Movement of triclopyr, picloram and aminopyralid down a river after blackberry spraying

John H. Moore[1], Brad Rayner[2] and Bret Vukelik[2]
[1] Department of Agriculture and Food Western Australia, 444 Albany Hwy, Albany, WA, 6330, Australia
[2] Department of Agriculture and Food Western Australia, Verschuer Place, Bunbury, WA, 6230, Australia
Corresponding author: john.moore@agric.wa.gov.au

Summary Movement of herbicides in water following spraying close to water courses concerns both the community and government regulators. Very few products are approved for use in or near aquatic environments due to application of the precautionary principle. Grazon Extra® contains aminopyralid, picloram and triclopyr and provides high levels of blackberry (*Rubus fruticosus*) control but is not specifically registered for use on river banks where much of the blackberry occurs. Blackberry plus the associated small river was sprayed with Grazon Extra and water samples taken at the spray site, 1 km downstream and 3.5 km downstream over the following 4 days. Salt was released into the river immediately before spraying to act as a tracer to determine when the herbicide was likely to pass the sampling points. Triclopyr was detected for short periods at 43 µg L^{-1} at the spray site, at 34 µg L^{-1} 1 km downstream and at 8.4 µg L^{-1} 3.5 km downstream. Aminopyralid and picloram were detected at the spray site but were not detected 1 or 3.5 km downstream. These levels are not expected to cause adverse environmental impacts.

Keywords Aminopyralid, blackberry, contamination, Grazon, herbicide, picloram, *Rubus fruticosus,* water quality, triclopyr.

INTRODUCTION

Movement of herbicides in water following spraying close to water courses concerns both the community and government regulators. Very few products are approved for use in or near aquatic environments due to application of the precautionary principle. Grazon Extra contains aminopyralid, picloram and triclopyr and provides high levels of blackberry control but is not specifically registered for use on river banks where much of the blackberry occurs.

Very few adverse experiences have been reported over many years of blackberry spraying with products containing triclopyr and/or picloram. Label statements such as 'Do not allow physical drift onto waterways …' (Dow 2007) have made some managers nervous enough to use less efficacious products specifically registered for aquatic environments.

This exercise intended to simulate a worse case scenario situation where blackberry plus the associated slow flowing river was sprayed and then the levels of herbicide contamination in the water and its movement downstream were determined.

MATERIALS AND METHODS

The experiment was conducted on a small blackberry-infested river running through private property in the south west of Western Australia. Stream velocity was measured at 60% of maximum depth at 10 equally spaced points across the stream together with stream depth to estimate the flow rate. The river was approximately 6 m wide and 0.5 m deep with a water velocity of 0.12 m s^{-1} at the spray site.

Two hundred kilograms of salt (sodium chloride) was mixed in 800 litres of water in open top drums and released over a 2 min period into the river just downstream of the area to be sprayed. A blackberry-infested area (200 m^2) was sprayed with a mixture of 1 L of Grazon Xtra in 100 L of water using two high pressure hand held nozzles (Hardi #20 at 400 psi) immediately after the salt release. This operation took 20 min to complete. Approximately half of the sprayed area was open water and this was also sprayed to simulate a worst case spraying situation. A high application rate of 5000 L ha^{-1} of spray solution (100 L over 200 m^2) was applied so that there was dripping of herbicide from the foliage into the water to again simulate a worst case scenario. The site was 20 m long by 10 m wide. Across the width there was a 3 m strip of blackberry and kikuyu on the south bank, 6 m of river with some over hanging blackberry and willows and a 1 m strip on the north bank with blackberry, willows and kikuyu. It is estimated that between 10–20% of the spray solution ended up in the river. This is equivalent to 0.8–1.6, 10–20 and 30–60 g a.i. of aminopyralid, picloram and triclopyr respectively.

