbed as it is released.

Based on the review of field studies discussed above, a rate of release that allows complete release of the herbicide within 14 to 21 days of application appears to optimize controlled release. A faster rate of release does not appear to result in modification of environmental behavior. A slower rate of release may result in poor initial weed control and increased persistence. A rate of release that would allow complete release of encapsulated herbicides in 14 to 21 days using the formulation technology used in this study (Carr et al., 1991) appears feasible for herbicides exhibiting a solubility in water of 20 to 300 mg L⁻¹. Use of different granule sizes can be used to adjust the release rates (Fig. 1) of herbicides within this range. For herbicides outside of this range of solubilities a different encapsulation technology (e.g. different matrix composition) may be needed.

Most of the field studies conducted with starch encapsulated herbicides have used atrazine and alachlor which is reasonable since they are two of the most commonly used herbicides and have demonstrated potential for environmental contamination. However, to better understand how starch encapsulation affects environmental behavior of herbicides and determine the viability of starch encapsulation technology, field experiments utilizing herbicides with other chemical properties need to be conducted and herbicide losses via the different dissipation pathways quantified and compared to those for commercial formulations of the same chemicals. Here we present criteria that can be used to select herbicides for use in future field experiments. We propose that modification of environmental fate by starch encapsulation will be most feasible when used on herbicides with solubilities in water between 20 and 300 mg L⁻¹. We propose that starch encapsulation will not significantly modify the environmental fate of herbicides with high water solubilities (> 300 mg L⁻¹) when compared to the commercial formulation. We also propose that starch encapsulation will greatly modify the environmental fate of herbicides with very low water solubilities in water (<20 mg L⁻¹) when compared to the commercial formulation. There are many commonly used herbicides within each of the three solubility classes proposed here (<20, 20 to 300, and >300 mg L⁻¹). An experiment comparing the environmental fate of three herbicides (one from each solubility class) applied as a starch encapsulated formulation to that of the same three chemicals applied as a commercial formulation would greatly improve our understanding of the potential for starch encapsulation technology.

REFERENCES


