Wool residue breakdown model: An example of how wool blending models can be used to estimate sale lot maximum concentrations and wool harvesting intervals.

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Summary

A blending method has been previously proposed to estimate maximum acceptable residue concentrations in wool sale lots to meet specified wool processing lot requirements. This report uses the method to provide revised estimates for sale lot maximum residues based on current (to March 2001) survey data.

This report also describes a Withholding/Blending method for determining wool harvesting intervals from processing lot targets in a single step. We have used this approach to estimate wool harvesting intervals, based on current information, to meet suggested UK and Australian environmental and marketing requirements. When residue targets are formally defined this may be a useful tool to determine wool harvesting intervals and to help wool producers and their advisers decide which products to use at particular times of the wool growing season.

The sale lot maximum residues and wool harvesting intervals reported here are more lenient than those suggested previously.

Keywords

Wool, pesticide, residue, breakdown, wool harvesting interval

Introduction

Pesticide residues in greasy wool may cause environmental problems due to the release of residues in wool scour effluent (Shaw, 1997). It is possible to calculate directly from the permissible environmental standards in water back to the maximum concentration of pesticide that should be permitted in wool processing lots (Russell, 2000). If wool processors can ensure that the average concentration in the daily wool processing batch remains below a given level, then the wool scour effluent will not cause environmental standards to be exceeded.

The environmental standards proposed for river and ocean water that are relevant for wool scouring operations are -

- Environmental quality standard (EQS). This is an annual average, based on average emissions for scouring plants under average river flows and takes into account the chronic exposure of aquatic organisms (Savage, 1998).
- Maximum allowable concentration (MAC). This is a maximum concentration which is allowable only for short periods of time and which is based on acute toxicity under conditions of low river flow (Savage, 1998).
- Australian limits are Environment Australia estimates based on acute toxicity figures, LC_{50} at 96 hours.

The EQS and MAC are UK standards but it is anticipated that they will be adopted in other EU counties.

Proposed environmental limits and the corresponding wool residue concentration for wool processing lots are summarised in Table 1. The wool scouring plant at Spenborough, which was used by Savage (1998) to estimate UK/EU residue limits has now closed and its relevance to current UK requirements is questionable. For that reason, the environmental requirements of the Calder River below Dewsbury were used by Russell to estimate UK residue limits. They may underestimate other European requirements. The UK EQS data are taken from Russell (2000), the Australian data are from Savage (1998) and the UK MAC data are based on Savage (1998) but with the adjustments made for the Calder river system, rather than the Spenborough, as described in Russell (2000). The data for the Calder are obtained by multiplying figures for Spenborough by 1.56 because the Calder is a larger river system.

Calculation of the maximum permitted concentration of pesticide residues in individual wool sale lots is more complex. Wool from different sale lots is blended into processing lots at the scouring plant. This blending is part of the normal scouring process and usually includes a range of different types of wool so that scouring of identical lines of fleeces from one location is relatively uncommon.

In order to consider the situation of individual wool sale lots it is necessary to model the blending process that produces the wool processing lots considered in Table 1.

While the National Registration Authority has yet to announce its position on this, we believe it is important to take into account the distribution of each pesticide on all Australian wool lots when setting standards for the residual pesticide concentration of individual sale lots. This distribution includes the proportion of the national flock treated with the chemical. The distribution results from the normal time and method of application of the product, since the range of values is based on the residues observed in actual practice. This distribution is obtained from the national wool residue survey data, which covers about 600 fleece wool sale lots each year (Williams and Brightling, 1999).

The wool blending model proposed by Shaw and Russell and described by Savage (1998), provides a statistically sound estimate of the maximum residue levels that can be tolerated in an individual sale lot in order to be confident that the scouring effluent will meet environmental standards. It is particularly suitable for existing products with a stable market share, but can be modified to allow for a growing market share, or for estimating the expected situation for new products.

Table 1. Proposed environmental limits and corresponding maximum processing lot limits.

