Transferability of Six Pesticides from Agricultural Sprayer Surfaces

CARMEL T. RAMWELL¹*, PAUL D. JOHNSON² and HELEN CORNS²

¹Central Science Laboratory, Sand Hutton, York, YO41 1LZ, UK; ²Health and Safety Laboratory, Harpur Hill, Buxton SK17 9JN, UK

Received 10 August 2005; in final form 2 November 2005; published online 2 February 2006

Secondary exposure to pesticide residues on the external surfaces of sprayers does not currently form part of the risk assessment process. A measure of the ease with which residues may be transferred from the sprayer surface to the operator would enhance the accuracy of any such assessment. This study quantified the dislodgeability of six pesticides from sprayer surfaces in order to calculate the transfer efficiencies. The transfer efficiency was compound dependent, ranging from 80% for azoxystrobin to <25% for flusilazole and tebuconazole. When the washed and unwashed surfaces were analysed separately, more pendimethalin and isoproturon residues were removed from the wet surface compared with the dry surface. The variation in results for the different compounds highlights the need to consider a range of compounds to form generic statements to support guidelines regarding operator exposure to pesticide residues on sprayers.

Keywords: agricultural sprayers; dermal transfer; pesticides

INTRODUCTION

During the normal process of applying pesticides using agricultural spraying equipment, a proportion of the spray will be deposited on the external surfaces of the sprayer. These residues can accumulate to levels >1 g m⁻², although doses vary between both the type of sprayer used and the compounds applied (Ramwell et al., 2004). When a pesticide compound is submitted for registration, the applicant must prove that the product does not pose an unacceptable risk when used as indicated on the label. Typical exposure scenarios assessed include opening, mixing, loading and applying the product. In addition, exposure to bystanders and other workers, such as harvesters, may also be considered. However, secondary exposure to external residues remaining on the sprayer does not currently form part of the risk assessment of a compound during the registration process. It may be perceived that risks from external residues are negligible compared with other aspects of the spray operation, particularly as it is known that potential exposure is greater when handling the concentrate, i.e. loading and mixing, compared with applying the diluted pesticide (Glass et al., 2002). If external residues are currently being perceived as insignificant, hygiene may be poor compared with when pesticides are knowingly handled; this will increase the potential for dermal exposure in particular, and subsequent ingestion.

A study investigating the quantity of residues transferred to cotton gloves when in contact with sprayer surfaces indicated that these quantities were not insignificant, and it was proposed that consideration should be given to either enhancing the accuracy of the exposure assessment and/or exploring the possibility of improving decontamination methods (Ramwell et al., 2005). Information on the frequency of contact with contaminated surfaces and some measure of the ease with which residues can be transferred during this contact is required for human health risk assessments, but there has been little work in this area in relation to external residues on agricultural sprayers. To address this shortfall, the current study examined the transferability of six pesticides from a representative sprayer surface, both before and after washing; the influence of surface wetness on the dislodgeability of residues was also investigated.

*Author to whom correspondence should be addressed. Tel: +44(0)1904 462485; fax: +44(0)1904 462111; e-mail: c.ramwell@cs1.gov.uk
MATERIALS AND METHODS

Test compounds

Stock pesticide solutions were prepared individually and gravimetrically using the formulated product and distilled water. The compounds were chosen to represent a range in physico-chemical properties of commonly used pesticides and details of the compounds are given in Table 1. The pesticides were applied using an airbrush (Morgam) fitted with a glass vial reservoir (1.8 ml). The products (Amistar, Folicur, Bavistin, Lyric and Trump) were applied in two batches, as 0.5 ml of each product was used. After each application, the spray lines and vial were rinsed with 0.25 ml of distilled water and the rinsings sprayed onto the test surface. The volumes used were the maximum that could be applied in a practical manner while avoiding the generation of any drips. The target application rate was 5 mg for each surface; this mass is comparable with the mean pesticide mass on the external surfaces of spray tanks and mudguards of field sprayers (Ramwell et al., 2004).

