Release of Fenamiphos, Atrazine, and Alachlor into Flowing Water from Granules and Spray Deposits of Conventional and Controlled-Release Formulations

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The release into water of active ingredients from spray deposits or granules of fenamiphos, atrazine, and alachlor was measured for commercial and experimental controlled-release formulations. Granules or spray mixtures of the pesticides were mixed with coarse sand and dried if necessary, and the mixture was placed in 5 mm × 35 mm stainless steel cylinders through which distilled water was then pumped for 24 h. Pesticide concentrations in the eluate were determined by HPLC analysis. The conventional formulations (emulsifiable concentrates, granulars, and dispersible granules) gave total release in 5−24 h and in some cases appeared to release particles into contacting water. Controlled-release starch-encapsulated formulations gave between 5% and 94% release in 24 h. Clay/alginate and clay/alginate/linseed oil formulations gave 0.3−100% release in 24 h, depending mainly on the aqueous solubility and lipophilicity of the pesticide. This simple technique provides comparative insights into the amounts and rates of release of pesticide active ingredients (and/or other chemicals such as oxidative degradates) when these formulations are contacted by flowing water. Initial results indicate that formulation can affect the potential of these pesticides to be water pollutants under severe rainfall conditions.

Keywords: *Atrazine; alachlor; fenamiphos; formulation; controlled release; spray deposit; water quality; runoff; leaching; granules*

INTRODUCTION

When a pesticide application is followed shortly by rainfall, the rate and degree to which the application deposit is soluble or dislodgable in flowing water may be an important factor in determining the potential of the pesticide to be a pollutant of runoff or leachate water. Many soil-applied pesticides are formulated as solid or liquid concentrates to be mixed with water and applied as sprays. When these sprays are applied to soils, unless conditions are very wet, spray water and emulsifying solvents (if present) quickly evaporate, leaving a deposit of mostly pure active ingredient. Rainfall will dissolve such deposits at a rate depending on the kinetics of dissolution of the active ingredient [e.g., Calvet et al. (1975)]. In contrast, granular pesticides are applied dry, and the granule must be wetted and the active ingredient diffuse out of the granule into soil water before it can move through the soil or be available for pest control.

Fenamiphos [ethyl 3-methyl-4-(methylthio)phenylisopropylphosphoramidate] is an organophosphorus nematicide with low volatility that is available in both granular and emulsifiable concentrate formulations. It is applied to the soil surface and incorporated after application. In the field, fenamiphos is readily oxidized to fenamiphos sulfoxide, which may then be oxidized more slowly into fenamiphos sulfone (Lee et al., 1986; Leonard et al., 1988, 1990; Ou, 1991; Ou and Rao, 1986; Schneider et al., 1990). All three chemical species are nematicidal (Waggoner and Khasawinah, 1974).

Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-1,3,5-triazine] and alachlor [2-chloro-2′,6′-diethyl-*N*-(methoxymethyl)acetanilide] are moderately mobile herbicides (Schoppet et al., 1989; Wauchope et al., 1992). Commercial formulations of these compounds are designed to be dispersed in water and applied as preemergence sprays to the soil surface. The relatively long persistence of atrazine in subsurface soils, and the extensive use of both compounds, have led to many instances of their presence in groundwater and surface water (Cohen et al., 1986; Goolsby et al., 1993; Holden et al., 1992; Leonard, 1990; Richards and Baker, 1993; U.S. Environmental Protection Agency, 1990; Wauchope, 1976). Both herbicides are typically applied as preemergence sprays to the soil surface.

Controlled-release formulations have been suggested as a means to decrease pesticide leaching, runoff, and volatilization while increasing persistence (Harris et al., 1983; Groenwold et al., 1980; Johnson and Pepperman, 1995; Lewis and Cowsar, 1977; Mehltretter et al., 1974; Osgerby, 1972; Scher, 1977; Schreiber et al., 1987; Ware, 1983; Wilkins, 1978). Controlled-release formulations of atrazine and alachlor have been evaluated for efficacy and pollution potential in the field (Dailey et al., 1993; Gish et al., 1991, 1994; Huang and Ahrens, 1991; Mills and Thurman, 1994; Schreiber et al., 1987, 1994; Negre et al., 1992; Wienhold and Gish, 1994). We obtained controlled-release formulations of fenamiphos, atrazine,

