1-1-1992

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Recommended Citation
Martin, Tony; Jacob, Robin; Davies, Marion; and Rutherford, Peter (1992) "How arsenic residues get in wool," Journal of the Department of Agriculture, Western Australia, Series 4: Vol. 33 : No. 2 , Article 8.
Available at: http://researchlibrary.agric.wa.gov.au/journal_agriculture4/vol33/iss2/8

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How arsenic residues get in wool

By Tony Martin1, Robin Jacob2, Marlon Davies3 and Peter Rutherford4

Wool can become contaminated with arsenic in various ways, and several different sources may each contribute to any individual arsenic residue problem.

Proven sources of arsenic contamination of the fleece are:
• dipping sheep in an arsenical dip (now illegal),
• dipping sheep in a non-arsenical dip in a contaminated dipping facility
• penning sheep on soil with high levels of arsenic before shearing.

Other possible sources include running sheep on land contaminated by gold mine tailings or exploration sites, and allowing sheep access to sites on the farm where arsenical compounds have been dumped, for example, rubbish dumps or sites where dip/sump sludge has been dumped.

Farmers can prevent wool arsenic levels above the Industry Standard by soil testing and sensible management of their dip and yards.

Background
Scouring wool during processing, removes any arsenic residue. The scouring effluent then contains arsenic, which can contaminate the environment at the time of disposal.

Importers of Australian greasy wool are concerned about these residues. In April 1989, the Australian Wool Corporation (AWC) introduced random testing of Australian wool clips for arsenic residues. Producers of wool containing 3.0 to 9.9 parts per million (ppm) arsenic received a warning, and those producing wool with 10 or more ppm arsenic received only 80 per cent of the market price for their wool.

In mid 1991, the AWC changed these arrangements. Wool now found to contain more than 9.9 ppm arsenic may not be marketed for export; producers of wool containing 3.0 to 9.9 ppm still receive a warning.

At the start of this program, the industry assumed wool containing more than 10 ppm arsenic must have come from sheep dipped in one of the arsenical sheep dips, the sale of which has been banned in all Australian states for some years.

The Department of Agriculture decided to investigate all cases of wool arsenic residues of more than 3 ppm identified by the AWC in Western Australia after April 1989. Initial investigations suggested that not all wool with more than 10 ppm arsenic came from sheep dipped in...
arsenic. We therefore planned our investigations of farms that had produced contaminated clips to:

- Determine whether arsenical dips had been used
- Identify the likely source of contamination on each property.

We also conducted on-farm experiments in conjunction with the CSIRO's Division of Wool Technology and the South Australian Department of Agriculture, to show whether wool could become contaminated with arsenic from farm sources other than arsenical dips.

This article presents the results of both the investigations into the sources of wool residues found by the AWC, and the experiments conducted on farms in Western Australia and South Australia.

Sources of residues

Sheep do not develop significant fleece contamination from eating or drinking arsenic-contaminated material. For practical purposes we can assume all arsenic in the wool results from direct contact with an external source.

On most sheep farms the commonest source is residue from arsenical dips used over decades until they were banned in 1987. The active ingredient in arsenical sheep and cattle dips is arsenic trioxide. This compound is stable, and residues in concrete or soil will remain there unless they are physically removed. Arsenic is found more than a metre deep under highly contaminated surface sites (see Table 1).

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**Table 1. Soil arsenic levels at different depths at a site in Western Australia**

<table>
<thead>
<tr>
<th>Depth (mm)</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 100</td>
<td>250</td>
</tr>
<tr>
<td>110 - 120</td>
<td>1400</td>
</tr>
<tr>
<td>210 - 400</td>
<td>520</td>
</tr>
<tr>
<td>410 - 600</td>
<td>430</td>
</tr>
<tr>
<td>610 - 800</td>
<td>180</td>
</tr>
</tbody>
</table>
Excluding these two high results (249 and 193 ppm), cases where sheep were not dipped in arsenic all gave arsenic levels of less than 100 ppm, but nine were more than 10 ppm. The highest level encountered (369 ppm) was in wool shorn prematurely, seven months after using an arsenical dip. For sheep shorn the usual 10 to 12 months after dipping in arsenic, the highest level was 225 ppm.

Nine farmers admitted dipping sheep in an arsenical dip while 44 claimed not to have used such dips. The highest wool arsenic level in this latter group was 249 ppm. If this case is excluded, the next highest level in sheep not dipped in arsenic was 193 ppm. These sheep were shower-dipped in a non-arsenical product straight after another group had been dipped in arsenic in the same facility.

We sought information concerning the group(s) of sheep involved; their shearing, dipping, and yarding history; their origins (whether bought in or home-bred); the history of any dipping facility present; current and past dipping practices; soil type, and possible sources of arsenic. The Agricultural Chemistry Laboratory of the Chemistry Centre of the Department of Mines performed the arsenic analyses.