Test surfaces

The test surfaces were new, 14 litre pure water tanks (Hardi International A/S) as used on agricultural sprayers. These consisted of a painted-metal frame supporting a polyethylene tank. Each surface was contaminated with the six actives (Test compounds section) and left to air-dry for 24 h. The washed surfaces were washed for 5 s using a pressure washer (Karcher 855S) giving a representative cleaning time of ~15 min for a whole sprayer. Separate surfaces were used to represent unwashed and washed surfaces and to quantify removable and dislodgeable residues (defined in Removable residues and Dislodgeable residues sections) with three replicates per test condition. Six test conditions were established: (i) removable residues—unwashed, dry surface; (ii) removable residues—washed, dry surface; (iii) dislodgeable residues—washed, dry surface; (iv) dislodgeable residues—washed, dry surface; (v) dislodgeable residue—unwashed, wet surface and (vi) dislodgeable residues—washed, wet surface. An unwashed, wet surface was created by applying 2.5 ml of distilled water using an airbrush that was sufficient to wet the surface without causing dripping.

Removable residues

In this study, removable residues were defined as the quantity of residues removed by wiping the test surface with a methanol-washed cotton swab wetted with methanol (5 ml). Three swabs were used to wipe the entire surface of the tank to form a composite sample and the swabs were placed in an HDPE bottle (250 ml). This was repeated a further two times on the same tank giving a total of nine swabs per composite sample. A test was undertaken to confirm the suitability of this sampling method. Six tanks previously wiped with methanol-wetted swabs (as described above) were nominally divided into one-third and re-wiped using swabs wetted with 5 ml of either methanol, ethyl-acetate or cyclohexane. The position (top, middle or bottom) of the area swabbed with each solvent was alternated between the tanks and each area was wiped twice with swabs wetted by the same solvent. All samples were stored at −18°C prior to analysis.

Dislodgeable residues

Dislodgeable residues were quantified using dry, methanol-washed cotton gloves. A glove was worn on each hand and the entire surface of the tank was rubbed for 3 min. Each glove pair was placed in an HDPE bottle (250 ml) and stored at −18°C prior to analysis.

Chemical analysis

The pesticide residues were extracted by adding methanol (50 ml for swabs and 100 ml for gloves) and sonication for 30 min. Carbendazim and isoproturon were analysed by liquid chromatography (LC). The main LC mobile phase (A) was prepared from acetonitrile (45%), deionized water (45%) and methanol (10%). Mobile phase (B) was deionized water and mobile phase (C) was acetonitrile. A Waters Symmetry Shield RP8 column, 3.9 × 150 mm, diode array detector and Millennium software was used. The flow rate was set at 1.0 ml min⁻¹ and the mobile phase was initially 5% (A), 25% (B) and 70% (C) at 40°C. After 10 min this was changed to 75% (A) and 25% (C) and after

<table>
<thead>
<tr>
<th>Product name</th>
<th>Active ingredient (a.i.)</th>
<th>Water solubility (mg l⁻¹)</th>
<th>Koc</th>
<th>Log Kow</th>
<th>Pesticide type</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amistar</td>
<td>Azoxystrobin</td>
<td>6</td>
<td>423</td>
<td>2.5</td>
<td>Fungicide</td>
<td>403.4</td>
</tr>
<tr>
<td>Bavistin</td>
<td>Carbendazim</td>
<td>8</td>
<td>225</td>
<td>1.6</td>
<td>Insecticide</td>
<td>191.2</td>
</tr>
<tr>
<td>Lyric</td>
<td>Flusilazole</td>
<td>54</td>
<td>1660</td>
<td>3.7</td>
<td>Fungicide</td>
<td>315.4</td>
</tr>
<tr>
<td>Trump</td>
<td>Isoproturon</td>
<td>70</td>
<td>139</td>
<td>2.5</td>
<td>Herbicide</td>
<td>260.3</td>
</tr>
<tr>
<td>Trump</td>
<td>Pendimethalin</td>
<td>0.3</td>
<td>15744</td>
<td>5.2</td>
<td>Herbicide</td>
<td>281.3</td>
</tr>
<tr>
<td>Folicur</td>
<td>Tebuconazole</td>
<td>32</td>
<td>1027</td>
<td>3.7</td>
<td>Fungicide</td>
<td>307.8</td>
</tr>
</tbody>
</table>

Source: http://www.inra.fr/Internet/Produits/agritox/.

Table 1. Pesticide properties
19 min this was changed back to its initial values. The injection volume was 20 µl and the total run time was 30 min.