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S0021-8561(95)00131-2

Table 1. Properties of Commercial and Controlled-Release Formulations

formulation	symbol	ai content[a] (%)	total ai in column[b] (mg)	species released	total ai released into flowing water in 24 h		
					n[c]	mg	%
fenamiphos							
commercial granular	G	15	10	fenamiphos	6	11.9 ± 0.4	
				fenamiphos sulfoxide	6	0.17 ± 0.02	
				fenamiphos sulfone	6	0.006[c]	
				total[d]	6	12.1 ± 0.4	121
commercial emulsifiable concentrate	EC	360[e]	10	fenamiphos	4	10.6 ± 0.7	
				fenamiphos sulfoxide	4	0.31 ± 0.11	
				fenamiphos sulfone	4	nd[f]	
				total[d]	4	10.9 ± 0.7	109
C-R clay alginate/linseed oil	CALO	0.126	10	fenamiphos	6	1.66 ± 0.14	
				fenamiphos sulfoxide	6	12.6 ± 1.3	
				fenamiphos sulfone	6	0.4 ± 0.2	
				total[d]	6	13.7 ± 1.1	137
atrazine							
commercial Nine-O dispersible granule	DG	0.9	10	atrazine	4	4.18 ± 0.18	42
C-R clay alginate/linseed oil	CALO	0.017	5	atrazine	4	0.015 ± 0.001	0.3
C-R pearl cornstarch	PC	0.0718	3.33	atrazine	5	1.60 ± 0.13	48
C-R starch encapsulated	SE	0.1	10	atrazine	5	0.51 ± 0.06	5
alachlor							
commercial emulsifiable concentrate	EC	479[e]	3.33	alachlor	5	3.2 ± 0.2	97
C-R clay alginate	CA	0.079	3.33	alachlor	5	1.17 ± 0.10	51
C-R clay alginate/linseed oil	CALO	0.056	3.33	alachlor	4	0.39 ± 0.02	12
C-R pearl cornstarch	PC	0.058	3.33	alachlor	4	3.1 ± 0.6	94

[a] ai content in percent by weight except as noted. [b] Total based on nominal ai content of formulation. [c] Incomplete or anomalous runs excluded. [d] Total expressed as milligrams of fenamiphos. [e] Grams per liter. [f] None detected.

and alachlor, formulated by encapsulation of the active ingredient within a polymeric matrix of alginate (Connick, 1982; Connick et al., 1983, 1984; Walker and Connick, 1983) or starch (Carr et al., 1991; Shasha et al., 1976, 1981; Trimnell et al., 1982).

Our objective was to develop a procedure to measure the amount and rate of release of pesticides from sprayer or spreader deposits on, or in, soil into flowing water. A simple packed column has been used to examine the release of fenamiphos, atrazine, and alachlor from simulated spray deposits of commercial and experimental pesticide formulations. Under such conditions the water carries away the solute as it is released and thus acts as an infinite sink, in contrast to stirred-batch release curve experiments such as those of Mills and Thurman (1994) and Wienhold and Gish (1992). In the field, if infiltration is equal to rainfall rate, a surface deposit of pesticide will be in contact with water flowing past at a rate equal (at least to a first approximation) to the rainfall rate. For practical reasons our procedure determined active ingredient release rates in water flowing at 20 cm/h, which is higher than a typical infiltration rate. Thus, we have probably produced release rates which are as high, or higher, than anything that would be observed under natural rainfall.

MATERIALS AND METHODS

The formulation release rates were determined for three formulations of fenamiphos and four formulations of atrazine and alachlor (Table 1). Commercial formulations of fenamiphos (Nemacur 15G granular and Nemacur 3 emulsifiable concentrate) and analytical standards for fenamiphos and fenamiphos sulfoxide were obtained from Miles (now Bayer), Inc., Agriculture Division, Kansas City, MO. Commercial atrazine (Aatrex Nine-O water-dispersible granules) and alachlor (Lasso emulsifiable concentrate) were from Ciba Corp., Greensboro, NC, and Monsanto Corp., St. Louis, MO, respectively. Clay/alginate and clay/alginate/linseed oil granular formulations (spherical; 1.6−1.8 mm diameter) were provided by the Agricultural Research Service (ARS) Southern Regional Research Laboratory, New Orleans, LA, and 20−40 mesh pearl cornstarch and starch-encapsulated formulations were provided by R. E. Wing and Baruch Shasha of the ARS National Center for Agricultural Utilization Research, Peoria, IL.

A disk of Whatman No. 1 filter paper was placed at the outflow end of Perkin-Elmer 5 mm × 35 mm stainless steel HPLC column cylinders having a flow cross section of 0.196 cm^2. Commercial and clay/alginate granular formulations were dry-packed into the cylinders, and unused volume was filled with 1 mm silica sand to hold the formulation granules tightly in place against the filter paper and to reduce dead volume in the rest of the column. The sand had been washed three times with methanol and dried. An arbitrary loading of 10 mg of active ingredient (ai) was sought, but low density or granule swelling on wetting often required that smaller amounts be used (see Table 1). Materials were weighed with a precision of better than 1%.

Starch-based granular formulations were mixed with dry sand before being placed into the cylinders since the starch formulations tended to swell and occlude the cylinder if the granules were clustered together. For the commercial formulations which are designed to be suspended in water, atrazine DG and fenamiphos EC were mixed with water to give 0.1 g/mL ai, and alachlor EC was mixed to give 0.033 g/mL ai. These mixtures are ∼3−10 times more concentrated than typical spray tank mixtures would be but allowed us to use smaller volumes of "spray" in the columns. The columns were first filled with dry sand, 0.1 mL of the mixtures was added using a pipet, and the columns were placed in a drying oven overnight (ca. 15 h) at 40 °C.

