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Dissipation of the Defoliant Tribufos in Cotton-Producing Soils

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Soil dissipation of the cotton defoliant tribufos was measured in laboratory incubations and on 0.2-ha research plots. Computed 50% dissipation time (DT_{50}) using nonlinear and linear kinetic models ranged from 1 to 19 days. Data indicated that exchangeable soil aluminum inhibited tribufos-degrading soil organisms. Nevertheless, measured DT_{50} values were 40 to 700 times less than the aerobic soil half-life ($t_{1/2}$) values used in recent tribufos risk assessments. DT_{50} values suggest that risk estimates were overstated. However, edge-of-field runoff concentrations measured on research plots exceeded invertebrate LOECs, thus some aquatic risk is indicated. Field data also suggested that volatilization may be a significant soil dissipation pathway. From this result, we conclude that volatilization should be included in simulation models used for pesticide registration. This will likely improve the accuracy of model outputs for products such as tribufos. Potential volatilization losses indicate a need to evaluate the atmospheric behavior of tribufos.

KEYWORDS: Defoliant; tribufos; soil; dissipation; kinetics

INTRODUCTION

Cotton producers routinely apply chemical defoliants to their crops prior to machine picking. In the United States, the most widely used active ingredient is tribufos (*1*). Its structure is shown in **Figure 1**. In crop-year 2000, an estimated 1.8×10^6 ha were treated, with application rates averaging 1 kg ha^{-1} (*1*). Recently the U.S. Environmental Protection Agency (USEPA) issued an Interim Reregistration Eligibility Decision (IRED) for tribufos (*2*). No major limitations to re-registration were identified; however, concerns were raised regarding acute risks to estuarine and marine fish, and acute and chronic risks to freshwater, estuarine, and marine invertebrates in "rainbelt" cotton-producing areas in southeastern and Mississippi delta states. Contributing factors were (a) high rates of precipitation in the region, which promotes pesticide runoff, (b) tribufos toxicity to aquatic life, and (c) the persistence of tribufos.

Potential for tribufos movement from treated fields in runoff and its relatively high toxicity to aquatic life is well-documented (*3*−*6*), but conclusions regarding its persistence are not. They were based on a single proprietary study (*7*). The soil half-life value reported in this study, 745 days, was used in the USEPA risk assessment. This value suggests that the compound is exceptionally stable and that it may accumulate in soil and aquatic environments and impact wildlife for extended periods. The USEPA risk assessment document noted that the compound was "unusually persistent".

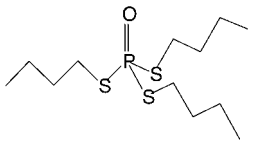

Figure 1. Tribufos (S,S,S,-tributylphosphorotrithioate).

Ambiguity in tribufos soil degradation rates pointed to a need for further study. Accurate data are required to ensure accuracy of risk assessments. Further, if degradation data used by USEPA are correct then tribufos may be accumulating at unacceptably high rates in soil and in aquatic environments impacted by runoff. This could have longterm negative ecological consequences and adversely impact crop yields. Thus, this study was conducted to evaluate tribufos dissipation kinetics in laboratory incubations with cotton-producing soils from Georgia, Mississippi, and Louisiana, and on field research plots located in south-central Georgia.

MATERIALS AND METHODS

Soil. Soils used for laboratory incubations included Tifton loamy sand (Tift County, GA), Tunica silty clay loam and Dundee silty clay loam (Stoneville, MS), and Norwood very fine sandy loam (Bossier City, LA). These soils support extensive cotton production (*8*).

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Table 1. Soil Properties (0–15 cm)[a]

	sand %	silt %	clay %	pH	C %	N %	Al μg g^{-1}	Fe μg g^{-1}	Mn μg g^{-1}	Ca μg g^{-1}	K μg g^{-1}	P μg g^{-1}
Tifton	94	2	4	6.1	0.49	0.02	130	10.6	5.6	311	52.5	46.8
Norwood spiked	62	32	6	7	0.34	0.03	47.2	16.7	11.1	808	48.8	73.9
Norwood unspiked post-defoliation	78	20	2	7.1	0.49	0.03	56.1	17.8	14.4	1070	66.1	82.1
Tunica	20	52	28	6	1.16	0.08	95.0	21.9	14.6	1940	141	69.9
Dundee	30	64	6	6.1	0.58	0.04	86.3	24.7	9.1	1410	77.7	85.3

[a] Analyses performed at University of Georgia Soil, Plant and Water Analysis Laboratory. Methods: soil not dispersed prior to textural analysis; pH measurements in distilled water; Al, Fe, Mn, Ca, K, and P concentrations determined in Mehlich 3 extract (*http://aesl.ces.uga.edu/protected/methods/stl-soil.html*).

