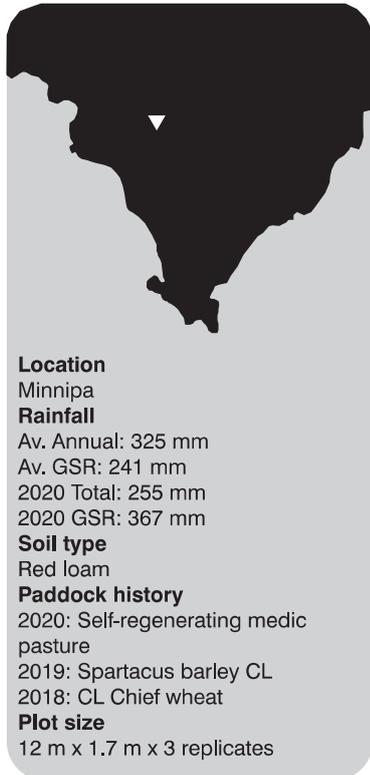


Persistence of the herbicide clopyralid in Eyre Peninsula soils

Mick Rose^{1,4}, Lukas Van Zwieten^{1,4} and Amanda Cook^{2,3,4}

¹NSW DPI Wollongbar NSW, ²SARDI Minnipa Agricultural Centre, ³University of Adelaide Affiliate Associate Lecturer, ⁴Cooperative Research Centre for High Performance Soils, Callaghan NSW



Key messages

- **Clopyralid herbicide carryover may harm some legumes - a sensitivity ranking of species to the herbicide has been established.**
- **Clopyralid persistence and crop toxicity is affected by soil type, rainfall and their interaction.**
- **Clopyralid can be released from stubble, so stubble management needs to be considered for managing potential carryover damage.**

Why do the trial?

The overall aims of this work are to determine the persistence of clopyralid herbicides over multiple seasons in different soil types and whether soilborne residues will injure subsequent crops.

Herbicides are a valuable tool for controlling weeds and reaching crop yield potential, but herbicide residues in soils can limit crop performance if not managed correctly. The recently concluded GRDC project DAN00180 (Rose *et al.*, 2019) found that between 5-15% of surveyed paddocks (n=40) contained residues of sulfonylureas or trifluralin that could lower seedling vigour of some crops. However, damage was avoided in most cases by growing crops tolerant to the herbicides (e.g. cereals or tolerant legumes in paddocks with SU residues). Growers also identified imidazolinone (group B) and clopyralid (group I) residues as potentially damaging to crops or constraining rotation options. However, the exact loss of productivity due to herbicide residues as a soil constraint has not been accurately determined due to the lack of tools to measure herbicide residues and quantify herbicide damage. It is difficult for growers and advisors to predict whether herbicide residues will cause issues beyond the “label” plant-back period, because the persistence and behaviour of these residues depends on numerous site-specific factors, including soil (chemistry, organic matter, microbial activity) and climatic conditions.

As part of a national Soil CRC project (4.2.001 Developing knowledge and tools to better manage herbicide residues in soil), we measured the persistence of clopyralid at several different sites in the 2019 and 2020 seasons. This article is an update on work

presented in the 2019 EP Farming Systems Summary, p 105. Here we present data from four sites for the 2019 season and carryover into the 2020 season.

How was it done?

The persistence of clopyralid was measured at four field sites during the 2019 growing season through until mid-2020. Site details, including soil characteristics and herbicide application details, are provided in Table 1.

Four soil samples comprising of homogenised sub-samples each were taken from quarter grids within a 100 m by 100 m georeferenced grid at participating farmer paddocks prior to sowing the 2019 winter crop (Mar-April 2019), at two depths: 0-10 cm and 10-30 cm. Repeated soil sampling occurred throughout 2019 and 2020 after the application of the clopyralid according to the following schedule: 1, 7, 21, 42, 84, 168, 364 days (d) after herbicide application. Soil samples were refrigerated and transported to NSW DPI, where they were dried at 40°C and then stored frozen until analysis for herbicide residues. Herbicides were extracted from soils, derivatized and analysed via GC-MS, with spike-recoveries for each soil type to ensure satisfactory sensitivity, accuracy and precision.

Table 1. Site locations, soil type and cropping details.