By November 1991, the AWC reported 91 cases in which arsenic levels exceeded 3 ppm originating from 80 producers; 28 of these levels were more than 10 ppm. We have completed investigations for 53 of the 91 cases, including 20 cases in which levels exceeded 10 ppm arsenic. Table 2 shows the presumed source of arsenic contamination of the wool, and the lowest and highest wool levels associated with each source, for the 53 cases investigated.

### Table 2. Investigators' assessments of the most likely sources of arsenic residues in wool detected by AWC tests

<table>
<thead>
<tr>
<th>Presumed source</th>
<th>Number of cases</th>
<th>lowest</th>
<th>highest</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipped in arsenic</td>
<td>9</td>
<td>38</td>
<td>369</td>
</tr>
<tr>
<td>Contaminated dip</td>
<td>11</td>
<td>3</td>
<td>133</td>
</tr>
<tr>
<td>Contaminated yards</td>
<td>11</td>
<td>3</td>
<td>37</td>
</tr>
<tr>
<td>Contaminated dip and/or yards</td>
<td>4</td>
<td>4</td>
<td>249</td>
</tr>
<tr>
<td>Sheep bought-in</td>
<td>6</td>
<td>3</td>
<td>44</td>
</tr>
<tr>
<td>Yards and/or bought-in</td>
<td>3</td>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td>Dip and/or bought-in</td>
<td>1</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Contaminated dump</td>
<td>1</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Soil (mining)</td>
<td>1</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Wool bought-in</td>
<td>1</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Unknown</td>
<td>5</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>Total</td>
<td>53</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Lowest and highest AWC residue levels (ppm)

'Some terms used

Dipping: either immersing sheep in a plunge dip or thoroughly soaking the sheep in a shower.

1 ppm is equivalent to 1 mg/kg

Industry standard wool arsenic level: 10 ppm.

We investigated cases of arsenic residues of 3 ppm or greater identified by the AWC random testing program until mid 1991. Investigations included a farm visit, interview, soil sampling, and mapping of sheep yards.

'Natural' soil arsenic levels in Western Australia are generally less than 5 ppm, although some sites, notably those associated with gold deposits, may have levels as high as hundreds of parts per million.

It is common practice to pump used dipping fluid out of the dip or sump onto the yards, or on to the ground beside the dipping facility. When arsenical dips were used, these practices contaminated soil in and around sheep yards.

Dip or sump sludge (the solid material that settles out at the bottom of used dipping fluid) is rich in arsenic when an arsenical dip has been used. This material may have been baled out of the dip or sump onto the same spot every year. If arsenical sludge is not cleaned out, it will contaminate non-arsenical dips.

The concrete of dipping facilities also absorbs arsenic from arsenical dipping fluids, and this arsenic then contaminates non-arsenical dips.

Property investigations

We investigated cases of arsenic residues of 3 ppm or greater identified by the AWC random testing program until mid 1991. Investigations included a farm visit, interview, soil sampling, and mapping of sheep yards.

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**Presumed sources**

Nine farmers admitted dipping sheep in an arsenical dip while 44 claimed not to have used such dips. The highest wool arsenic level in this latter group was 249 ppm. If this case is excluded, the next highest level in sheep not dipped in arsenic was 193 ppm. These sheep were shower-dipped in a non-arsenical product straight after another group had been dipped in arsenic in the same facility.

Excluding these two high results (249 and 193 ppm), cases where sheep were not dipped in arsenic all gave arsenic levels of less than 100 ppm, but nine were more than 10 ppm.

The highest level encountered (369 ppm) was in wool shorn prematurely, seven months after using an arsenical dip. For sheep shorn the usual 10 to 12 months after dipping in arsenic, the highest level was 225 ppm.
In 10 cases all or part of the group of contaminated sheep was bought during the year before shearing.

The highest soil arsenic level found around the sheep yards on each property investigated varied from 9 to 25,000 ppm.

On one property the sump of the shower dip had been cleaned out since an arsenical dip had last been used, but the dip replenishment tank had not been cleaned, and the fluid contained a high level of arsenic.

We found no relationship between the arsenic level in wool and the highest level in soil around the yards.

The present situation

Over the three-year period since the AWC began testing wool clips for arsenic residues, the proportion of Western Australian clips tested that has contained more than 9.9 ppm has fallen (see Table 3).

Research

We wanted to determine whether arsenic residues in the wool could result from penning sheep on contaminated soil in sheep yards before shearing, or from dipping sheep in non-arsenical fluid in facilities contaminated from previous use of arsenical dips.

