Bull Environ Contam Toxicol (2008) 81:355–359
DOI 10.1007/s00128-008-9414-9

Calculation of Pesticide Degradation in Decaying Cotton Gin Trash

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Received: 19 February 2007 / Accepted: 16 March 2007 / Published online: 24 July 2008

Abstract Pesticide residues were measured in stockpiled cotton gin trash (CGT) over a 2-year period. Samples were analysed by GC/MS/MS and interpretation of the results was aided by the presence of DDE residues, remnant from prior DDT use. Fourteen pesticide residues from current agricultural practice were detected in CGT. Several of these, including indoxacarb, profenofos, chlorpyrifos, propargite, bifenthrin, ethion and cyhalothrin, were more persistent than expected on the basis of published data for soil dissipation. The results showed a complex pattern of pesticide residue decay over time because of the simultaneous decomposition of the CGT matrix.

Keywords Cotton gin trash (CGT) · Pesticides · Dissipation · Compost · Half-life

Cotton gin trash (CGT) is a complex mixture of woody fragments of cotton bolls, stalks, knotted cotton fibre residues, mulched leaves, soil and dust particles. CGT comprises about 30–40% of the harvested cotton by mass, separated from the cotton fibre (lint) during the mechanically intensive ginning process. In the absence of clear guidelines for legitimate use in Australia, CGT has often been stockpiled and allowed to decompose, a process that can take several years.

Despite potential use of CGT as a valuable by-product, several hazards need appropriate management. Pesticide residues contained in CGT will restrict its re-use. Studies involving GCT containing DDT residues (DDE plus DDD) fed to cattle showed bioaccumulation of these residues in fat tissues (Martin et al. 1976). A highly notable case of contamination of beef cattle from feeding of CGT was the Helix (chlorfluazuron) incident in Australia. Residues of chlorfluazuron were detected in export beef and because there were no tolerances set at the product destination all residue detections above 0.2 mg kg^{-1} were considered unacceptable (Spence et al. 1998). Damages to the beef industry in the order of $100–200 million were awarded in 1997 in a successful legal class action against the chemical supplier and the chemical was subsequently restricted for use in cotton.

The widespread stockpiling of gin trash has recently raised concern with respect to the potential of residues to leach into the environment. To inform and help develop management strategies of CGT, this study examined the pattern of pesticide residue concentrations in CGT with time.

Materials and Methods

This study primarily reports data from sampling trash stored over a 2-year period, 2002–2004. CGT from one week of ginning (roughly 600 t) was collected from a large gin facility in the Namoi Valley of north-east NSW, Australia. The fresh CGT was distributed into windrows approximately 1.5 m high. Ten replicate samples were collected from the trash within one week of ginning (t0) and then at 60, 162, 265, 377 and 748 days following collection of the first samples. Each replicate sample consisted of 10 grab samples taken randomly throughout the segregated trash pile.

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Samples were collected in clear glass jars (5 L), sealed and refrigerated (0–4°C). The samples were delivered directly to the laboratory for extraction and chemical analysis. Each replicate sample was analysed for 27 pesticides used in cotton production. Sub-samples were extracted by shaking (1 min) and then soaking overnight in pesticide grade acetone/hexane (Mallinckrodt® 1:1) with 400 µL DEF (4H-cyclopenta[def]phenanthren-4-one) (10 µg mL^{-1} in toluene) as an internal standard. The mixture was then filtered through 90 mm Whatman GF/C glass fibre filters (Whatman #1822 090) using a Büchner apparatus. The filtrate was evaporated to dryness and the residue redissolved in a hexane/acetone (2:1) solution using ultrasonication. The residue solution was then eluted under vacuum though a SPE column (Bond Elut Jr SAX/PSA, 500 mg, Varian Aust. #12166052B) preconditioned with 40 mL of pesticide grade acetone and 10 mL of column eluent (2:1 pesticide grade hexane/acetone). The columns were washed with four volumes of sample eluent and all aliquots were collected and then evaporated to dryness. The residue was redissolved in toluene (2 mL Mallinckrodt pesticide grade) using an ultrasonic bath to dissolve wall adhering solids. At least 1 mL of the residue solution was transferred to a GC vial, capped and analysed by GC/MS (Hewlett-Packard 6890 GLC equipped with a 5972 MSD and a 30 m × 0.25 mm fused silica column coated with HP-5MS). To correct for loss of dry matter from the CGT matrix during the study, highly persistent DDE residues were used as an internal standard, as indicated in the "Results and Discussion" section.