Composite samples over the depth increment 0−15 cm were obtained prior to defoliant application to cotton fields in September 1999. In the case of the Norwood soil, a sample also was collected 1 day after tribufos was applied. Soil samples were maintained in field-moist condition and shipped 24 h after collection to Tifton, GA where incubations were conducted. Where the Tifton soil was collected, a pre-plant application (ca. 2000 kg ha^{-1}) of poultry litter was made in April 1999. This site was the same site where field dissipation samples were collected in Fall 2000 (see below). Cotton crops at all sites where soil samples were collected were treated with tribufos in prior growing seasons. Selected properties of each soil are shown in **Table 1**.

Laboratory Incubations. Samples (50 g) of soil passing a #10 stainless steel sieve were transferred to 250-mL French square glass bottles, and their moisture was adjusted to field-moist capacity with distilled−deionized water. Bottles were sealed with Teflon-lined screw caps and allowed to stand overnight. All samples except the Norwood collected after defoliant application were then fortified with 200 mg of quartz sand. It had passed a #60 sieve, been mixed with a solution of acetone and tribufos, and allowed to evaporate to dryness. Tribufos concentration determined by methylene chloride extraction and GC−NPD analysis of 15 200-mg sand samples was 238 μg g^{-1} with relative standard deviation (RSD) of 3.4%. The nominal soil-spiking rate was 1.0 μg g^{-1}. This approach was taken because tribufos solubility was too low to permit spiking at this level with an aqueous solution. Its water solubility is reported to be 2.3 mg L^{-1} (*9*). Through use of sand, a carrier solvent was avoided. To 3 bottles selected randomly from each treatment, 50 mL of methylene chloride was added. Bottles were then capped and placed in a −20 °C chest freezer. These were "time-zero" samples. All remaining bottles were capped, thoroughly shaken, and placed in a dark laboratory incubator maintained at 29 ± 1 °C. One, 4, 7, 14, 28, 42, 62, 92, 122, and 666 days later, 50 mL of methylene chloride was added to 3 bottles from each treatment. They were then placed in the −20 °C freezer. Prior experience with this incubation technique with Tifton soil showed that degradation conditions remained aerobic for extended periods (*10*). Suzuki et al. (*11*) reported that closed soil incubations with the same soil−air space volumetric ratio remained aerobic for at least 180 days. Their soil had 4.7% organic carbon and was obtained under turf. Organic carbon content in the soil used in the current study ranged from 0.4 to 1.0% (**Table 1**). Thus, the current samples were expected to have lower oxygen demand.

Field Dissipation. Tribufos was applied to a mature cotton crop on six 0.2-ha research plots located in Tift County, Georgia on August 28, 2000. Bosch et al. (*12*, *13*) described the plots and their management. A sample taken from a plot maintained under conventional tillage was used for the laboratory incubation study described above. The tribufos source was a commercial formulation DEF 6 (Bayer). It was tank mixed with two other products (Dropp 50WP (Aventis) and Super Boll (Griffin)) and applied with 100 L ha^{-1} of water using a tractor-mounted boom sprayer. The nominal tribufos application rate was 0.3 kg ha^{-1}. Actual rates were measured by attaching 6 spray targets (7.0-cm diameter Whatman #2 filter paper) to the topmost leaf on randomly selected plants on each plot. The filters were collected within 1 h after defoliant application, wrapped in foil, and returned to the laboratory where they were stored at −20 °C. Filter papers were subsequently thawed, sequentially extracted three times with 25 mL of methylene chloride, and analyzed by GC−NPD. Composite soil samples were collected periodically on each plot at three depth intervals: 0−2, 2−8, and 8−15 cm. Samples were collected 1 h and 1, 3, 17, 22, 35, 64, 94, and 133 days after defoliant application. Samples were collected with a stainless steel trowel and a coring device. The trowel was used to collect the 0−2 cm depth increment samples. The coring barrel was then pressed into the soil to 13 cm. The soil core was subdivided into the 2−8 and 8−15 cm depth increments. Sampling began at planting in May 2000 and continued to January 2001 (*13*). All samples were passed through a #10 stainless steel sieve. Subsamples of 50 g each were combined with 50 mL of methanol in 250-mL glass French square bottles (same as for the soil incubations). For quality control, three replicates and a tribufos matrix spike at 1 μg g^{-1} were prepared using 0−2 cm samples from a conventional and a strip-tillage plot for each sampling date. After the contents were mixed with solvent, the bottles were capped and held at −20 °C until extraction was completed. Methanol was used for the field dissipation samples to facilitate extraction of other target analytes.