Azoxystrobin, flusilazole, pendimethalin and tebuconazole were analysed by gas chromatography (GC). The GC system consisted of a Hewlett Packard (HP) 6890 GC fitted with a BPX-50 MS column (30 m × 2.5 mm, 2.5 µm film thickness) and an HP 5973 Series Mass Selective Detector (MSD). The injection volume was 1 µl. The injection (splitless) and transfer line temperatures were 250 and 280°C, respectively. The oven temperature programme was 100°C for 1 min, ramping at 25°C min⁻¹ to 300°C and holding for 6 min; total run time was 15 min. Helium (>99.996%) was used as the carrier gas, and electronic pressure control in constant flow mode delivered 0.98 ml min⁻¹. The MSD was operated in Selected Ion Monitoring (SIM) mode and data were collected between 8 and 20 min.

The limits of detection ranged from 0.1 to 2.5 µg and recoveries were within the range of 73–84%, which is considered acceptable for residue determinations (Hill, 1997).

Data analysis

Data from the three replicates of the surfaces wiped with methanol-wetted swabs were used to provide a mean value of removable residues. The transfer efficiency was calculated by dividing the dislodgeable residues for individual tanks by the mean removable residue for each compound. Students-t test was used for statistical analysis where applicable.

RESULTS

Removable residues

The quantity of pesticide removed by three sequential swabs using methanol-wetted swabs varied between compounds ranging from ~2000 µg for carbendazim, isoproturon and pendimethalin to ~3500 µg for azoxystrobin and tebuconazole (Fig. 1).

Efficacy of sampling technique

Following the sequential swabbing with methanol, the surfaces were wiped again with different solvents and the results illustrated in Fig. 2. The mean quantities of pesticides on re-swabbing with ethyl acetate, methanol and cyclohexane were 9.7, 5.2 and 5.3 µg, respectively. In relation to the removable residues, the quantity of pesticides that could be removed by further swabbing was <3% of the removable residues on the whole. There was little difference between the performance of methanol and cyclohexane in removing residues, but significantly (P < 0.05) more residues were removed by ethyl acetate compared with methanol for all compounds. However, in absolute values, the differences were small (~5 µg).

Dislodgeable residues

With the exception of azoxystrobin, the maximum quantity of pesticide that could be dislodged was in the order of 1500 µg (Fig. 3). As could be expected, more residues were dislodged from the unwashed surfaces compared with the washed surface, but there were differences between the compounds. For example, washing removed over 70% of tebuconazole residues compared with only ~30% for carbendazim and 50% for azoxystrobin.

Bulking the data for washed and unwashed surfaces, there was no significant difference in dislodgeable residues depending on whether the surface was initially dry or wet. However, when the washed and unwashed data were analysed separately, for washed surfaces, significantly (P < 0.05) more residues of isoproturon and pendimethalin were dislodged when the surface was wet compared with dry.

Fig. 1. Removable residues showing the mean ± 1 SE.
Transfer efficiency

There were large differences in the transfer efficiency between compounds (Fig. 4). The values for flusilazole and tebuconazole (~20%) were less than half that for carbendazim, isoproturon and azoxystrobin (>50%). Azoxystrobin had the highest transfer efficiency with an overall mean for both washed and unwashed surfaces of 80%. There was a tendency for the transfer efficiency to be greater for unwashed surfaces compared with washed surfaces, however, this difference was not significant with the exception of pendimethalin ($P < 0.05$) where the mean transfer efficiencies for washed and unwashed surfaces were 29 and 49%, respectively.

DISCUSSION

Comparison of the different solvents (methanol, ethyl acetate and cyclohexane) demonstrated that methanol might not remove all ‘available’ residues with three sequential wipes. Although ethyl acetate
can remove more residues, this solvent also removed paint and would thus be unsuitable for conducting any studies in the field. Likewise, both ethyl acetate and cyclohexane reacted with rubber, which again would not be suitable for use on real sprayers given the quantity of rubber hosing present. Consequently, the use of solvents other than methanol was deemed impractical. Nevertheless, when considering the quantity of residues remaining on the surface (<3% of ‘removable residues’) after three sequential wipes with methanol-wetted swabs, and the time taken to sample a single surface (~10 min), the proposed method for quantifying removable residues was deemed to be both practical and reasonable.

