Imazapic and diuron availability and toxicity in different soils

Michael Widderick[1], Annie Ruttledge[1], Kerry Bell[1], Lukas Van Zwieten[2] and Michael Rose[2]

[1] Queensland Department of Agriculture and Fisheries, Toowoomba, QLD
[2] NSW Department of Primary Industries, Wollongbar, NSW

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Take home message

- Herbicide residue levels can be measured in soil, but to interpret what soil analysis results mean for the subsequent crop, information about crop toxicity thresholds, and soil-specific herbicide availability is needed.
- An approach has been developed to derive toxicity thresholds and predict herbicide availability in different soils to provide a prediction of safety for cropping.
- Soil analysis for herbicide residues is not a replacement for using herbicides according to label requirements.
- Additional ground truthing of this proof-of-concept research across a wider range of soil types and environments will strengthen the predictions.

Background

Residual herbicides are an important tactic for the extended control of weeds in Australia's northern grain region (NGR) cropping systems. The use of residual herbicides, for both fallow and in-crop weed control, has increased in recent years, with up to 45% of the cropped area routinely receiving a pre-emergent herbicide application (Llewellyn et al. 2016). This increase is largely in response to an observed increase in resistance to glyphosate in difficult to control summer weeds including feathertop Rhodes grass, flaxleaf fleabane, common sowthistle and awnless barnyard grass. The persistent nature of residual herbicides can cause damage to subsequent, susceptible crops. This is a key consideration in northern region farming where both summer and winter crops can be grown.

While residual herbicide labels clearly state plant back periods for susceptible crops, the duration of persistence can extend beyond label claims, based upon the environment in which the herbicide exists. External factors such as rainfall, temperature and soil type all affect the duration of a residual herbicide (Figure 1). There have been cases where residual herbicides in prolonged hot and dry environments have persisted beyond the label recommended time for safety, and damage of the subsequent crop has occurred. Herbicide labels are legally binding documents, and the purpose of this research was to explore extended herbicide persistence, not to shorten the plant back.

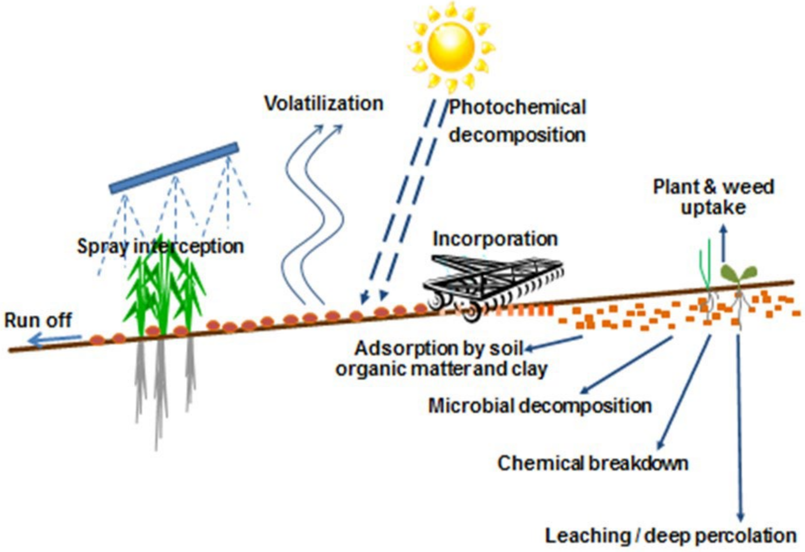


Figure 1. Interactions, loss and breakdown pathways of soil applied herbicides (Source: Congreve, M. and Cameron, J. 2019).

There are limited useful approaches to accurately predict the safety of cropping after the application of a residual herbicide. Commonly, a soil sample is submitted to determine how much herbicide is present. However, a soil test will only provide information on the total amount of herbicide present but will not tell how much herbicide is available to the plant. Furthermore, a soil test will not provide information on whether the amount of herbicide present will cause damage to the subsequent crop.

To address this issue, proof-of-concept research has been conducted toward developing a tool to assist in decision making for safe re-cropping post residual herbicide use. This research has been conducted on two test herbicides, imazapic and diuron. Both herbicides can persist in the soil for lengthy periods (12 – 24 months) at levels that can impede the growth of winter (e.g. barley, wheat, chickpea) and summer (e.g. maize, sorghum, mungbean) crops (Fleming et al. 2012).

Laboratory research has been conducted on:

- determining toxicity thresholds for imazapic and diuron on commonly grown summer and winter crops, and
- predicting the bioavailability of these herbicides across a range of soils.