Water was pumped through the columns at a rate of 4 mL/h using a peristaltic pump, giving a "percolation rate" of 20 cm/h. This flow rate allowed us to collect samples of 2 mL every 0.5 h. Water flow was maintained for 24 h.

Concentrations of atrazine, alachlor, fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone in the eluted water were determined by HPLC analysis utilizing a C_{18} column and a 55% acetonitrile−45% water mobile phase at a 1.3 mL/min flow rate. Analytical wavelengths were 225 nm for fenamiphos sulfoxide and fenamiphos sulfone (approximate retention times of 1.8 and 2.3 min, respectively), 250 nm for fenamiphos (approximate retention time of 4.4 min), and 240 nm for atrazine and alachlor (approximate retention times of 2.7 and 6.9 min, respectively). Detection limits were relatively high (ca. 1 mg/L) since direct injections of the eluate water were used.

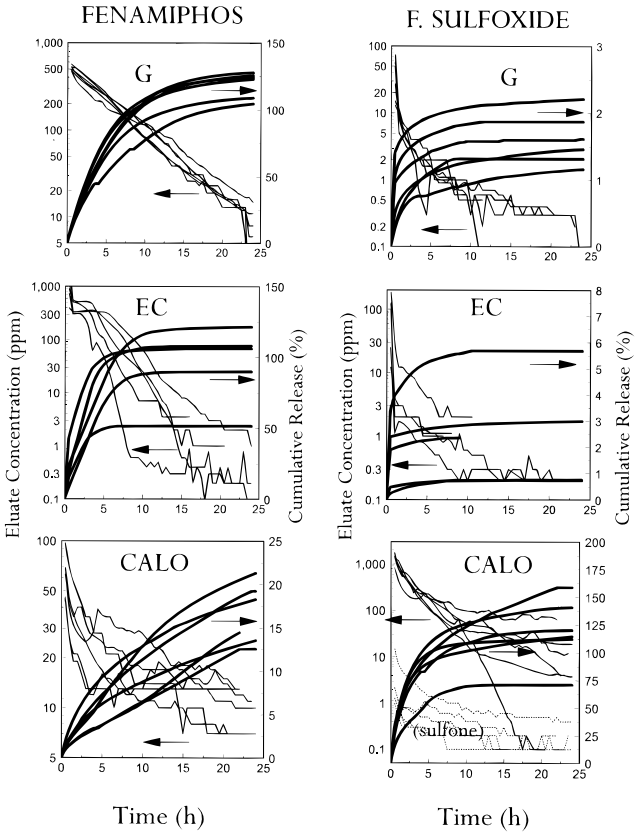

Figure 1. Release from fenamiphos formulations: ai concentration in packed-column eluate water (left scale) and cumulative release curves as percent of the total ai expected (right scale) of fenamiphos and its oxidative product fenamiphos sulfoxide. G, commercial granular (Nemacur 15G); EC, commercial emulsifiable concentrate (Nemacur 3); CALO, a clay/alginate/linseed oil controlled release granule.

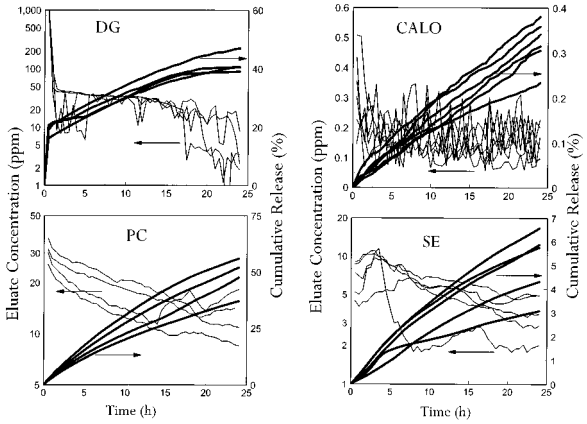

Figure 2. Release from atrazine formulations: ai concentration in packed-column eluate water (left scale) and cumulative release curves as percent of the total ai expected (right scale). DG, commercial dispersible granule (Aatrex Nine-O); CALO, PC, and SE, clay/alginate/linseed oil, pearl cornstarch, and starch incapsulated controlled-release granules, respectively.

Four cylinders were used at one time, and the formulations of each pesticide were run in randomized-complete blocks which were replicated in time. Three blocks were used in an experiment, and the experiment was repeated.