Site	Location	Soil type	Crop	Product	Date of application	Product Rate (L/ha)
SA1	Minnipa	Red loam	Barley (cv Spartacus)	Lontrel Advanced 600	25 June 2019	0.075
SA2	Poochera	Grey alkaline sandy loam	Wheat (cv Scepter)	Lontrel Advanced 600	25 June 2019	0.05
SA3	Minnipa	Sand	Self-regenerating medic pasture	Lontrel Advanced 600	23 July 2019	0.045
SA5	Mt Cooper	Red loam	Wheat (cv Scepter)	Lontrel Advanced 600	4 July 2019	0.04

In conjunction with the field trials, dose-response bioassays were conducted for clopyralid in washed pool sand or soil taken from the trial site at Minnipa Agricultural Centre, paddock N7 (SA1). Large volume topsoil samples taken in 2019 prior to herbicide application were transported to NSW DPI Wollongbar, air dried, homogenised and sieved to <2mm. Subsamples (20 kg) were then spiked with increasing concentrations of either herbicide, with six levels ranging from 0 - 100 ng/g (with ~50 ng/g equivalent to an application rate of 0.125 L/ha of Lontrel Advanced 600, distributed in top 0-10 cm profile). Residue levels were confirmed by liquid chromatography/mass spectrometry. Wheat (cv Scepter), barley (cv La Trobe), canola (cv Diamond), lupin (cv

PBA Batemen), field pea (cv PBA Butler), chickpea (cv PBA Slasher), faba bean (cv Nasma) or lentil (cv PBA Bolt) were sown into pots (dimensions 65 mm by 65 mm and 160 mm depth, filled with 140 mm soil kept moist to 80% field capacity by mass). Plants were harvested 21 d after sowing by cutting shoots at the soil surface, drying them at 60°C for 2 days and weighing to determine dry weight. Dose-response thresholds were determined for sand or soil by fitting shoot dry weight data to sand/soil clopyralid concentrations using 4 parameter log-logistic curves and the 'effective dose' for 20% shoot biomass reduction (ED20) was calculated, using the package 'drc' (Ritz *et al.*, 2015) in the R statistical soft-ware environment (R Core Team, 2019).

What happened?

As expected, bioassays showed that wheat, barley and canola were all tolerant to soil residues of clopyralid at rates representative of label rates (Table 2). The legumes tested were all sensitive, with the order of tolerance (from least to most sensitive in terms of shoot biomass at 21 d) being lentil ~ field pea < chickpea < faba bean < lupin (Table 2). Toxicity thresholds in the Minnipa soil (6% clay) were approximately 5 times higher than when the crops were grown in pure (washed pool) sand, showing the role that soil type can have on the bioavailability and hence toxicity of herbicide residues (Figure 1). This type of information is currently not widely available but is necessary to be able to interpret results from soil testing for herbicide residues.