Soil and Water Sample Extraction. Bottles containing soil and solvent were brought to room temperature and placed on a bed-shaker operated at 210 rpm for 30 min. Prior to shaking samples with methylene chloride, approximately 30 g of anhydrous sodium sulfate was blended with the soil. The solvent, either methylene chloride or methanol, was decanted through a glass fiber filter (Whatman GF/F) on a Büchner funnel support under vacuum. Two additional extractions were performed with 50-mL aliquots of the respective solvents. After the third extraction, soil was transferred to the Büchner funnel and rinsed with 2 10-mL aliquots of solvent. The vacuum was maintained until the soil was dry. Combined filtrates were concentrated to 10 mL under high-purity nitrogen. Aliquots of 1 mL were fortified with 5.0 μg of the internal standard, 2-chlorolepidine, prior to analysis. Water samples collected from wells, tile drain, and during runoff at the field site were glass-fiber filtered (Whatman GFF, 0.7 μm) and solid-phase extracted (*3*).

Extract Analysis. Sample extracts were analyzed using a Hewlett-Packard model 6890 gas chromatograph equipped with an NPD detector (*3*). The column oven was fitted with a 30 m × 0.25 mm DB-5 fused silica capillary column obtained from Alltech (Deerfield, IL). The column's liquid film thickness was 0.25 μm. The carrier gas (helium) head pressure was maintained at 100 kPa with injection in the splittless model. The initial oven temperature, 100 °C, was held for 1 min, then the temperature was increased to 260 °C at 25 °C min^{-1} and held for 4 min. The detector was used with a TID-2 (black ceramic) supplied by DeTector Technology (Walnut Creek, CA). Nitrogen was the detector makeup gas. The limit of detection (LOD) based on concentration of the lowest concentration standard analyzed during calibration was 0.003 μg g^{-1} for soil and 0.01 μg L^{-1} for water. Peak identification was confirmed by GC−MS.

Standards and Chemicals. Tribufos was purchased from Chem-Service (Chester, PA), and the internal standard, 2-chlorolepidine, was obtained from Sigma-Aldrich (Milwaukee, WI). Optima grade methylene chloride and methanol, anhydrous sodium sulfate, and filter papers were purchased from Fisher Scientific (Suwannee, GA).

Quality Control. All laboratory incubation samples were analyzed in triplicate. Among the 55 sample sets analyzed, the relative standard

Table 2. Kinetic Parameters: Linear First-Order Model

	length of incubation (days)					
	666	122	92	62	42	28
			Tifton			
$t_{1/2}$ (days)	75	29.7	26.2	21.4	17.8	16.1
r^2	0.713	0.862	0.857	0.917	0.972	0.967
			Tunica			
$t_{1/2}$ (days)	76.7	21.3	18.6	15.3	13.6	11.8
r^2	0.182	0.850	0.860	0.927	0.911	0.894
			Dundee			
$t_{1/2}$ (days)	70.2	15.8	12.8	10	8.2	6.7
r^2	0.504	0.645	0.740	0.848	0.911	0.950
			Norwood (spiked)			
$t_{1/2}$ (days)	70.4	14.5	11.4	8.7	6.6	4.7
r^2	0.034	0.181	0.301	0.404	0.503	0.680
			Norwood (unspiked, post-defoliation)			
$t_{1/2}$ (days)	109.3	27.8	24.1	24.4	17.9	12.7
r^2	0.323	0.689	0.655	0.621	0.218	0.386

Table 3. Kinetic Parameters: Non-Linear Model DT_{50} (Days)

	length of incubation (days)					
	666	122	92	62	42	28
			Tifton			
DT_{50} (days)	18.8	14.5	14.2	14.8	15.8	16.1
r^2	0.992	0.987	0.981	0.917	0.972	0.967
			Tunica			
DT_{50} (days)	7.5	8.8	8.7	9.3	8.4	8.1
r^2	0.992	0.993	0.990	0.987	0.982	0.968
			Dundee			
DT_{50} (days)	2.5	3.5	3.8	4.2	4.3	4.6
r^2	0.970	0.992	0.994	0.997	0.997	0.997
			Norwood (spiked)			
DT_{50} (days)	0.8	1.1	1.2	1.1	1.3	1.6
r^2	0.940	0.959	0.956	0.944	0.937	0.946
			Norwood (unspiked, post-defoliation)			
DT_{50} (days)	6.7	8.2	7.2	5.1	4.7	4.9
r^2	0.894	0.853	0.805	0.968	0.971	0.972

deviation (RSD) averaged 13%. Low RSD indicated high measurement precision. Accuracy was indicated by tribufos recovery from time-0 samples. For Tunica, Dundee, and Norwood soils it was quantitative. The average was 99% (RSD = 2%). For Tifton soil, recovery averaged 76.2% (RSD = 0.5%). The cause of the relatively low recovery was identified as a failure to sequentially extract this sample. Only a single extraction was made. A follow-up study was conducted by spiking Tifton soil with tribufos and sequentially extracting. Percent recovery of three replicates averaged 104% (RSD = 3.5%). In calculations described below the time-0 Tifton soil concentration values were adjusted to reflect 100% recovery. Field dissipation sample matrix spike recoveries ($n = 35$) averaged 95.6% (RSD = 15.4). The average RSD for the field dissipation sample replicates ($n = 36$) was 13.6%. Data indicated that extraction was quantitative with high precision.