RESULTS

General. The technique generally produced reproducible release curves (Figures 1−3). Concentration ranges over 2 orders of magnitude during runs were often obtained, and the wide dynamic range of the HPLC detector was helpful. In some cases concentrations approached detection limits. Occasionally column flow stopped due to swelling of the starch, and in three cases one of six replicate runs gave much higher or lower total release than the other two (data not shown). This usually occurred when a suspension or emulsion was loaded on the column in liquid form and dried (alachlor and fenamiphos emulsions and atrazine dispersed granule)—apparently, this was difficult to do reproducibly.

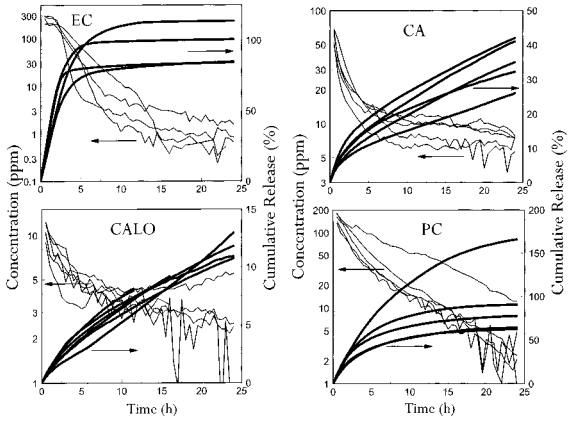

Figure 3. Release from alachlor formulations: ai concentration in packed-column eluate water (left scale) and cumulative release curves as percent of the total ai expected (right scale) for alachlor formulations. EC, commercial emulsifiable concentrate (Lasso 4L); CA, CALO, and PC, clay/alginate, clay/alginate/linseed oil, and pearl cornstarch controlled release granules, respectively.

Three types of behavior were exhibited by the pesticide formulations: *I, complete release in 5−10 h* (fenamiphos and alachlor emulsifiable formulations); *II, complete release in 24 h* [fenamiphos granular and clay/alginate/linseed oil (the latter releases the sulfoxide completely but not the parent), alachlor pearl cornstarch encapsulated]; and *III, incomplete release in 24 h* [all atrazine formulations, alachlor clay/alginate and clay/alginate/linseed oil, and fenamiphos clay/alginate/linseed oil (releasing the parent compound); release ranged from <1% to 51%].

Two main effects appear to control release under the conditions of this experiment. *Diffusion* slows release from the granular formulations, and *solubility/partitioning effects* slow release from the atrazine and clay/alginate/linseed oil formulations (Connick, 1982; Schreiber et al., 1987; Wienhold and Gish, 1992).

Fenamiphos, Fenamiphos Sulfoxide, and Fenamiphos Sulfone. The solubility of fenamiphos has been reported to be 329, 400, and 700 mg/L (Davies et al., 1990; Heller and Herner, 1990; Royal Society of Chemistry, 1983; Wauchope et al., 1992). Our emulsion formulation data (EC, Figure 1) suggest a saturation (solubility) limit of 300−500 mg/L. Fenamiphos and its two oxidation products each produced a distinct peak in the HPLC analysis, and thus we were able to monitor simultaneously the release of compounds with different solubilities from the same formulation.

Commercial Granular and Emulsifiable Formulations. The granular formulation consists of fenamiphos deposited on mixed montmorillonitic and kaolinitic clay particles, which are irregular granules ~0.5−1 mm in diameter (J. Lin, Mobay Corp., Kansas City, MO, personal communication, 1994). Our results indicate the formulation was near 18% fenamiphos, and 98% of the fenamiphos was present as the parent. The gran-

ules act like a controlled-release formulation, at least in comparison to emulsion deposits. They control release in a manner similar to a starch-encapsulated formulation (compare the pearl cornstarch formulation of alachlor), requiring about 24 h for complete release. An initial stirred-batch experiment in our laboratory (data not given) gave very similar release curves for fenamiphos 15G and a 14 mesh cornstarch-encapsulated formulation prepared by Dr. Jack Swarthout of Illinois Cereal Mills, Inc. The shapes of the curves are fundamentally different, however; this is discussed further below.

Commercial Emulsifiable Concentrate. Release was relatively rapid and complete (Table 1). Emulsion formulations leave a deposit of crystalline pesticide, formed by the drying of solvent/pesticide emulsion droplets (Royal Society of Chemistry, 1983). The result is probably crystals of pesticide mixed with a residue of surfactant. In our experiments, on first contact of these deposits with flowing water there was an initial high concentration of released pesticide, followed by a period of elution with constant concentration, followed by a rapid concentration decline as the residue is depleted (Figure 1). The short period of high concentration is likely an effect due to the residue of emulsifier: as water flows through the column, the highly soluble emulsifier is quickly removed but initially solubilizes the fenamiphos at much higher concentrations than the solubility.

Both commercial formulations of fenamiphos had measurable amounts of the sulfoxide (1−3%) but only traces of the sulfone oxidation products. For the granular formulation about 1 ppm of sulfone was observed during the first few hours of the first test. The sulfoxide was released almost immediately from both formulations, suggesting it was at the surface and due to air oxidation.