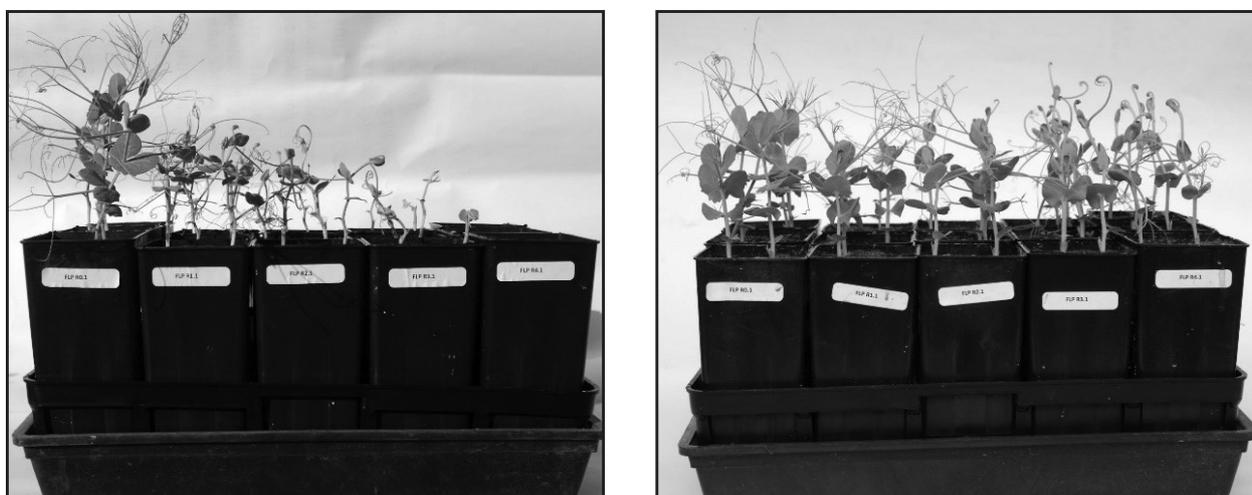


Figure 1. Phytotoxicity dose-response of clopyralid residues toward field peas in (Left) sand and (Right) soil (sandy loam, Minnipa, SA). Within each photo, the clopyralid dose increases from control (no clopyralid) on the far left, to label rate (~ 50 µg/kg) on the far right.

Table 2. Preliminary phytotoxicity dose thresholds (ng/g) for 20% shoot biomass reduction (ED_{20}) for different crop species growing in sand or soil spiked with clopyralid. Note that these data have not yet been finalised and may be slightly different depending on best model fits.

Species	Sand	Minnipa Soil (6% clay)
Lentil	0.5	3.4
Field pea	0.6	1.9
Lupin	8.8	54
Chickpea	0.5	6.2
Faba bean	3.2	25
Wheat	> 100	> 100
Barley	> 100	> 100
Canola	> 100	> 100

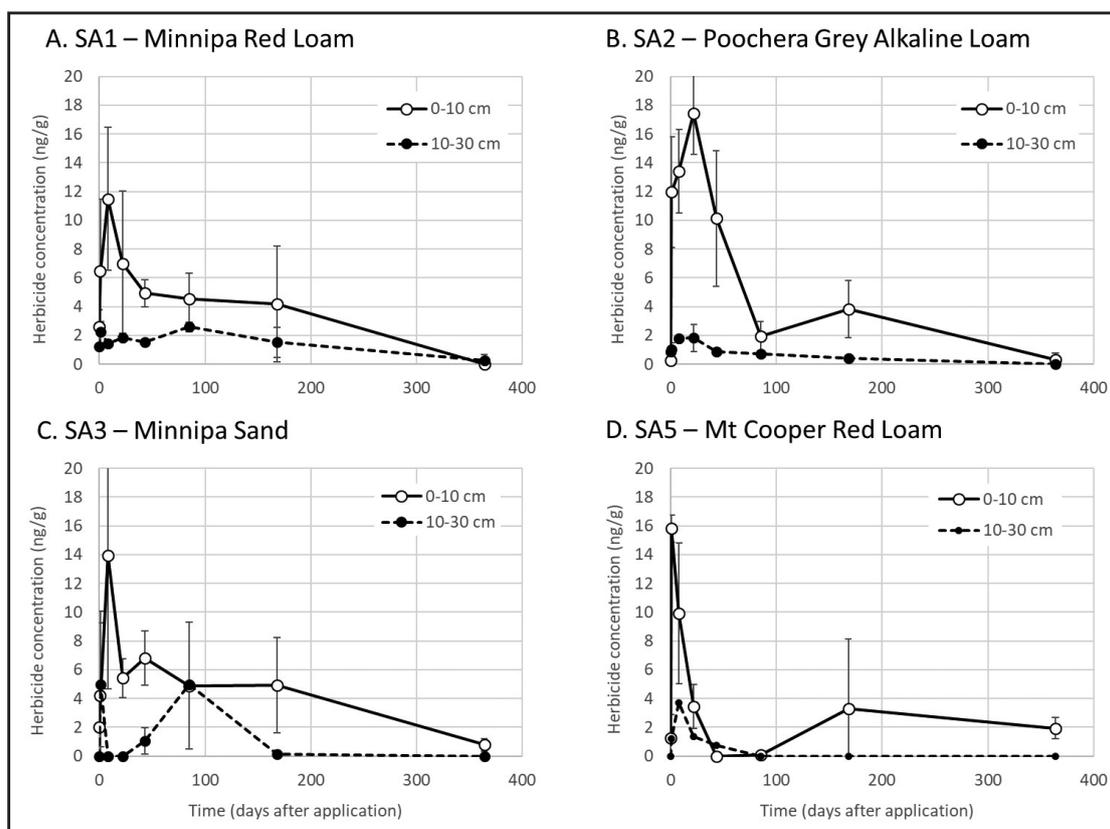


Figure 2. Clopyralid residue concentrations in 0-10 cm layer (white points, solid line) and 10-30 cm layer (black points, dashed line) at four EP monitoring sites. Points represent average residue levels of three field replicates, error bars are standard deviations. Line are a visual guide and are not statistical model fits.