Water sampling points were set up at the spray site, 1 km downstream and 3.5 km downstream. The stream velocity was measured and the time taken for the contaminated water to reach the downstream sampling points estimated. At the spray site, samples were taken from before spraying then every 20 min for 4 h, then hourly for 4 h, then approximately 4-hourly for 20 h, then daily for the next 2 days. At the 1 km sampling site, samples were taken at half hourly intervals from 1 h after spraying until the spike in salt concentration was detected, then at 20 min intervals for 3 h then hourly, 4-hourly and daily similar to the spray site. At the 3.5 km sampling site, sampling started 4 h after spraying at hourly intervals for 2 h then at 20-min intervals for 6 h followed by 4-hourly then daily sampling similar to the spray site. There were 88 samples taken, of which 60 were analysed for aminopyralid, picloram and triclopyr. New 20 or 50 mL disposable syringes were used to collect water so that many aliquots were taken to sample the width and depth of the water. Samples were collected in new brown glass bottles and stored in a cool room for 1–3 days before delivery to the Chemistry Centre of Western Australia. At the spray site, 1 L surface water samples were also taken by holding the bottles just below the surface of the water and moving across the width of the stream at the lower extent of the sprayed area. These were taken just before spraying then at 20 min intervals for 5 h, hourly for 4 h and 4 hourly for 20 h.

Salinity, temperature, pH and dissolved oxygen were sampled at various times and sites using a portable Hydrolab. The salinity measurements were taken to determine when the water from the sprayed site arrived at the downstream sampling sites.

RESULTS

The flow rate of the river was 249 to 335 L s^{-1}, the water temperature was 18.3 to 21.4°C and the pH was 6.7 to 7.1. The natural salt concentration as measured by water conductivity was 1.22, 1.28 and 1.54 mS cm^{-1} at the spray site, 1 km and 4.5 km sampling sites respectively. The water conductivity increased by approximately 0.1 mS cm^{-1} as the salt released at the spray site passed the sampling points.

The maximum concentration of triclopyr detected was 43 µg L^{-1} at the spray site immediately after spraying. This dropped to the level of detection within 80 min of spraying or 1 h after the end of spraying. At 1 km downstream the concentration of triclopyr increased between 3 and 4 h after spraying to reach a maximum concentration of 34 µg L^{-1} and was only just detectable at 7 h after spraying. At 3.5 km downstream the maximum level detected was 8.4 µg L^{-1} at 13 h after spraying. At 4 h earlier none was detectable and 4 h later it was just detectable at 2.4 µg L^{-1} (Figure 1). This peak occurred around midnight when sampling was only being done 4 hourly. However, the salt peak and surrounding values indicate it was close to the true peak. No triclopyr was detected at any site for the following 3 days. The level of detection is 2 µg L^{-1}.

The maximum concentration of triclopyr fell linearly with distance from the source (Figure 2).

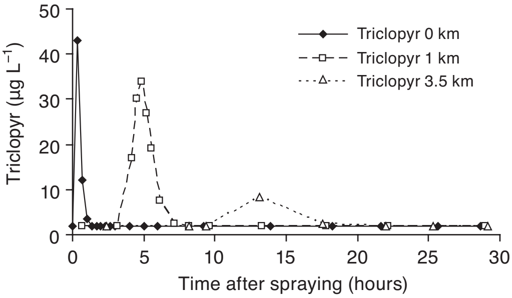

Figure 1. The concentration of triclopyr (µg L^{-1}) over time at the three distances downstream. The flat line at 2 µg L^{-1} is the level of detection.

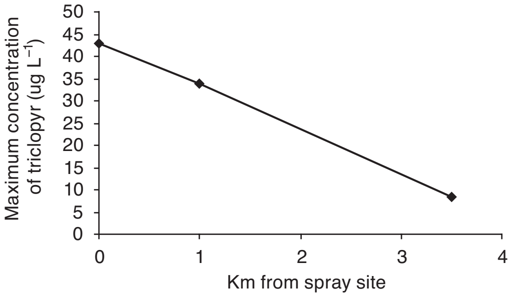

Figure 2. The maximum concentration of triclopyr at various distances downstream from the spray site.

Aminopyralid and picloram were not detected in any of the bulk water samples. The only detections recorded were 3.9 µg L^{-1} of aminopyralid and 25 µg L^{-1} of picloram, along with 580 µg L^{-1} triclopyr, in the surface water samples taken 20 min after the completion of spraying at the spray site. Aminopyralid and picloram concentrations had fallen to the level of detection within 1 h of spraying and triclopyr within 2 h of spraying (Figure 3).

The level of dissolved oxygen in the water at the various sites over the duration of the experiment is shown in Figure 4. There is the normal diurnal pattern and no obvious effect on aquatic microorganisms caused by the treatment.