Complete release of the fenamiphos emulsion deposit required about 8 h, whereas the granular required about 24 h. This suggests that these formulations could have significantly different field characteristics.

Clay Alginate/Linseed Oil Formulation. Apparently during the production of this formulation fenamiphos was oxidized, producing 87% conversion of fenamiphos to the sulfoxide. Linseed oil has been reported to be reactive (Pepperman and Kuan, 1992), but given the sensitivity of fenamiphos to oxidation, conversion to the sulfoxide could have occurred at any stage in the production process. For example, the formulation beads are dried for 10−14 days before storage.

This formulation combines alginate with a lipophilic oil which controls active ingredient release into water by a partitioning process that is much slower than the simple dissolution into water that would occur with the alginate matrix alone. It is revealing to see how much better this works with the more hydrophobic parent fenamiphos than with the sulfoxide—even in the same granule. The sulfoxide was essentially completely released in less than 10 h, whereas fenamiphos was only about 10% released in the same period of time. This formulation also released measurable amounts of the sulfone (about 3% of the total for all species) in a curve very similar to that of the sulfoxide. Note, however, that both the sulfoxide and the sulfone are released much more slowly from the clay/alginate/linseed oil formulation than from the emulsion and granular formulations. This indicates that both of these species are distributed throughout the granule; i.e., oxidation of the parent to the sulfoxide occurred, and then both species were incorporated into the granule.

Atrazine. *Dispersible Granule.* Atrazine is the most insoluble of the active ingredients in this study and, in addition, has some clay-binding capability (Bailey and White, 1964; Gilchrist et al., 1993; Goring and Hamaker, 1972; Harris and Hurle, 1979). The Nine-O commercial dispersible granule formulation consists of a finely ground powder of atrazine prilled into small spherical granules with a water-soluble binder (H. M. LeBaron, Ciba-Geigy Corp., Greensboro, NC, personal communication, 1992). These granules instantly disperse in water to form a fine suspension. Thus, when this suspension was added to the column and dried, a deposit of fine atrazine crystals resulted. When water first begins to flow over this deposit, apparent concentrations of 1000−2000 ppm result (Figure 2). This is approximately 50 times the aqueous solubility of atrazine (33 ppm; Wauchope et al., 1992). We hypothesize that microscopic crystals (small enough, apparently, to pass through the filter paper at the end of the column) are removed from the deposit and ultimately injected into the HPLC, where they are dissolved in the mobile phase.

In spite of this heterogeneous behavior, four of the five completed runs gave quite reproducible release curves (Figure 2). After an initial short-lived high concentration "spike" of atrazine (which generated half or more of the entire 24 h release in the first 30 min), subsequent water samples dropped in concentration to near the solubility limit, indicating that the flowing water was being saturated. By the end of the 24 h experiment, concentrations were somewhat lower than the solubility, suggesting that the approximately 50% removal of atrazine may have decreased the amount of exposed crystal surface to the point that saturation was incomplete. Apparently it would take many days for complete removal of the atrazine deposit.

Starch-Encapsulated Formulations. These materials are reported to exhibit excellent release control over a wide range of release rates (Dailey et al., 1993; Gish et al., 1991, 1994; Wienhold and Gish, 1994). In our experiments there were fluctuations in release, probably due to variability in the swelling of the starch matrix. There was approximately a 2 times variability in the total mass of pesticide released due to inhomogeneities in the formulation. Wienhold and Gish (1992) showed that a starch-encapsulated SE formulation required about 2 h to swell completely and that it showed greater control of atrazine release than alachlor release.

Clay Alginate/Linseed Oil Formulation. This formulation gave very reproducible—but very slow—release. Linseed oil is used to increase control over release in clay alginate formulations (Pepperman et al., 1991; Pepperman and Kuan, 1993) by adding a water-immiscible solvent medium to the granules to partition the pesticide away from water. This partitioning effect would be expected to affect the active ingredients in inverse order of their aqueous solubility (or hydrophobicity); i.e., the effect would increase in the order fenamiphos sulfoxide < fenamiphos < alachlor < atrazine, as was observed. Atrazine concentrations in the eluate from this formulation were close to the detection limit and were essentially constant, probably a direct reflection of the linseed oil/water partitioning equilibrium of atrazine.

Alachlor. *Commercial Emulsifiable Concentrate.* Similar to the fenamiphos emulsion, on first contact with water there was an initial high concentration of

released herbicide followed by a period of elution near the solubility limit—alachlor has an aqueous solubility of 240 ppm (Wauchope et al., 1992)—followed by a rapid decline. One alachlor EC column gave almost 3 times as much alachlor release as any of the others (270% of the 3.33 mg expected). Our only explanation for this is a probable inhomogeneity of the EC/water mixture used to charge the column. Note that, although the solubility of alachlor is less than that of fenamiphos, depletion of alachlor was faster because only one-third as much chemical was placed in the column.