Data Analysis. Dissipation data were evaluated using eqs 1, 2, and 3.

$$\ln (C/C_o) = -kt \quad (1)$$

$$\ln(C/C_o) = -Kc \times \ln(1 + t/c) \quad (2)$$

$$DT_{100x} = [(1 - x)^{-1/Kc} - 1]c \quad (3)$$

Equation 1 is the well-known first-order rate expression. In this case $C_o = C$ (time 0), k is the degradation rate constant (days^{-1}) and $t_{1/2} = 0.693/k$. Data were fit to this equation by simple linear regression. Equation 2 was derived from the nonlinear kinetic model proposed by Gustafson and Holden (*14*). They describe this model as an extension of the first-order kinetic model in which soil is divided into a series of compartments within which first-order kinetics are operative. In this case $C_o = C$ (time zero) and K and c are fitting parameters. K may be interpreted as a spatially weighted degradation constant and $1/c$ is an index of the spatial heterogeneity. As $1/c$ increases decreased spatial homogeneity may be inferred. When $1/c$ approaches zero, eq 2 reduces to eq 1 and $K = k$. Equation 3 is an extension of eq 2. It provides the dissipation time as function of the fraction of the compound remaining $(1 - x)$ and the two fitting parameters. Using this equation, the time to 50% dissipation = $[0.5^{-(1/Kc)} - 1]c$ (DT_{50}). K and c were determined by linear regression of $\ln(C/C_o)$ vs $\ln(1 + t/c)$ for selected values of c. The slope of this line is equal to $-Kc$. The best-fit value of $-Kc$ was set equal to the result when maximum r^2 values were obtained. K was computed using the c value, which gave this result. All computations were performed using data analysis functions in the spreadsheet program Excel (*15*).

RESULTS AND DISCUSSION

Laboratory Incubations. Kinetic parameters and regression coefficients for laboratory incubations are shown in **Tables 2** (linear model) and **3** (nonlinear model). Decay curves for one of the Mississippi soil samples (Dundee) are presented in **Figure 2**. Results from other soil incubations were similar with the exception that the closeness of the fit of the linear model varied as indicated by the r^2 value.

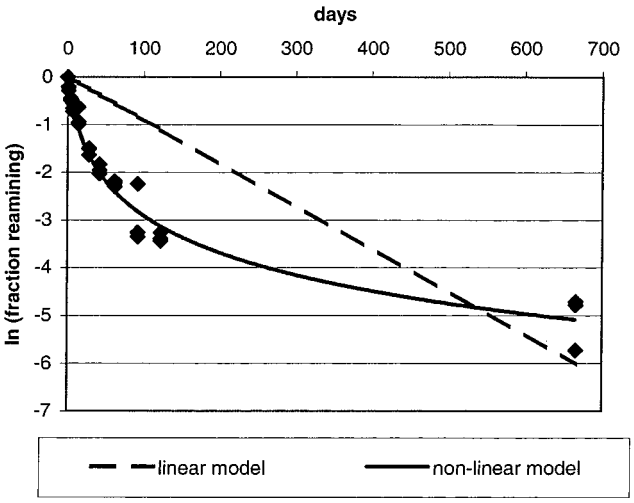

Figure 2. Tribufos dissipation during laboratory incubation in Dundee silty clay loam.

These data represent recovery of decreasing amounts of the parent compound with time, and it is inferred that biodegradation was the primary process responsible. This is based on reports that the compound is relatively stable to abiotic hydrolysis (*7*) and the fact that incubations were in enclosed containers. This limited volatilization losses of the parent. However, there were no sterile controls and tribufos was not ^{14}C-labeled, thus, definitive statements about biodegradation cannot be made. In addition, degradates were not specifically targeted in this study, and their accumulation and decay are not presented. Unpublished registrant data indicate that formation of stable degradates during aerobic metabolism is unlikely. These data were summarized by USEPA (*7*). The principal degradate detected was 1-butane sulfonic acid. It was a maximum of 9.9% of tribufos applied. Relatively rapid metabolism of this compound in soil and aquatic environments is likely.

In these tables, DT_{50} for the nonlinear model, the corresponding value for the first-order model, $t_{1/2}$, and r^2 are shown for 28, 42, 62, 92, 122, and 666-day incubation periods. Data were handled in this way to evaluate the impact of the length of

incubation period on computed results. With the linear model, an increasing trend in computed $t_{1/2}$ with incubation period was observed. A wide variation in the magnitude of the regression coefficients was also noted, as it ranged from 0.034 to 0.972. Values increased with decreasing length of incubation period.