A toxicity threshold is the amount of herbicide above which plant damage will occur. The threshold can be set at any percentage of damage and an ED (Effective Dose) value identified. For example, an ED_{20} value will be the concentration of herbicide resulting in 20% reduction in growth. Bioavailability is the amount of herbicide available to the plant and will differ for different soil types. By having a knowledge of both toxicity threshold and bioavailability (exposure), a prediction of safety can be determined for a specific soil type and crop (Figure 2).

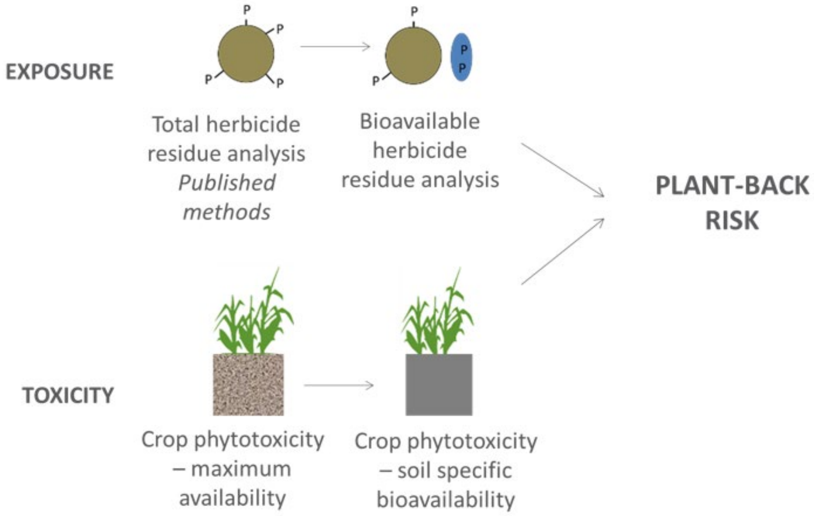


Figure 2. Framework to improve prediction of plant-back risk.

Through this research an approach to determine both crop toxicity thresholds and herbicide bioavailability for soil applied, pre-emergent herbicides has been developed. This information can be used to develop a decision support tool for residual herbicides.

Methods and results

Bioavailability

Herbicide bioavailability differs between soil types as the amount of herbicide bound to the soil (sorption) will differ. In a soil with greater sorption, less herbicide will be available to the plant. Sorption is quantified by the sorption coefficient (known as K_d), which is defined as the proportion of bound (unavailable) herbicide divided by the proportion of soluble (bioavailable) herbicide. A low K_d indicates the herbicide is more available.

Physicochemical properties can be used to determine a soils K_d value. Soils can be characterised by wet chemistry methods in a laboratory to determine factors such as pH, soil carbon, and organic matter, however, this process is very time consuming. An alternative method of characterising soils is via using mid-infrared reflectance (MIR) spectrum, which is relatively cheap and quick. MIR spectroscopy is a technique that uses a beam of MIR light through the sample and measures transmission and absorption of the light (Su and Sun, 2019). MIR integrates information about the soil's texture, carbon content and mineralogy. Together these characteristics can explain most of the variation in herbicide sorption and therefore bioavailability.

Diuron and imazapic K_d values of 42 different soils were determined via laboratory sorption experiments covering the range of soil types typically encountered in the NGR. Each soil was also scanned using MIR, and the MIR spectra calibrated against the laboratory-determined K_d value (Figure 3). It was confirmed MIR spectra were an accurate approach for prediction of K_d values.