Pearl Cornstarch Encapsulated. Total alachlor release varied from 62% to 166% of the 3.33 mg expected, but the shapes of the release curves were consistent (see below), indicating nearly complete release from each sample near 24 h (Figure 3). Clearly the concentration of alachlor in the starch matrix varied considerably between samples. This material is similar to the atrazine PC, and column loadings were the same. As with the atrazine PC, the eluate was initially near the solubility of the ai but declined smoothly. This suggests that the starch matrix contains crystals or small patches of ai crystals near the surface of the granules, and these are able initially to nearly saturate the flowing water until they are depleted. Alternatively, swelling of the starch granules at the surface may produce an initial fast release followed by slower release as the alachlor toward the surface of the granules is depleted. Subsequently, the diffusion required to bring solute to the surface of the granule limits the release rate, but because alachlor solubility is much higher than that of atrazine, mass transport within the granules is greater. The overall result for alachlor was approximately twice the release rate of atrazine—nearly 100% vs 50% in 24 h.

Clay Alginate and Clay Alginate/Linseed Oil Formulations. Having both formulations for alachlor allows a comparison of the effect of linseed oil on release from the clay granule: the clay/alginate/linseed oil release rate was about one-fourth of the clay/alginate rate.

Statistical Analysis. The curves in Figures 1–3 indicate that most of the release rates are determined by (a) the total amount of material available to be released and (b) solubility, diffusion, and granule-swelling mechanisms, each of which may be rate-limiting in a given case. When the individual release curves are normalized in terms of the fraction of the total released in 24 h, agreement between replicate release curves is much improved (Figure 4–6). The data were treated as follows:

(a) The total mass of ai released in the 24 h of leaching was calculated for each sample, interpolating any missing sample concentrations.

(b) The mass of ai in each 2 mL (0.5 h) eluate sample was calculated as a percentage of the 24 h total.

(c) The resulting data for "normalized" 0.5 h releases, computed as percentages of the 24 h totals, were combined for all replicates. The standard errors for the means at each sampling time are presented in Figures 4 and 5.

Figures 4–6 indicate that even though individual samples of the granular formulations gave somewhat different release curves, a single equation can be found that is well within the standard error of the means for most of the combined data. The emulsion deposits and atrazine dispersible granule data were not treated in this manner—their behavior is clearly limited by solubility.

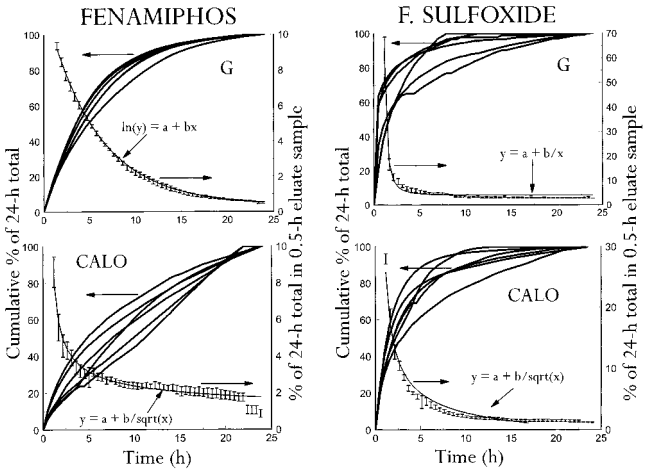

Figure 4. Granular formulation release curves for simultaneous fenamiphos and fenamiphos sulfoxide release: cumulative release plotted as percent of the total released in 24 h (left scale) and standard errors (bars) of the means of the percent of the 24–h totals released by each 0.5-h eluate sample (right scale). Curves drawn through the error bars are labeled with the equation used—parameters are given in Table 2.

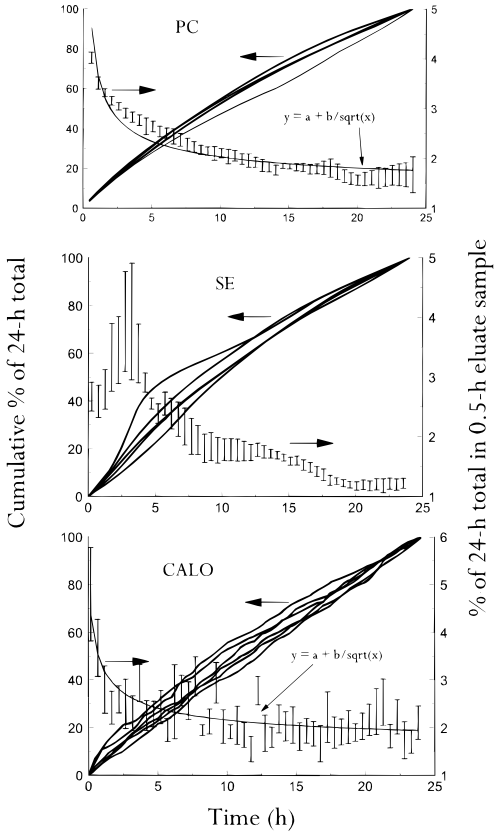

Figure 5. Granular atrazine formulation release curves: cumulative release plotted as percent of the total released in 24 h by the sample (left scale) and standard errors (bars) of the means of the percent of the 24-h totals released by each 0.5-h eluate sample (right scale). Curves drawn through the error bars are labeled with the equation used—parameters are given in Table 2.