	UK EQS (ng/L)	Scour lot maximum (mg/kg wool)	UK MAC (ng/L)	Scour lot maximum (mg/kg wool)	Australia (ng/L)	Scour lot maximum (mg/kg wool)
Organo-phosphates	30	2.6	470	12.6	1000	3
Synthetic pyrethroids	0.1	0.1	3.1	0.84	50	1.5
Triflumuron	18	7.9	550	70	3500	70
Diflubenzuron	6	1.3	160	4.2	1000	7.4
Cyromazine	5000	44	1.45×10^6	3,900	93×10^6	97,000
Dicyclanil	310	1.75	17,000	46	1.1×10^6	1,100

Source: UK EQS estimates, except dicyclanil, (Russell, 2000), UK MAC and dicyclanil UK EQS (Savage, 1998, adjusted as in Russell, 2000), Australia (Savage, 1998). These residue targets are not official.

The Russell/Shaw Wool Blending Model (Savage, 1998; Savage and Russell, 1999)

Procedure

- Using the national wool residue survey data to represent the national clip, take sample sale lots 10 or 20 at a time to generate 1000 processing batches. For small processing plants (UK) 10 sales lots a day would be processed, while larger plants (Australia) would process at least 20 lots a day. A larger number of lots per day decreases the risk of large effects by averaging out the small number of high residue lots with a larger number of low residue lots.
- Calculate how often these sample processing batches exceed the required processing lot maximum (the limit which would cause the required environmental standards to be exceeded).
- If the proportion of sample processing batches which exceed the limit is too high then exclude the sale lots with the highest residues, as would be the case if prescribed residue limits were imposed.
- Generate a further 1000 processing batches to find how often the environmental standards would be exceeded.
- If the proportion exceeding the limit is still too high then more high residue lots are excluded and the process repeated.

- By progressively excluding the highest residue lots it is possible to determine the maximum residue concentration for sale lots that would ensure that processing batches would remain within required limits.

The process of progressively eliminating the highest residue sale lots can be automated to quickly find the cutoff point below which the processing lots will meet the environmental requirements shown in Table 1.

Some limits, such as the UK EQS, which are based on chronic toxicity data are annual average limits. It is permissible to exceed the EQS relatively often, provided that the average residue over the year does not exceed the EQS. To determine maximum wool residue limits it is only necessary that the 1000 sample processing lots generated do not have an **average** exceeding the specified limit.

Other limits, such as the UK MAC indicate the maximum pesticide concentration that can be tolerated in stream water at any one time, and for that reason, are derived from acute toxicity data. In this case it is necessary that the sample processing lots generated do not exceed the required processing lot limit more than 5% of the time. The Australian wool residue standards are also determined on a maximum allowable residue basis, and again acute toxicity figures are used, although more lenient target figures are considered appropriate (e.g. LC_{50} rather than LC_0) because of the rapid dispersion and dilution that occurs at ocean outfall (Geelong).

Survey data adjustments

The report by Savage (1998) included estimates of the sale lot maximum concentration corresponding to the specified processing lot concentrations determined for that report. This was based on wool residue data from The Woolmark Company's Australian fleece wool survey from July 1997 to June 1998. More recent survey data is now available and was used here to generate current estimates.

If a product is rapidly increasing market share it is possible to model the future situation. This is done by increasing the proportion of lots containing that product to reach any expected market share before using the data to estimate sale lot limits. The wool blending model requires survey results and so is not directly suitable for new products, although if the expected pattern of use is known a dummy set of survey data can be generated.

For all products except cyromazine the analysis used the most recent data available - April 2000 to March 2001 (Brightling, 2001). Over the last two years the average concentration of organophosphates (OPs) has been low. It is not clear whether this is due to greater attention to residues from these products, the availability of insect growth regulators with greater safety for the user or less severe fly seasons. It is possible that a higher "normal concentration" should be considered for these products. Synthetic pyrethroid (SP) wool residues have also declined over the last few years but this may be due to replacement by newer treatments, so current survey data may be appropriate rather than the higher figures found in the past.

For cyromazine, there is some doubt that the most recent survey data represent the "average" residues. Results for the last year have been lower than in previous years and it is believed that previous results are more representative of the use of this product (Brightling, 2001). Therefore the survey data from July 1999 to June 2000 were used rather than the most recent results.