DT_{50} data obtained with the nonlinear model showed no discernible trends with length of incubation, and regression coefficients were uniformly high, 0.805 to 0.997. Wolt et al. (*16*) have noted that a limitation of the first-order linear kinetic model is that kinetic parameters may vary with the length of incubation. The tribufos data provide support for this argument and the observation that nonlinear models may provide more accurate descriptions of pesticide dynamics in soil. This is because more rapid initial degradation rates and higher residue levels persisting for longer periods than are predicted by the first-order linear model are often observed.

That the nonlinear model presented a more uniform data fit was not surprising. Increasing the number of empirically derived fitting parameters will almost always improve data fit. It should be noted that the best-fit values of kinetic parameters derived with the nonlinear model varied with length of incubation. This is obscured by the relatively uniform DT_{50} values. As indicated by eq 3, DT_x is a nonlinear function of the parameters K and c.

It also may be argued that soil incubation in an enclosed container for nearly two years was inappropriately long. Isolating soil in this manner is expected to impact the diversity and stability of microbial communities that are responsible for pesticide degradation. This brings use of the day-666 data points in question. Although the day-666 values may be problematic, we note that the length of our incubation was motivated by reports that the tribufos $t_{1/2}$ may be up to 745 days (*2*, *7*), and simulations used to assess the potential for water contamination are usually carried out over annual cycles.

Overall, our data indicate that an appropriate value for soil tribufos $t_{1/2}$ or DT_{50} is on the order of 5 to 20 days for soil maintained at 29 °C and field moist capacity. This is based on use of incubation data for up to 62 days. Procedural guidelines for soil biodegradation studies recently proposed jointly by USEPA and the Office of Economic Cooperation and Development (OECD) recommended 64 days as the maximum length for laboratory-based incubations (*17*).

In this time frame, the first-order linear model behaved reasonably well for the Tifton, Tunica, and Dundee soils. A relatively poor data fit was observed for the Norwood soil, both spiked and unspiked. For the spiked soil, this poor fit was due to the fact that degradation of added tribufos was exceptionally rapid. Use of the nonlinear model indicated that the time to 50% dissipation was about 1.3 days. An excellent fit of the data was indicated by $r^2 = 0.946$. For the unspiked soil, the DT_{50} was 5.1 days with r^2=0.968. The difference in tribufos behavior between the spiked and unspiked soil may be attributed to a number of factors. A 10-fold lower initial tribufos concentration in the unspiked sample stands out. Because the initial concentration was lower, a greater fraction of the mass of compound in the soil may have been biologically unavailable. This is assuming that the Norwood, like other soils, can sequester biologically available substrates with the amount related to soil properties such as organic matter content and time (*18*, *19*).

It is clear from these results that the linear first-order model had some limitations in describing tribufos degradation kinetics in these soils. However, its use has some advantages. Regression equations are available to adjust laboratory-incubation data to less optimal moisture and temperature conditions which may be encountered in the field (*20*, *21*). The effect of temperature is most frequently described by the Arrhenius equation.

$$\ln(t_{1/2})_1/(t_{1/2})_2 = (E_a/R) \times ((1/T_1) - (1/T_2)) \qquad (4)$$

Temperature (T) units are degrees K and R is the gas constant. E_a is the activation energy and is compound-dependent. To our knowledge no values for tribufos are available. Thus, its $t_{1/2}$ temperature adjustment requires use of literature-derived E_a values. A recent review reported an average $E_a = 54$ kJ mol^{-1} (*21*). In the absence of tribufos specific data, this is a reasonable approximation for the tribufos E_a. Moisture effects are taken in account with a power function as follows:

$$(t_{1/2})_1/(t_{1/2})_{fc} = ((\theta_1)/(\theta_{FC}))^{-B} \qquad (5)$$

Like E_a, B is compound-specific, and it appears that no values have been reported for tribufos. A literature default value, 0.7, provides the best approximation (*21*).

Detailed soil moisture and temperature records are available for the location where the Tifton soil sample was collected (*13*). The average temperature of the surface soil for the month of September 2000 was 25.4 °C, and the average volumetric moisture content was 75% of field capacity. Using these values and default values for E_a and B, the tribufos $t_{1/2}$ (62-day incubation) adjusted for field conditions was determined to be 34 days.

Regressions for the nonlinear model parameters K, c, and DT_x with temperature and moisture have not been developed, although Morton et al. (*22*) indicate that it is feasible. They applied the nonlinear kinetic model to dissipation of 7 insecticides on stored grain. Uniformly good data fits were reported and K values were found to be linear functions of temperature. It remains to be determined whether similar relations can be identified for soil pesticide dissipation.