We used the TableCurve curve fitting program (Jandell Scientific Software, San Rafael, CA) to fit each data set to various two-parameter and three-parameter nonlinear power and exponential functions and then ranked all equations by *F* statistic. Some of the equation fits are shown in Figures 4 and 5, and the resulting regression results are given in Table 2.

For all but two experiments (Table 2), the two-

Table 2. Curve Fitting for Granular Formulations

		equation F statistics			parameters for $y = a + b/\sqrt{t}$	
formulation	total d.f.	$y = a + b/\sqrt{t}$	best eq[d]	F for best eq	$a \pm$ se	$b \pm$ se
fenamiphos						
G	283	1808	$\ln y = a + bt$	18570	2.217 ± 0.008[c]	−0.167 ± 0.002[c]
CALO	268	880	−[e]	−[e]	0.30 ± 0.07	4.99 ± 0.17
fenamiphos sulfoxide						
G	185	314	$y = a + b/t^2$	895		
G: 1st eluate						
sample deleted	179[f]	532[f]	$y = a + b/t$	711	2.7 ± 0.2	11.6 ± 0.5
CALO	268	3811	−[e]	−[e]	−4.24 ± 0.12	17.1 ± 0.3
atrazine						
PC	180	652	$y = a + b \ln t$	1123	1.24 ± 0.04	2.29 ± 0.09
SE	230		noisy data; linear fit $F = 436$		2.93 ± 0.05[a]	−0.075 ± 0.004[a]
CALO	282	69	$y = a + b/t$	70	1.46 ± 0.09	1.70 ± 0.21
alachlor						
PC	239	2497	−[b]	−[b]	−1.87 ± 0.09	10.7 ± 0.2
CA	239	2842	$y = a + b/t$	4616	−0.42 ± 0.06	6.84 ± 0.13
CALO	239	456	−[e]	−[e]	0.93 ± 0.06	3.13 ± 0.15

[a] Parameters for linear fit. [b] Better equations were all complex functions of both y and t. [c] Parameters for logrithmic equation. [d] Best equation with simple functionality in either y or t. [e] Inverse sqrt(t) was best of all equations. [f] $t = 0.5$ value deleted.

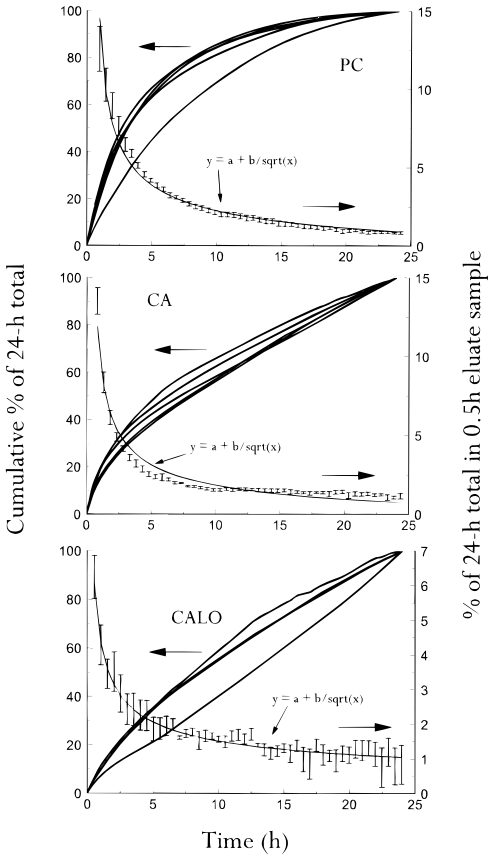

Figure 6. Granular alachlor formulation release curves: cumulative release plotted as percent of the total released in 24 h by sample (left scale) and standard errors (bars) of the means for the percent of the 24-h totals released by each 0.5-h eluate sample (right scale). Curves drawn through the error bars are labeled with the equation used—parameters are given in Table 2.