DISCUSSION

Aminopyralid and picloram disappeared from the water very quickly and are unlikely to cause any adverse effects at the levels and durations detected. The most sensitive aquatic species listed for the herbicides used are diatoms to triclopyr butoxyethyl ester producing growth inhibition with an EC_{50} of 193–1170 µg L^{-1} and

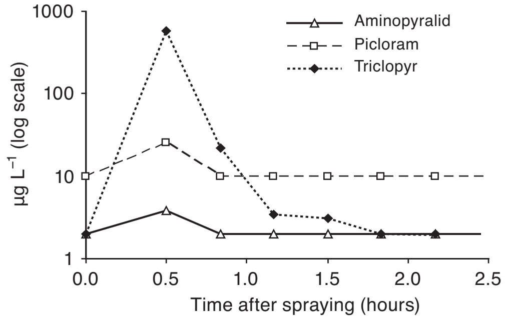

Figure 3. The concentrations of the herbicides (µg L^{-1}; log scale) over time in surface water at the spray site. The straight lines at 10 and 2 µg L^{-1} are the levels of detection.

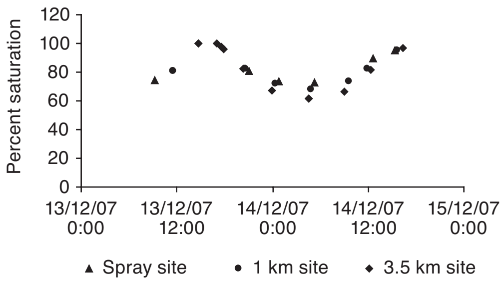

Figure 4. The level of dissolved oxygen as percentage saturation over the time of sampling.

some fish with an LC_{50} of 100–1000 µg L^{-1} (Moore and Moore 2009). The maximum levels of triclopyr detected in bulk water samples were less than a half of these levels and only persisted for short periods. Surface water sample levels of triclopyr may have exceeded the lower level for around 30 min but again are unlikely to have significant effects under field spraying conditions.

There was a linear reduction in maximum concentration of triclopyr from the spray site downstream (Figure 2). This result indicates dilution, and by extrapolation triclopyr would probably be undetectable more than 4–5 km from the source for this level of contamination in this type of stream.

Triclopyr fell to undetectable levels in the bulk water samples at the spray site within 1 h of spraying. At 1 km downstream triclopyr arrived about 2.5 h after spraying then increased to a maximum concentration 4.5 h after spraying and had fallen below the level of detection 7.5 h after spraying. At 3.5 km downstream it arrived approximately 11 h after spraying and had fallen to undetectable levels about 19 h after spraying. Water velocity in the river varied between 0.1 m s^{-1} and 0.5 m s^{-1} and could be used to predict approximately when the first detection of herbicide was likely.

Overall these data indicate that spraying blackberry or similar weeds along rivers with Grazon or products containing triclopyr, picloram and/or aminopyralid is unlikely to have any adverse effects on the aquatic life, stock drinking water or irrigation. While the effects of larger scale spraying will depend on the situation it is unlikely that normal blackberry spraying operations along rivers will cause observable deleterious effects due to the herbicide.

The logistics of the spraying operation and good practice using hand held equipment will normally ensure no adverse effects. In this exercise, worse case techniques were simulated resulting in a considerable amount of herbicide entering the water. The site was continuously sprayed with two hand leads delivering 400 L h^{-1}, over a short period, right on the banks and across the water. In normal situations there will be considerable amounts of spraying away from the immediate banks of the river and interruptions to spraying allowing sufficient time for dissipation to very low levels in the water.

Control of large infestations overhanging rivers using multiple crews or rapid application techniques may need assessment. Working in stages or separating crews by few kilometres should usually be sufficient.

ACKNOWLEDGMENTS

Andrew Reeves and Simon Merewether helped with various aspects of this study and the larger project. Funding for this work was supplied by the Department of Agriculture and Food Western Australia and under a Defeating the Weed Menace, National Heritage Trust, WA component of the National Blackberry Strategic Management (Eradication and Control) of Isolated and Outlier Infestations Project supported by the National Blackberry Taskforce.

REFERENCES

Dow (2007). Grazon Extra label. (Dow AgroSciences Australia Limited, NSW). www.dowagrosciences.com.au.

Moore, C.B. and Moore, J.H. (2010). HerbiGuide – The Pesticide Expert on a Disk. (HerbiGuide, Box 44, Albany, WA 6331). www.herbiguide.com.au.