Finally, it should be noted that all soil samples had been exposed to tribufos during its application to cotton crops in prior years. This was consistent with the objective of the study to evaluate tribufos dissipation under normal use conditions. This includes its repeated annual use. The preexposed soil may have developed pre-acclimated tribufos-degrading microbial populations. In turn, this may have increased the rates of tribufos transformation. Further study is required to determine the significance of this process. Health Canada and USEPA jointly proposed guidelines for field dissipation studies (*23*) recommend that a site selected for dissipation investigations should not have a history of test substance use for 3 prior years. This is in recognition of impacts of prior exposure that have been observed for some compounds.

Relationship between Kinetic Parameters and Soil Properties. Relationships between soil characteristics and kinetic parameters for spiked laboratory incubations using both models for the 62-day long incubation data set were evaluated by linear regression. Among the two Norwood samples only spiked sample data were included. This was done to ensure comparability with other incubations. Regression coefficients (r^2) for $t_{1/2}$ derived with the linear model ranged from 0.007 to 0.848. The maximum r^2 was for extractable aluminum. All other values were <0.46.

A surprising result was that r^2 for %C was only 0.049. Published tribufos K_{oc} values are in the 5000−10000 range (8). Thus, strong binding to soil organic carbon with reduced bioavailability in soils with highest organic carbon content was

anticipated. In turn, higher $t_{1/2}$ values were expected. This was not the case.

Scow and Johnson (*24*) recently reviewed the literature on the effect of sorption on biodegradation of soil pollutants. They describe a number of studies which identified an inverse relationship between sorption and rate of biodegradation but note that the relationship is often weak. In the case of tribufos, a factor which likely played a role in the failure to observe a relationship between $t_{1/2}$ and organic carbon was the relatively low organic carbon content of the soils. The maximum value was 1.2%. Nam et al. (*18*) reported that the bioavailability of aged phenanthrene, a strongly sorbing compound, was reduced in soils with >2.0% organic carbon but not in soils with lower organic carbon content.

The relatively rapid rate at which tribufos was degraded in the current study may also have played a role. A slower degradation rate would have permitted time-dependent inter-aggregate diffusion and possibly prolonged degradation. The amount of phenanthrene sequestered (not bioavailable) in soils was shown to be inversely related to the initial rates of degradation (*19*).

Nonlinear model kinetic model parameters were also poorly correlated to soil properties with the exception of pH and extractable aluminum. The aluminum r^2 ranged from 0.791 to 0.916, and for pH r^2 ranged from 0.474 to 0.977.

Taken together, these results suggest that aluminum may inhibit populations of soil organisms responsible for tribufos degradation. Alexander (*25*) classified exchangeable aluminum as one of the few fungistatic agents characterized in soil. The connection to pH is expected because increased soil acidity, which is directly related to exchangeable aluminum, has also been shown to change soil microbial community structure. Pennanen et al. (*26*) reported that increasing acidity shifted the bacterial community in forest soils to acid-tolerant gram-positive bacteria.

Field Dissipation. Using measured application rates as determined by analysis of spray targets and the time-zero surface (0−2 cm) soil samples, the fractional tribufos mass applied that reached the soil surface was calculated for the six plots. It ranged from 5.3 to 49% with an average of 19.9%. The high value was from a plot that was partially defoliated prior to tribufos application. Drought and nematode infestation were identified as causative factors (*13*). If the high value is rejected then the tribufos fraction reaching the soil surface for the remaining 5 plots averaged 14.0%. This is within the computed range for the Norwood soil site. In this case, tribufos application rates were not measured. However, it is assumed that an agronomically effective amount, 0.3−1.5 kg ha^{-1}, was applied. Given this, the fraction reaching the soil surface based on analysis of the time-zero post-defoliation sample used in the laboratory incubation study was in the 2−6% range. This sample was held at ambient conditions for 3 days during shipment and sample processing prior to extraction. Thus, some tribufos postapplication degradation likely occurred. Using the DT_{50} computed with the nonlinear model (1.5 days), data indicate that four times more tribufos reached the soil surface than was measured in the time-zero soil analysis. This places the tribufos fraction reaching the soil in the 8−24% range.

To our knowledge, there are no other published values on the mass of applied tribufos which is intercepted by the canopy and which reaches the soil surface during spraying. Thus, the range of values reported can serve as first-approximation for fate and transport modeling.

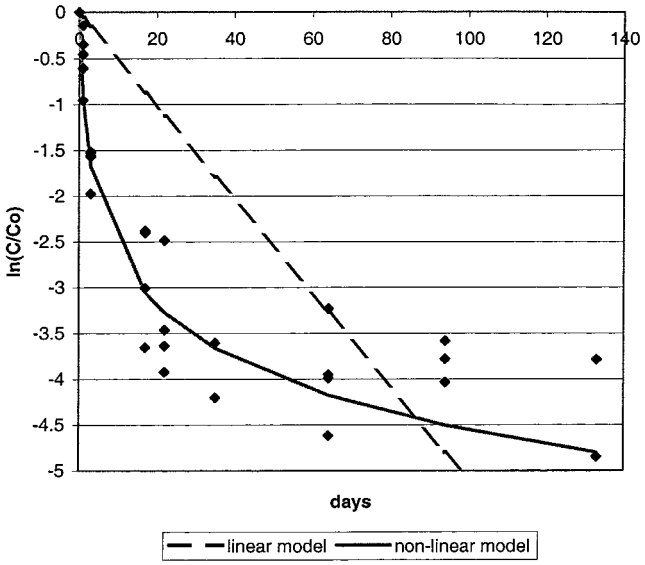

Figure 3. Tribufos field dissipation.