In the case of cyromazine and dicyclanil, using the survey data without further adjustment, it was not possible to find situations in which any of the environmental limits were exceeded. However, the use of these products could increase if there are restrictions on other products. Therefore an increased market share was simulated to determine whether some limits might need to be used in the near future. For cyromazine, all the samples with positive cyromazine residues were replicated three additional times and all samples below the detection limit were removed. This simulates the situation that would occur if **all** wool producers used cyromazine, using the same methods as are currently in use by those leaving measurable residues. At present about 25% of wool samples are positive for cyromazine, so this simulates a 4-fold increase in usage.

Products containing dicyclanil have only recently been marketed for sheep flystrike control and survey figures for this chemical are available from July 1999. Only 1.2% of wool samples are above the detection limit for this chemical so the entire period from July 1999 to March 2001 was used to obtain enough positive results for a meaningful analysis. With this data a 10-fold increase in market share was simulated by using 10 copies of each dicyclanil positive result, while removing an equivalent number of dicyclanil negative samples from the test batch.

Table 2 summarises the residue details for the data set used for each chemical or group. Table 3 shows the maximum wool residue in sale lots that would avoid exceeding the limits in Table 1.

Table 2. Mean wool residue and proportion of positive sale lots in the National wool residue survey for April 2000 to March 2001 (cyromazine data are for July 1999 to June 2000).

	OPs	SPs	Triflumuron	Diflubenzuron	Cyromazine	Dicyclanil
Mean residue (mg/kg wool)	1.7	1.5	8.2	5.3	5.1	0.11
% Positive	51%	17%	29%	15%	25%	1.6%
Adjusted					x 4	1999-01 x 10

The 'Adjusted' row shows the changes made to the current survey data for this analysis.

Table 3. Proposed wool sale lot maximum limits using the wool blending model (mg/kg wool).

	OPs	SPs	Triflumuron	Diflubenzuron	Cyromazine	Dicyclanil
UK EQS	56	**2.8**	**80**	**32**	**>>130***	**>>24***
UK MAC	>75	10	170	**32**	na	na
Australia	**48**	52	170	70	na	na

*For cyromazine and dicyclanil the highest results in the survey were 130 and 24 mg/kg wool, respectively. It is not possible to estimate how much higher the limit should be than these values.
na: no estimate is available because there is no survey result high enough to exceed the relevant limit even with a 4 to 10-fold increase in market share.
Figures shown in bold are the most limiting value for that chemical or group.
Wool sale lot maximum residue limits shown here are those required to meet the processing lot criteria in Table 1. The processing lot targets are not official and therefore the sale lot targets are not official.

Wool Residue Limits vs Wool Harvesting Intervals (WHIs)

The term wool harvesting interval is used for the recommended period between application of the treatment and the following shearing. This term is used to avoid confusion with "withholding periods" which are a requirement for the registered use of a product and must be observed, whereas it is expected that "wool harvesting intervals" will be recommendations, not mandatory.

The Russell/Shaw Wool Blending Model generates a sale lot maximum residue limit, such that if all sale lots above that limit are excluded, the remaining wool will be suitable for the specified market. This would be the appropriate method if all or most wool was tested for wool pesticide residues and the actual concentrations of all lots were known. Wool buyers could then purchase only the wool with residues below the limit they require. This is not the same as imposing a wool harvesting interval to allow buyers to purchase wool that has been collected by observing some specific time limit between treatment and the next shearing.

Wool producers who treat sheep and then shear at or close to the wool harvesting interval will not have an exact known wool residue concentration. Both experimental studies (Campbell *et al.*, 1998) and surveys of wool residues (Horton *et al.*, 1999, Morcombe *et al.*, 1999) show that normal biological variation will result in a wide range of possible wool residue concentrations after any specified treatment. This results from differences between sheep, climate variation, equipment used etc.

The effect of this variation is that if any given wool harvesting interval is used, then the actual sale lots resulting from that wool will have a wide variation. Most will be below the required residue concentration, but some higher residues will be observed. Further enhancement of the method is required to determine wool harvesting intervals to meet the processing lot requirements.