Results and Discussion

The decomposition of gin trash significantly changes its volume and consistency. During this study composting was not assisted because of severe widespread drought. However, composting can be accelerated by the addition of water with mechanical mixing to reach thermophilic temperatures (Büyüksönmez et al. 2000).

Of the 27 pesticides analysed, 14 were detected in CGT samples (Fig. 1). Immediately obvious is the large temporal variation shown by the 95% confidence intervals indicating large variation between replicates. These initial observations suggest that the chemical concentrations in CGT are relatively stable, with no significant degradation within the first year, despite large fluctuations between replicates. At first sight, these data excite concern with respect to pesticide persistence in CGT and the potential for environmental contamination.

We initially concluded that the half-lives could be lengthened because of very limited availability of water, resulting in minimal microbial degradation. The samples were collected during severe drought (Bureau of Meteorology 2005). Microbial activity is limited by low water availability because of limited substrate diffusion and desiccation (Prescott et al. 1999; Büyüksönmez et al. 2000); the associated microbial degradation of pesticides could also be limited, as observed by Parkin and Shelton (1994).

Another concerning observation with these data was the DDE content (Fig. 1). Although permission to use DDT as

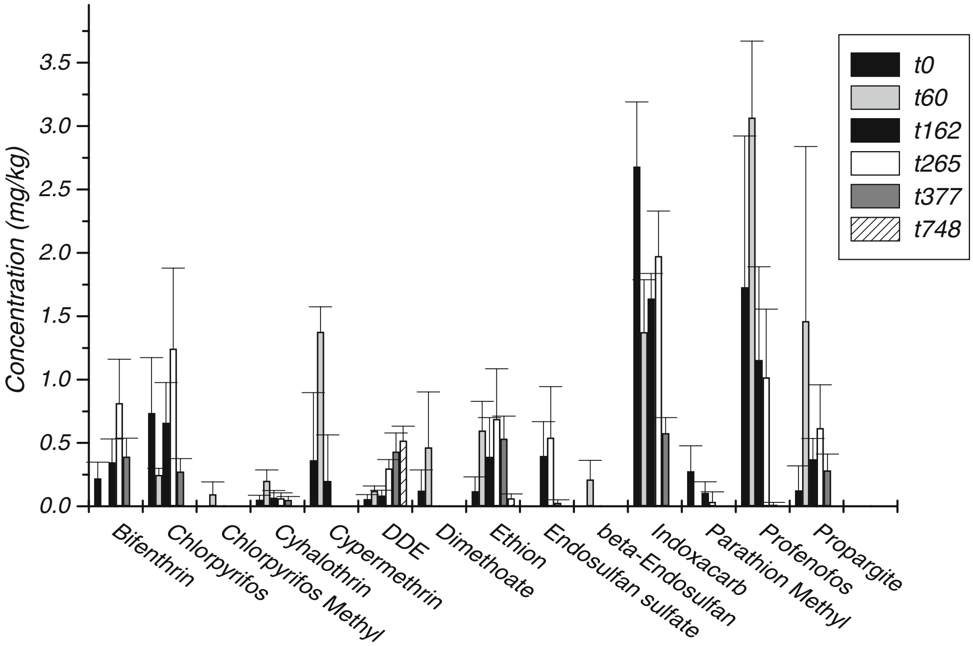

Fig. 1 Concentration of pesticide residues in fresh trash at the Namoi Valley cotton gin. Time (t_{days}) intervals correspond to period after initial sampling (t0) which occurred within a week of ginning; error bars show 95% confidence intervals

an insecticide for cotton production was withdrawn in October 1981 (Pesticides Act 1978 Cth.) its primary breakdown product, DDE, is still widely detected in soils of the region (Shivaramiah et al. 2002). The half-life for DDT in tropical and temperate soils ranges between 6–75 weeks and 10–35 years, respectively (Foght et al. 2001). Half-life values for DDE range from 151 to 271 days in tropical soils to greater than 20 years in temperate climates (Racke et al. 1997). A study conducted in the 1980s reported that dissipation half lives in this geographical region were about 3–4 years for DDT and over 15 years for DDE (McDougall 1992).

We conclude that DDE detected in CGT is bound to dust and soil particles removed from the lint during the ginning process then incorporated with the other waste material into the trash pile. Evidence supporting this conclusion was obtained when DDE residues were detected in soils used for cropping about 0.5 km from the trash stockpiles at concentrations of 0.6 ± 0.04 mg kg^{-1} of soil. By comparison, the concentration of DDE residues in the waste stockpile after 2 years (0.9 ± 0.02 mg kg^{-1}) indicates the long-term consequences of stockpiling CGT.