The fact that the quantity of removable residues differed between compounds is worthy of note. It is possible that there were losses due to drift during application that differed when the two mixes were applied. However, if this were the case, it could be expected that the observed differences in removable residues would mirror the mix of compounds as applied (i.e. flusilazole, isoproturon, pendimethalin or azoxystrobin, carbendazim, tebuconazole); this is not borne out in the results. It is more probable that the physico-chemical properties, such as volatility, octanol:water partition coefficient ($K_{ow}$) and solubility, influence the tenacity of the compounds. These results highlight the importance of investigating the behaviour of a range of compounds to enable more generic inferences to be made.

The transfer efficiencies (20–80%) were generally high compared with other published data (e.g. Byrne et al., 1998; Snyder et al., 1999; Williams et al., 2002). This finding may be attributable to a number of factors including the hardness of the surface sampled and the sampling technique. Roff and Wheeler (2000) reported higher transfer efficiencies from glazed tiles (22%) and rough tiles (28%) than from absorbent surfaces (1–2%) such as wood or carpet (Roff and Wheeler, 2001). This effect was attributed to the fact the compounds applied to absorbent materials can disperse into the matrix, thus reducing the quantity of residues on the top surface available for transfer. In the current study, the treated surfaces were relatively hard and smooth, and therefore residues should be readily available for transfer. This may explain why the results were similar to that of Slayton et al. (1998) who reported a study where the transfer rate of polychlorinated biphenyls (PCBs) from glass or painted metal (22–84%).

The sampling technique used in the current study of rubbing the surface is likely to result in a higher transfer of residues compared with simply pressing the sampling media (cotton gloves) on the surface. Slayton et al. (1998) found that more PCBs were removed from a concrete surface with rubbing than without. The contact time (3 min) may also account for higher transfer efficiencies in the current study compared with other reported values; Roff and Wheeler (2000) noted a linear increase in transfer efficiency of compounds from hard surfaces within the range of 5–30 s (the maximum time investigated). The differences in the sampling technique used here could therefore contribute to the higher transfer efficiencies for pesticides from sprayer surfaces even if...
there is a limit to the linearity of a relationship between contact time and transfer efficiency.

It is acknowledged that the sampling technique used in the current study would not be suitable for determining residue transfer during incidental contact with the sprayer. However, there are several parts of the sprayer where the contact would be a grabbing action and pressure applied, such as handles, and other sprayer parts during maintenance. Consequently, it was considered that the method used represented a worse case for maintenance, and the data demonstrate that residues can be relatively easily removed from sprayer surfaces. Nevertheless, to make an accurate assessment of potential operator exposure more data would be required on the contact type, frequency and duration.

The differences in transfer efficiencies between the compounds were not related to the water solubility of the compound, but there was an inverse relationship between transfer efficiency and the (Log) octanol-water partition coefficient ($P < 0.01; R = 0.57$). This could indicate that some residues are lightly bound to the polyethylene surface of the spray tank (or dust particles therein), so the higher the $K_{ow}$ of a compound the more difficult it is to remove in the absence of a suitable solvent, hence the lower transfer efficiency. However, owing to the small sample size, further work with a larger number of compounds would be required to give more confidence in this theory.

The difference in results for the washed and unwashed surfaces (i.e. with lower and higher initial doses, respectively) indicated that, on the whole, there might not be a linear relationship between pesticide loading and transfer efficiency. This is in contrast to the findings of Roff and Wheeler (2000) where the transfer of strontium tended to be higher at low surface loadings. The difference in these findings may be attributable to a number of factors including the compounds used and the sampling methods. For the current exposure scenario, further work with a wider range in pesticide loadings would be required to substantiate this theory. In relation to operator exposure to residues on the external surfaces of sprayers, it is unlikely that residues, on the whole, are more available for transfer while the surface is wet after washing.

**CONCLUSION**

The current study has provided novel data on the transfer of agricultural pesticides from hard surfaces. The data could be used as measures of transfer efficiencies for basic risk assessment models if data were also available on contact frequencies and duration with the sprayer surface. The data could be used to estimate probable exposures and raise awareness of the significance of external residues. This would assist in reducing exposure to pesticides if the operator then takes relevant precautions. The variation in results for the different compounds highlights the need to consider a range of compounds to form generic statements to support guidelines regarding operator exposure to pesticide residues on sprayers.

Acknowledgements—The authors are grateful to the Health and Safety Executive for funding the study and to Hardi International A/S for supplying materials.

**REFERENCES**