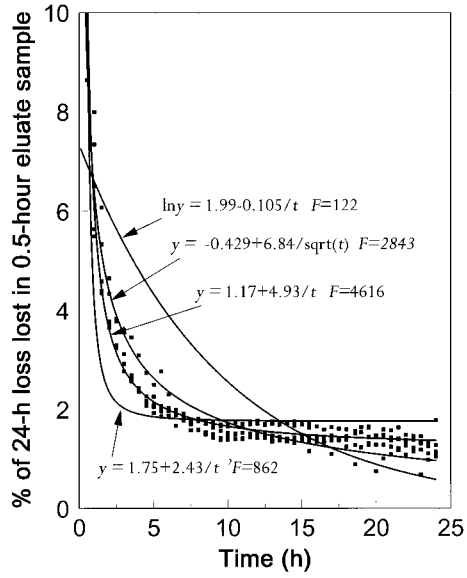

Figure 7. Alachlor release from the CA (clay/alginate) granular formulation. Individual losses as a percent of the total lost in 24 h are shown for each 0.5-h eluate sample (standard error bars for these data are shown in Figure 5). Degrees of fit of four model equations are shown.

parameter equations that fit the data best were of the form $y = a + b/t^{\alpha}$, where y is the mass of pesticide released into a 0.5 h eluate sample, t is the time of the eluate sample, and α is 0.5, 1, or 2. An $\alpha = 0.5$ dependence ($1/\sqrt{t}$) was the best fit, or tied for best fit, for all the CALO experiments. Atrazine PC fit several other equations better, but the $\sqrt{t}$ form also fit the data well. Atrazine SE exhibited a complex behavior probably due to an unusually large swelling effect.

An equation with $1/\sqrt{t}$ dependence has the form of the equation often quoted for diffusion of solute from a spherical source (Higuchi, 1961). This implies that release from these formulations is controlled by diffusion of solute from the interior to the surface of the granules and that the solute is homogeneously dispersed in the granules. Formulations with a $1/t$ or $1/t^2$ dependence have a more rapid initial mass release. This is illustrated for the Alachlor CA data in Figure 7. Alachlor CA, the fenamiphos G, and the fenamiphos sulfoxide G with the earliest (0.5 h) eluate sample data deleted all gave significantly better fit to a $1/t$ equation than to a $1/\sqrt{t}$. Possible explanations for this include a higher concentration of the pesticide toward the exterior of the granules, or the initial swelling somehow accelerating release. In the case of fenamiphos sulfoxide in the commercial granules it appears that most of the chemical is near the surface of the granules: the majority of the release was complete in the very first eluate sample, and this was the curve that required a $1/t^2$ form to fit. If the first data point was excluded, then a $1/t$ form fit well. Note that this same formulation also gave a unique release curve for the parent fenamiphos release—a

semilogarithmic curve was a near-exact fit to the data. We do not have an explanation for this unique release curve shape.

DISCUSSION

These results have relevance for runoff and leaching studies in the field, especially "worst-case" studies, in which fresh application deposits are exposed to short but intense simulated rainfall. With the exception of the atrazine dispersible granule, it takes several hours for any of the formulations to release a significant fraction of active ingredient, even though our flow rates are higher than would be likely to occur except in the most extreme storms. Thus, large storms of short duration (e.g., 5 or 10 cm in 2 h; Wauchope et al., 1993; Burgoa and Wauchope, 1991) would release only a fraction of the pesticide present. Emulsifiable concentrate formulations, which are typically used with highly insoluble chemicals, will be limited by solubility. The commercial granular fenamiphos behaves rather similarly to the starch and clay controlled-release formulations.

In contrast, the atrazine dispersible granule formulation not only releases atrazine by dissolution but appears to form fine particles which are easily flushed from the deposit—it behaves in fact like a wettable powder (Wauchope, 1976). This may or may not significantly increase leaching (however, if the fine particles can pass through filter paper, they will certainly take advantage of macropore flow), but it is very likely it will have a significant effect on runoff. Given the current concerns with atrazine runoff, it appears that this feature of the commercial formulation might be examined further. Mills and Thurman (1994) have shown that starch encapsulation can decrease runoff losses of incorporated atrazine applications by 40%. It is probable that in the more typical case—application to bare soil surfaces without incorporation—a starch encapsulation or other granular, dustless formulation could have a much greater effect in controlling runoff—unless the granules themselves are washed off the field.

Cramer (1976) and Hance (1976) reported that soil may behave like a controlled-release formulation because of its adsorption−desorption characteristics. Soil adsorption and aggregate structure may reduce the effect of controlled-release formulations in soils (Connick et al., 1984). Controlled-release formulations have reduced pesticide movement in soil (Baur, 1980; Fleming et al., 1992; Gish, 1991; Schoppet et al., 1989; Wauchope et al., 1990), but this has not been clearly demonstrated to be due to different rates of release from formulations.

ACKNOWLEDGMENT

We are grateful to Dr. Jack Swarthout of Cereal Mills, Inc., and to Dr. R. E. Wing of the USDA-ARS, Peoria, IL, laboratory for providing starch formulations for fenamiphos and the herbicides, respectively.

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Received for review March 7, 1995. Revised manuscript received October 23, 1995. Accepted June 12, 1996.[⊗]

JF950131X

[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1996.