It was observed during the period of sample collection trash that the volume of the trash piles decreased substantially. We postulate that this reduction in volume is accompanied by decreasing mass of the CGT matrix, explaining the incongruent “decay” curves of the pesticide concentration within CGT, similar to previously reported evidence (Vandeervort et al. 1997; Büyüksönmez et al. 2000). All analytical data is expressed in terms of the mass of the matrix. As a result, if the rate of mass decrease of the matrix was similar to the rate of decay of the pesticides, then no significant change in concentrations would be observed, leading to an apparent but erroneous increase in their persistence.

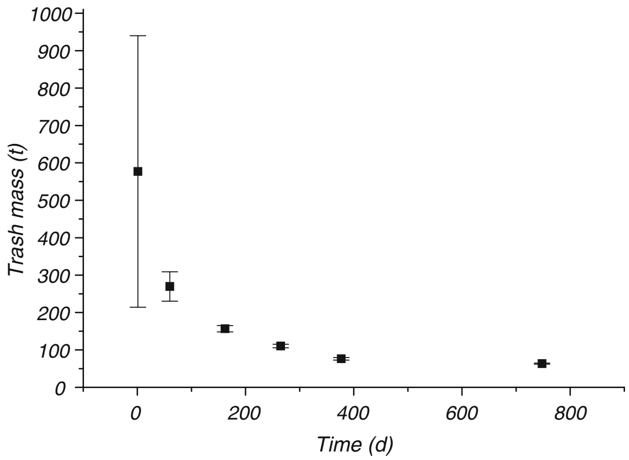

Fig. 2 Calculated mass of gin trash stockpile over the 2-year sampling period (estimated from the increase in concentration of DDE residues over this period)

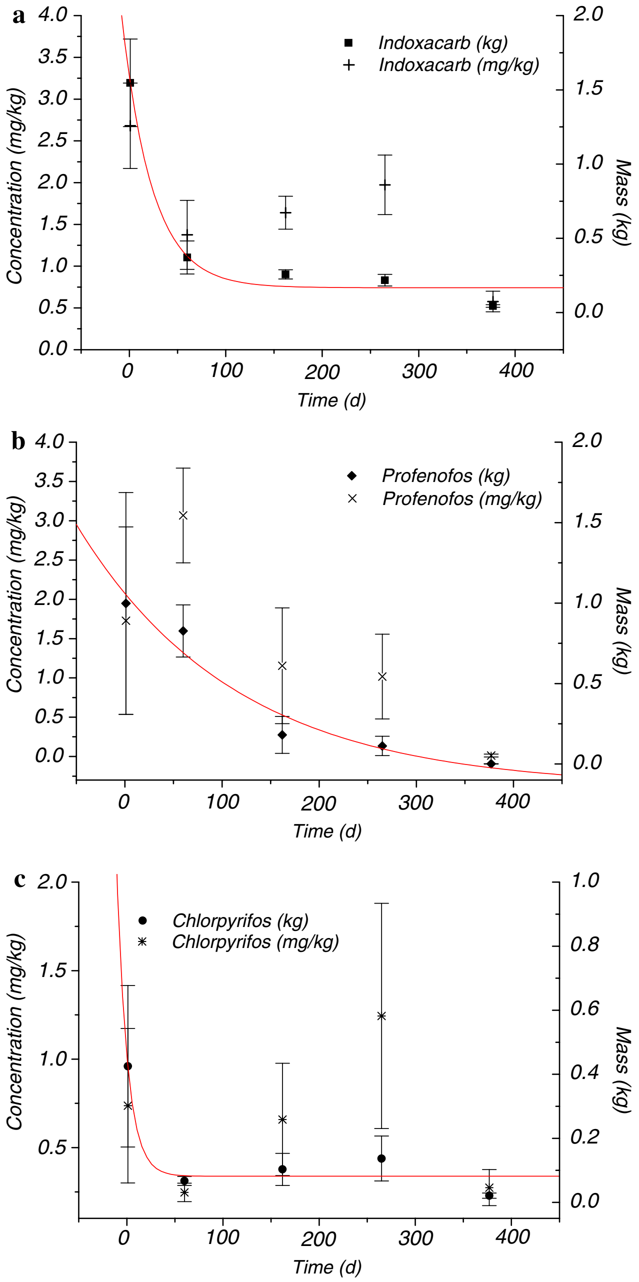

Fig. 3 (**a**, **b**, **c**) Concentration and calculated mass of indoxacarb, profenofos and chlorpyrifos in CGT