Three properties in Western Australia and three in South Australia were used in the experiments. The properties selected were known to have arsenic contamination of both soil and dipping facility. Wool of experimental sheep tested negative for arsenic before the experiments began.

In dry conditions in Western Australia, fleece residue levels of 50, 605 and 31 ppm arsenic resulted from this process. Sheep taken straight to the shearing shed, with no possibility of contact with high-arsenic soil, had average fleece arsenic levels of less than three ppm on all properties. Wool and associated soil arsenic levels are shown in Table 4.
Any of the three levels of fleece contamination achieved in this experiment could contaminate a wool clip above the ‘Industry Standard’ (10 ppm or greater), depending on the management of the rest of the flock, and the make-up of individual bales of wool.

**Residues from the dipping facility**

We dipped 10 sheep on each property, six weeks after shearing, using a non-arsenical dipping fluid. Five of the dipping facilities were showers, and one (property 4 in South Australia) was a plunge dip. Sheep did not contact any arsenic-contaminated soil in the yards.

Wool samples were taken two days later, then again at one, three to five, and 10 to 12 months after dipping. Results from these sheep were compared with those from another group of 10 sheep which was not dipped.

On five properties wool contamination exceeded 10 ppm two days after dipping, but the arsenic levels varied greatly (see Table 5). The property with the plunge dip, which had not been cleaned out since an arsenical dip had been used, had the highest average fleece level — 1794 ppm arsenic in the dipped sheep. Undipped sheep on all properties had less than 4 ppm.

Levels of wool arsenic immediately after dipping are of interest, but the critical level is that remaining when the sheep are next shorn.

All arsenic levels in dipped sheep declined during the year (see Table 5 and Figure 1). Only property 4 had fleece levels more than 10 ppm 10 months after dipping; the average fleece level in the dipped sheep was 22 ppm.

Levels of arsenic in wool decline over time as wool grows, and from weathering (loss of arsenic from the fleece).

Arsenic levels in the surface concrete from dip sumps of properties 1 and 3 were about 3000 ppm; comparable measurements are not available for the other properties.

Penning wet sheep straight after dipping on soil with high levels of arsenic for 48 hours doubled the residue from dipping on one property (3, Western Australia) but had little effect on other properties.

We also looked at the effect of a cursory cleaning of dipping facilities on wool arsenic residues.

After dipping the sheep described above, the dipping facility on each property was emptied, and sludge baled out by hand. Concrete and pipes were washed with clean water, which was then emptied out; the dip was recharged, and a further group of five sheep dipped.

This cursory cleaning had little effect on five properties: wool arsenic levels in sheep dipped after cleaning were similar to those of sheep dipped before. However, when the heavily contaminated plunge dip was cleaned out, average post-dipping levels of arsenic in the fleeces fell from 1794 to 9 ppm.

The arsenic level of dipping fluid was not directly related to arsenic levels in the wool of dipped sheep, so it is not possible to predict the level of wool arsenic contamination from a sample of dipping fluid.

**How farmers can avoid high levels of arsenic in wool**

The commonest sources of fleece contamination with arsenic are arsenic-contaminated soil and arsenic-contaminated dipping facilities.
Farmers can investigate the extent of contamination in their own sheep yards and dipping facilities by following the Department of Agriculture's testing procedures. These are available on request from Departmental district offices.

They should then follow these steps:

- Avoid pens with high levels of soil arsenic when yarding sheep, especially for shearing.
- Consider covering contaminated pens with 'clean' material, for example, gravel or concrete.
- Do not treat sheep for lice if they have no lice.
- Use an effective back-line treatment for lice.
- If sheep are to be dipped, avoid using a contaminated dipping facility if possible: contractors with portable showers are a sensible option.

If a contaminated dipping facility must be used:

- Empty out all sludge, scrub concrete surfaces with detergent and water, and then thoroughly rinse with water before use.
- Dip sheep within six weeks after shearing.
- Do not shear prematurely the following year.

If these guidelines are followed, it is unlikely that arsenic residues in wool acquired from the dip will, on their own, cause clip contamination of more than 10 ppm.

Acknowledgements

The Australian Wool Corporation funded the experimental work, which was coordinated by Geoff Smith of CSIRO's Division of Wool Technology, who also performed all arsenic analyses.

The South Australian experiments were coordinated by Dr Bob Robinson of that Department of Agriculture.

Investigations and research in Western Australia were directed by the Arsenic Residue Policy Group, chaired by Ashley Mercy. On-farm investigations were conducted by the Department. The help of the five farmers and staff of Merredin Research Station was much appreciated.

Figure 1. Decline in average fleece arsenic levels (ppm) over a year after dipping 10 sheep on each of six Australian sheep farms in a non-arsenical dipping fluid.