Table 3. Soil properties, clopyralid application date and clopyralid dissipation at four monitoring sites (SA1, SA2, SA3, SA5).

Location	Soil Clay (%)	Soil pH	Soil OC (%)	Precipitation 0-180 d post-spray (mm)
SA1	6	7.8	1.0	120
SA2	6	7.9	1.0	75
SA3	<1	7.0	0.2	108
SA5	10	7.1	1.7	117

There was some variation in the persistence of clopyralid at the four different sites monitored from mid-2019 to mid-2020 (Figure 2). At all sites except Poochera, baseline residues of clopyralid were detected at 1-2 ng/g prior to the application of clopyralid in-crop in 2019. After clopyralid application, concentrations in topsoil (0-10 cm) increased to maximum levels of 12-18 ng/g, depending on the site. At the Minnipa sites, there was a steady decline in clopyralid over the 364 d after application, with approximately 30% of the clopyralid remaining at the 6-month sampling in January 2020. In contrast, at the Poochera and especially the Mt Cooper sites, dissipation was faster in the initial 3 months to day 84, to the point where clopyralid could no longer be detected in topsoil at Mt Cooper. However, clopyralid residues increased again at both sites at the 6-month sampling date and remained detectable (but low) at 1-2 ng/g by 364 d.

This pattern fits field observations (and product labels) that clopyralid can be released from crop stubble where clopyralid herbicides have been applied in crop. Thus, even though clopyralid breakdown/dissipation from soil can be rapid in some soils where rainfall and organic matter is sufficient (e.g. Mt Cooper, SA5), clopyralid residues may still be present in soil at sowing of the following crop (Table 3).

Another important point to note is the high variation in clopyralid concentrations at each time point,

particularly at 168 d after spraying. Repeat analysis of the same soil sample (i.e. lab replicate) showed that analytical variation was low, suggesting that there is high variation across field replicates. This means that although the average concentration in one paddock could be 3.5 ng/g (i.e. Mt Cooper SA5 at 168 d), the actual concentrations at different points across that paddock could vary from 0 - 10 ng/g or more.

What does this mean?

This project has generated seedling toxicity thresholds for the effect of soilborne clopyralid residues on different legume species. Although there will be variation in these thresholds across different soil types, the values can give an indication as to when seedling injury may occur if soil clopyralid testing is conducted.

For the sites monitored in this project, residue levels would likely have been, on average between 2-5 ng/g at the different sites, but concentrations at particular points within a paddock show variation and could have been greater. It is unlikely that any of the crops planted in 2020 in these paddocks would have suffered damage from clopyralid residues, but alternative legumes like field peas or lentils could have been injured. The data from this project also confirm field observations that remobilisation of clopyralid from senescing crops or crop stubble occurs, and more research is required to determine where and when this may cause issues.

This research is currently being repeated for the 2020 cropping season and samples will be taken in April 2021 to determine clopyralid carryover. Additional research aims to predict how toxicity thresholds and persistence might vary from soil to soil, depending on clay content, pH, organic matter or other soil properties. Finally, the project is examining whether injured plants can be analysed to determine if a herbicide residue is responsible for causing the injury, as a diagnostic tool to help growers avoid herbicide residue damage in future. It is hoped that through a better understanding of factors that contribute to persistence combined with modelling, growers will have greater confidence in decisions relating to plant-back periods provided on product labels and be better able to consider the potential impacts of current herbicide use on future rotations.

Acknowledgements

This work has been supported by the Cooperative Research Centre for High Performance Soils whose activities are funded by the Australian Government's Cooperative Research Centre Program, as part of the 'Improved management of herbicide residues in soil' project (4.2.001). More information https://soilcrc.com.au/current-projects/#project_4_2_001 Thanks to Lee Kearney, Terry Rose, Scott Petty, Kelvin Spann, Ian Richter, Steve Jeffs and Katrina Brands for technical support.



Department of Primary Industries



AIR EP
Ag Innovation & Research
Eyre Peninsula



Government of South Australia
Department of Primary Industries and Regions