The Withholding and Blending model

Procedure

- The national wool residue survey data is used as a basis of the method as before.
- The residue concentration of each of the sale lots is converted to an estimated time from treatment to shearing for that lot using the model developed by Campbell *et al*. (1998). This cannot be estimated precisely, due to the variation noted above, so for each sale lot, 10 new sale lots are generated with their **average** residue concentration the same as the specified sale lot, but with the log normal distribution expected for the treatment under consideration. The standard deviation for the log distribution is 76% for OPs and SPs, 73% for triflumuron, 46% for diflubenzuron, 61% for cyromazine and dicyclanil. The time from treatment to shearing that would result in that residue is estimated for each of the 10 sale lots.
- Starting with 600 survey lots, this provides 6,000 sample lots with the same average wool residue and the same distribution of wool residues as the original survey data set and a distribution of time intervals between treatment and shearing that would have produced that set of data.
- The Wool Blending Model is used on these samples as before until the criteria for processing lots are met. However, rather than progressively eliminating the highest residues in turn, we progressively eliminate those with the shortest time from treatment to shearing. The result will be an estimate of the wool harvesting interval that would be required to meet the wool processing lot criteria.
- In some cases the EQS may be satisfied by reasonable average concentrations, while the MAC may sometimes be exceeded even though its limit is higher. Therefore both criteria should be tested.

The method is essentially the same as the Russell/Shaw Wool Blending method, apart from the extra step of converting wool residue concentrations to estimated time periods, with allowance for the normal variation inherent in the method of application. The sale lot residue is only an intermediate target – the true target is the processing lot maximum. Therefore it is not essential to actually meet any specified sale lot maximum so long as it can be shown that the processing lots will be within the limits required. The Withholding and Blending Model ensures that if an occasional wool sale lot has a higher than expected residue (for a given WHI) then it will be balanced by corresponding low residue lots. If the WHI is observed then the average of all such sale lots will be within the required limits. Table 4 shows the WHIs for a range of common treatments based on the processing lot limits in Table 1.

The method of Horton and Campbell (1999) set the WHI such that the **average** sale lot would have equalled the concentration determined by the wool blending method (the limit given in Table 3). Due to the skewed distribution of residues in wool this would allow about 40% of results to exceed this limit. Others had objected that the method proposed did not include any margin for the variation in expected residues and that the WHI should be set so that there was only a 5% probability of exceeding the maximum residue limit. However, this ignores some of the safety margins for normal variation already existing in the Russell/Shaw blending model. When the Withholding/Blending model is used as described here, it sets a WHI such that about 7-16% of sale lots would exceed the concentration specified by the blending model. This method is therefore intermediate between the previous proposal (by Horton and Campbell, 1999) and the more stringent requirement that 95% of estimated residues remain below the sale lot limit.

The proposed method would result in a longer WHI than recommended previously (Savage, 1998, Savage and Russell, 1999) except that this has been more than offset by the use of more recent survey data and the increase in processing lot targets described by Russell (2000). As a result, all the WHIs in Table 4 are more lenient than those in Savage (1998).

Table 4. Suggested days from treatment to shearing using the Withholding/Blending Model.

	UK EQS	UK MAC	Australia
Organophosphates - Current data			
Diazinon off-shears backliner	26	24	**43**
Diprite® short wool dipping	0	0	**81**
Diazinon lice dipping	65	63	**98**
Diazinon fly control dipping	80	72	**118**
Diazinon jetting	0	0	**64**
Synthetic Pyrethroids			
Deltamethrin off-shears	**175**	105	60
Lambdacyhalothrin off shears	**215**	133	79
Alphacypermethrin off-shears	**238**	151	88
Cypermethrin off-shears	**265**	172	100
SP long wool backliner	**>365**	357	207
Triflumuron			
Short wool backliner	**101**	45	11
Diflubenzuron			
Off-shears backliner (400mg/50kg)	244	**263**	112
Off-shears backliner (500mg/50kg)	297	**303**	175
Long wool backliner	**>365**	**>365**	290
Lice dipping (low dose)	**314**	313	181
Lice dipping (standard dose)	**>365**	**>365**	331
Flystrike dipping	**>365**	**>365**	343
Jetting for lice	**330**	326	0
Jetting for flystrike	352	**356**	32
Cyromazine			
Jetting	**0**	0	0
Spray-on	**<23***	0	0
Dip	**<193***	0	0
Dicyclanil			
Backliner	<54*	**<56***	0

*The WHIs for cyromazine and dicyclanil only apply in the case of a 4-fold and 10-fold increase (respectively) in use of these chemicals. At current use no WHI is required.
Figures shown in bold are the most limiting value for that chemical or group.
The WHIs shown here are those required to meet the processing lot criteria in Table 1. These residue targets are not official and therefore the WHIs are not official.