Tribufos dissipation data expressed as $\ln(C/C_o)$ versus time, that were obtained from 5 of the 6 plots studied are summarized in **Figure 3**. It includes fits of the data using the linear and nonlinear models. Data from one field plot were omitted. The time-zero sample on this plot had lower tribufos concentration than samples collected 1 and 3 days postapplication. Analysis of archived samples, which had been kept frozen since collection, showed the same result. No explanation is available for what appear to be anomalous values.

Data were combined from plots in two tillage treatments, conventional and strip, and only results from the 0−2-cm surface soil samples were used. Examination of the data by tillage treatment did not indicate any tillage−tribufos dissipation relationships. Only the topsoil data were used as there was no indication of tribufos leaching during the study. During three years of monitoring, it was neither detected (MDL = 0.01 μg L^{-1}) in samples collected in shallow (4 m) monitoring wells installed in plots nor in samples collected at the outlet of tile drains which intercept shallow subsurface flow (Potter et al., unpublished results). In the soil samples collected at the 2−8-cm and 8−15-cm depth intervals in the plow layer, tribufos concentration in 53 of the 108 samples collected after tribufos application was below the MDL of 0.003 μg g^{-1}. In total, the concentration in only 4 of the 108 samples was above 0.015 μg g^{-1}. This is our estimate of the practical quantitation limit (PQL) in the analysis (5× the MDL). Finally, the average tribufos concentration in corresponding samples collected 32 days prior to defoliant concentration, 0.004 μg g^{-1}, was not significantly different ($P = 0.001$) from the average of samples collected after. Tribufos detected in the pre-spray samples presumably was a residual from its application to the 1999 crop. It was defoliated with the same tank mix at the same nominal rate as used in crop-year 2000 (*12*, *13*). The low tribufos residual may reflect the fraction sequestered in the soil, i.e, made biologically unavailable by physical "protection" by the soil matrix.

In preparing **Figure 2** and in data analysis to determine kinetic parameters, the combined surface soil data set was censored by eliminating all results that were below the detection limit. This included 9 of 60 reported results. Results below the PQL but above the MDL were retained. These points are reflected on the plot for $\ln(C/C_o)$ values <−3.5. Values below the PQL have relatively high analytical uncertainty. This is indicated by noise in this region of the plot.

In terms of dissipation kinetics, the plot shows that the nonlinear model provided an accurate description of the process. The r^2 of $\ln(C/C_o)$ versus $\ln(1 + t/c)$ was 0.843 and DT_{50} calculated from best-fit regression parameters was 0.6 days. A very poor fit was obtained with the linear model, $r^2 = 0.023$, indicating that it was not suitable for analyzing these data. European Union guidelines suggest that first-order linear models should not be used if $r^2 < 0.700$ (*16*).

The field dissipation DT_{50} was 25× less than the value obtained from the laboratory incubation for soil collected at this site (**Table 3**). It was 58× less when compared to the $t_{1/2}$ adjusted for average site soil temperature and moisture. Specific reasons for these large differences are not clear. Comparison of field and laboratory data available in the literature for other compounds show that in some cases field values exceed laboratory values, while in other circumstances the opposite is observed (*16*). Generalizations are difficult because of the varied nature of fate and transport processes which may be operative in field experiments.

As indicated above, data show that tribufos leaching losses were minimal during the study period. Some runoff losses were observed as indicted by analysis of samples collected during events 7, 8, 21, 28, 42, and 84 days postapplication. Automated samplers positioned at the outlets of runoff flumes were programmed to collect flow-weighted composites; thus, concentrations reported represented averages for each event (*12*, *13*). Long-term data records indicate that the pattern of storm events observed during the field dissipation study was not unusual. For the nearby Little River Watershed, Bosch et al. (*27*) reported that during September, return intervals averaged 13.7 h for intense storms that may generate runoff. They examined a 30-year data record and considered storms over the entire 334-km^2 watershed.