To measure the change in mass of the trash pile empirically would be difficult given that its weight was approximately 600 t. However, we were able to estimate the rate of reduction in mass of CGT from the increasing concentration of DDE. This calculation involves the key assumption that the rate of DDE degradation in CGT is negligibly slow compared to the decomposition rate of the organic material. Based upon the percentage increase in DDE concentration and the reported mass of gin trash from each bale of cotton produced (ca. 90 kg/per bale, Gordon

Table 1 First-order decay parameters (with adjusted R^2 and standard errors) and dissipation half-life for selected chemical detected in gin trash

Chemical	Parameters for equation: $y = A + B(R^x)$			Percent variation (Adj. R^2)	Standard error	Half-life in CGT (d)	Reported values in soil[b] (d)
	R[a]	B	A				
Indoxacarb	0.969	1.423	0.167	96.6	0.111	26	4–5
Profenofos	0.994	1.205	−0.145	90.9	0.137	96	7 (mean)
Chlorpyrifos	0.915	0.375	0.082	85.3	0.061	11	1.5–33
Ethion	1.004	−0.027	0.065	61.6	0.016	133	90
Cyhalothrin	0.999	0.094	−0.053	22.5	0.018	–	–
Bifenthrin	0.996	0.099	0.026	4.4	0.042	–	–
Propargite	1.004	−0.130	0.330	–	0.186	–	–

[a] Where $R = e^c$

[b] (BCPC 2002–2003)

et al. 2001) and the number of bales ginned corresponding to the trash pile, we estimated the reduction of CGT mass (Fig. 2) during the sampling period.

Exponential decay models fit these re-calculated data DDE well, with a second order model giving a slightly better fit ($R^2 = 99.9$) than a first order function ($R^2 = 98.3$). In such a model it would be expected that only the organic fraction of the gin trash would degrade, leaving DDE bound to non-degradable soil particles intact. This analysis shows that about 80% of the CGT material was metabolised to volatile products. This value falls within the reported range of 63–95% loss of weight for organic matter decomposition (Kim et al. 2004).

Considering CGT as a dynamic matrix, the total masses of the persistent pesticide residues detected beyond 180 days were calculated. More typical exponential pesticide degradation patterns can now be observed in Fig. 3a, b and c for indoxacarb, profenofos and chlorpyrifos, respectively (plotted together with original concentration data). Table 1 contains the equation of the fitted function and the adjusted R^2 values and standard error for all regressions. Propargite, bifenthrin and cyhalothrin concentrations were too close to the limit of quantification, and this combined with the variable distribution within the matrix, did not show good fit with the first-order model. However, the major effect of the degradation of the matrix was clearly observed within this dynamic matrix. The resultant close fit to a first-order regression confirms our supposition that the concentration of DDE residues provides a serendipitous internal standard, without which the measurement of decay rates would be very difficult.

By using the calculated total mass of chemicals we observed patterns of dissipation strongly supporting our conjecture that both the matrix and pesticides were degrading. The degradation of these residues appears to be bi-phasic, with the characteristic second-order asymptotic curve clearly visible in Fig. 3a and c. It can be concluded that the concentration data presented in the figures combine the net outcome of the rate of matrix decay and the respective rates of pesticide degradation.

Pesticides have been previously reported in composts, including those of cotton trash (Winterlin et al. 1986; Blewitt et al. 2005). Concerns have been primarily with phytotoxicity when the composts were used for soil augmentation. Pesticides detected in compost have reportedly dissipated to below 1 mg kg^{-1} within 3 weeks of composting (Lemmon and Pylypiw 1992). Whereas others have shown that residues can be detected for up to a year (Vandervoort et al. 1997). The data showed that concentrations of residues might initially increase (Vandervoort et al. 1997; Blewitt et al. 2005), but because the data were scattered and insufficient measures of variability were presented, it was difficult to interpret half-live values or to decide whether such observations were statistically relevant.

The data presented in this study clearly shows that the rates of degradation and dissipation are dependent upon the action between each chemical and matrix. Such interactive forces are characterised by the physical and chemical properties of each phase and solute (Kennedy et al. 2001). Half-life values for the chemicals detected were typically 2–10 times longer than when compared to values in soil (Table 1). Assessment of concentration alone does not provide a clear understanding of the dynamic nature of pesticides within CGT, nor the associated environmental risk. Potential end-uses and subsequent regulation of CGT need to be carefully considered with respect to chemical load (concentration and mass), environmental behaviour and bioavailability.

Acknowledgements The authors would like to acknowledge the valuable input from Mr. Bruce Pyke, Dr. Vic Edge and financial support from the Cotton Research and Development Corporation, Australia. Residue analyses were conducted at Agrisearch Analytical.

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