Comparison between methods for setting sale lot limits

Wool processors could restrict all purchases to wool with measured wool residue concentration and only consider wool that is below a specific concentration. The concentration limit should be the level determined by the blending model (Table 3).

If there is limited data available at sale on actual wool residue concentrations the wool buyers will not be able to use measured wool residues to meet processing lot requirements. Instead they will need to purchase wool that has not been treated within some specified time before shearing. This could be through a general declaration that all Australian wool meets the required criteria, if registered withhold periods were shown to be adequate. Alternatively, the specification might be by declarations from wool QA schemes or by individual producers. The time period could be determined by the Withholding/Blending Model as described here (Table 4).

The maximum residue method is a more precise method, which would allow wool processors to come closer to the residue limit without exceeding it. However, this would require every sale lot to be tested, and so is more expensive. In the short term the use of a WHI rather than maximum residue limits will allow wool processors to find wool that meets their requirements without the need to test every lot.

Advisory information for wool producers

When the environmental limits are enforced and wool processors have specific residue targets that must be met, suitable wool can be identified to buyers in two different ways.

Provision of actual wool residue results.
Wool producers can have their wool tested so that wool processors can select wool that meets their criteria, e.g. by purchasing only wool below the specified target. The wool test is relatively expensive, so most wool producers will only request a residue test if they are reasonably confident that the wool will provide a low result. They can be assisted in this decision by programs to estimate the wool pesticide residue from the treatment used. Alternatively they may use the model before carrying out a treatment to decide the risk that the resultant treated wool will exceed the limit when it is tested.

Declaration of low residue treatments
If wool producers have observed the required WHIs, they may make a declaration when their wool is sold that they have not used any high residue treatments. Such declarations would need a reasonable level of random testing to confirm that they were reliable. Wool marketing groups who wish to target specific low residue or eco-wool markets may be able to provide reliable low residue wool in this way without testing all lots. If high residues are found the model can be used to compare the measured result with the wool residue expected if the registered method has been used at the stated time.

Disclaimer

WHIs are not expected to be compulsory and should not be used to prevent the use of applications necessary for the welfare of the sheep while protecting the safety of the operator. It is anticipated that methods recommended for some situations may exceed the limits suggested here.

Both methods described here (for wool residue limits and for WHIs) assume a background residue concentration similar to the average Australian wool clip. Some regions may differ in chemical usage, and if a processor purchased wool exclusively from a local area then that processor might need to establish background residues from that area. It should not be necessary for all wool producers in all other areas to observe stricter limits merely because some processors on some occasions process large lots from an area with unusual product usage.

The model used here assumes the pesticide breakdown rate calculated for sheep in New South Wales. The breakdown rate is affected by the environment (Campbell *et al.*, 1999), so the WHIs developed may not be suitable for all states. Models can be calculated using any relevant breakdown rate as required.

The WHIs given here are those corresponding to the wool sale lot targets published previously for UK and based on results from current wool residue surveys. If the targets are altered or are different for other markets, or the usage of these products changes, then the WHIs would be different from those suggested here but could be recalculated using the same procedure. Other methods of estimating WHIs may give different results.

Russell *et al* (2001) have reported that the removal of diflubenzuron in sewage treatment may be 90% rather than 80% as previously used. This would halve the mass of diflubenzuron coming out of the sewage system and therefore double the permitted limit for wool processing lots. In addition the time taken for diflubenzuron to move through the sewage system may be longer than previously thought, so that averaging of lots over more than 24 hours may be required. This allows occasional high levels to be averaged out with other low residue wool sale lots. If these changes are included in the model they would allow more lenient limits for diflubenzuron, or allow a two-fold increased market share while using the limits suggested in our paper.

This paper has considered only environmental limits for wool processors. In some cases occupational health and safety requirements for protection of shearers and others handling the raw wool may require lower target residues and longer periods between treatment and shearing.

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