For events 7 and 8 days after application the dissolved tribufos concentration ranged from 1.3 to 12 μg L^{-1} in runoff from 3 conventional tillage plots and from 0.3 to 6.8 μg L^{-1} for 3 plots under strip-tillage management. Using sediment loads in the samples and sediment−water $k_d = 30$, particulate-phase concentrations were estimated. They ranged from 0.04 to 0.57 in conventional-till plot runoff and 0.03 to 0.33 in strip-plot runoff. The k_d used was an average of values determined experimentally in samples collected during prior rainfall simulation-runoff studies at the site (Potter et al., unpublished results). Dissolved tribufos concentration in samples collected during events 21 and 28 days postapplication ranged from <0.01 to 0.3 μg L^{-1} with computed particulate phase concentrations in the <0.001−0.05 μg L^{-1} range. Dissolved and particulate phase concentrations were uniformly <0.01 and <0.001 μg L^{-1} in samples collected during later events.

Values measured in 5 of the 12 day-7 and day-8 samples exceeded 3 μg L^{-1}; which is the lowest observed effect concentration (LOEC) for freshwater invertebrates identified by EPA in tribufos risk assessments. All measured concentrations exceeded the LOEC for marine/estuarine invertebrates (*7*). Thus, potential for ecological impacts of runoff are indicated. However, the time window for impacts appears to be relatively short. Tribufos concentration measured in all subsequent events was below the freshwater invertebrate LOEC and only two samples exceeded the marine/estuarine LOEC of 0.3 μg L^{-1}.

Flow and concentration data were used to compute estimates of the fraction of applied tribufos lost in runoff. The total was 1.0−4.0% on conventional-till plots and 0.45−2.33% on strip-till plots. Differences between tillage treatments were not significant ($P = 0.05$). From 92 to 99% of all tribufos loss in runoff occurred in the first two events after application. It included material deposited directly on the soil surface during spray application and wash-off from the plants and leaves, which had dropped to the soil surface. Separation of these sources in terms of the tribufos concentration in runoff is beyond the limits of available data. These data do indicate that tribufos dissipation via runoff in this study was a relatively small fraction of the total applied and which reached the soil surface during spraying.

This focuses attention on volatilization and biodegradation as dissipation pathways. Biodegradation is indicated by the laboratory incubation data. Measured degradation rates, although rapid in the context of default values used in USEPA risk assessments, were slow when compared to field dissipation rates. Given this, the data suggest that volatilization was a primary pathway. This is inferred from the current study and behavior of other moderately volatile pesticides described in the literature. In their summary of field volatilization measurements, Taylor and Spencer (*28*) reported that losses of active ingredients applied to bare soil in periods ranging from 7 h to 120 days were 2 to 90%. Losses were related to pesticide Henry's constants (K_H), soil temperature, organic carbon and moisture content, and pesticide placement. These data and other studies have shown that when pesticides are placed on the soil surface and moist conditions and warm temperatures prevail, volatilization losses can be high even when Henry's constants are low (*29*). The reported tribufos K_H is 1.2×10^{-5} (*2*). Whang et al. (*30*) reported volatilization losses of up 74% of chlorpyrifos applied to bare soil at a field site in Maryland during 26 days of monitoring. The reported chlorpyrifos K_H was 1.7×10^{-4}. Müller et al. (*31*), using a laboratory microcosm, reported volatilization of up to 11% of Fenpropimorph applied to bare soil in 4 days. Its reported K_H was 1.0×10^{-7}. These data, and the fact that soil temperature and moisture conditions during cotton harvest may be relatively high in southern Georgia, support the conclusion that the fraction of tribufos volatilized was high. Our estimate, after adjusting for biodegradation using site-specific soil $t_{1/2}$, was that >70% of the tribufos which reached the soil during spraying was volatilized.

CONCLUSIONS

Tribufos laboratory and field dissipation data indicated that the aerobic soil half-life value used in recent USEPA risk assessments, 745 days, was inappropriately high by up to 100× when growing conditions on the Atlantic Coastal Plain in southern Georgia, the Mississippi Delta, and the Red River Valley in northern Louisiana are considered. This geographic area spans much of the cotton "rainbelt" in the southeastern U.S. The data also indicate that tribufos is not accumulating in cotton-producing soils in the region. Using measured dissipation values in this study in simulation models used for risk assessments will likely reduce estimates of surface water contamination from runoff and reduce risk quotients for sensitive aquatic species. Nevertheless, field data indicated that tribufos levels in runoff may present ecological risks to aquatic life if runoff is discharged undiluted into ponds and streams. As is the case for most pesticides, storm events that occurred closest to the time of application were found to pose the greatest risk in this regard. Field studies also indicated that volatilization may be a quantitatively significant tribufos dissipation pathway. Many screening models used for pesticide registration, including those

used by USEPA, do not take volatilization losses into account when evaluating surface water and groundwater contamination risks (*32*, *33*). Thus, risks may be overestimated. Finally, data indicate that the magnitude of tribufos volatilization, its atmospheric residence time, and potential for re-deposition need to be quantified on a regional basis.

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