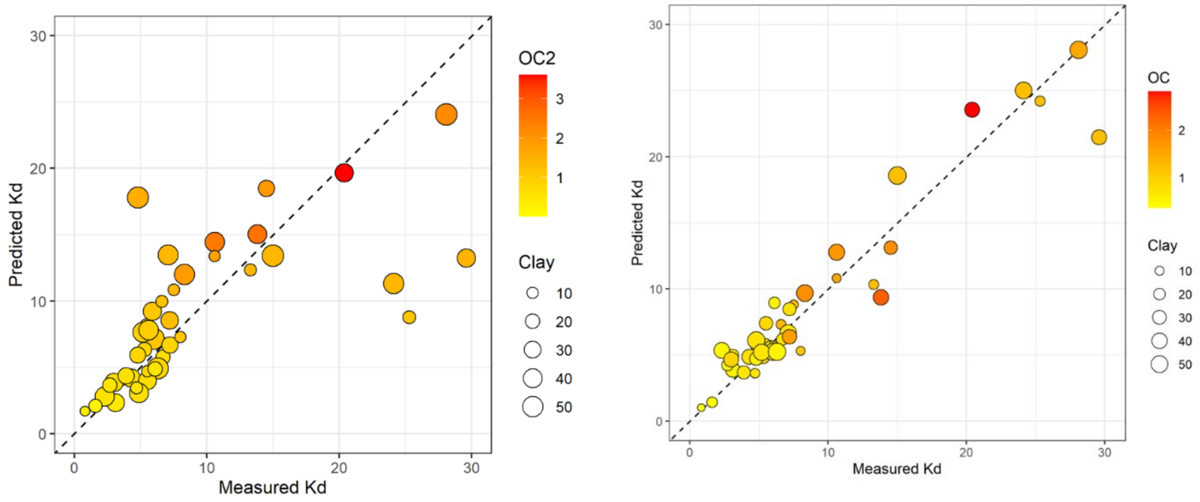


Figure 3. Measured versus best-fit predictions of soil sorption coefficients for diuron for 42 contrasting soils from the northern grains regions. A) using wet chemistry, B) using MIR. The dashed line represents a perfect prediction.

These sorption models can be used to characterise other soils and predict their K_d. Accurate prediction of herbicide sorption to soil, combined with knowledge of herbicide residue level in the soil, should allow for site-specific phytotoxicity risk assessment.

Toxicity thresholds

For this pilot study, the lower concentration levels of imazapic and diuron that cause crop damage were determined via seedling bioassays on key summer (including maize, mung bean, sorghum) and winter (including barley, wheat, chickpea) crops (Figure 4). The bioassays were carried out on washed river sand as a negligible sorption control (i.e. negligible herbicide sorption due to low organic carbon and clay). Shoot and root biomass were measured to determine toxicity thresholds (Figure 5).

Determining potential for herbicide damage via this proposed approach for other herbicides will require establishment of baseline dose response curves for each specific combination of herbicide x crop.

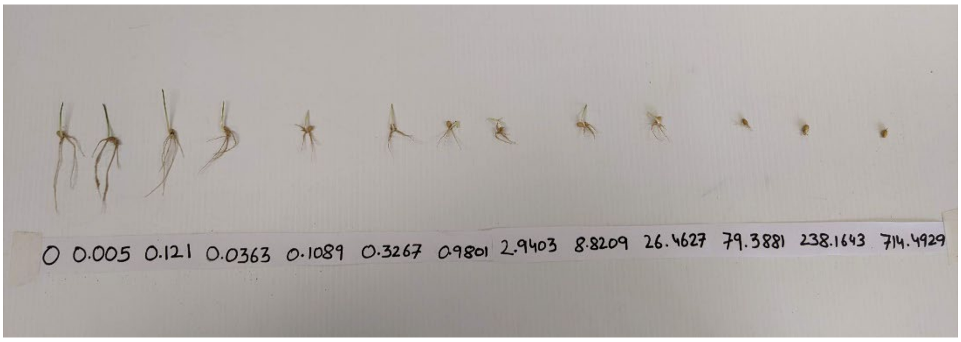
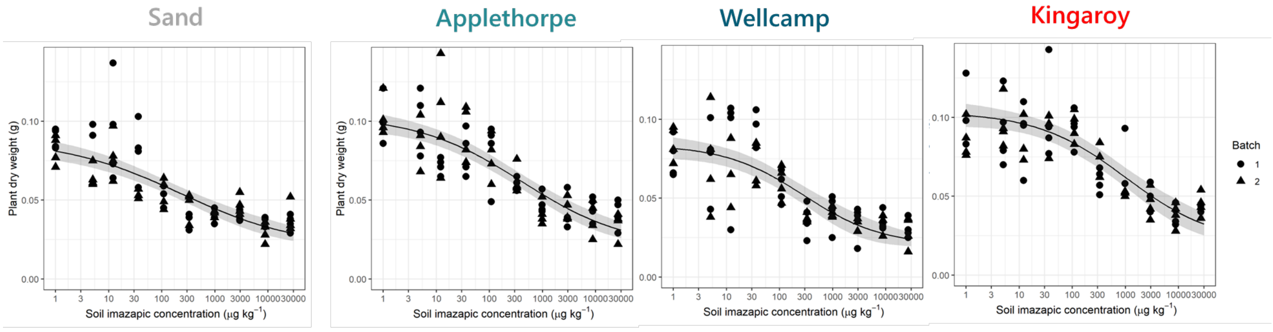


Figure 4. Imazapic dose response for wheat grown in river sand. Shoot and root length and biomass were determined.



ED$_{20}$ in soil 11 ng/g

ED$_{20}$ in soil 22 ng/g

ED$_{20}$ in soil 26 ng/g

ED$_{20}$ in soil 74 ng/g

Figure 5. Imazapic dose-response curves for wheat growing in different soils and the ED$_{20}$ value for dry weight biomass for each soil. X-axis = Soil imazapic concentration (g kg^{-1}) and Y-axis = Plant dry weight (g).

Secondly, bioassays were carried out on an additional three soil types (Table 1) to assess the effects on crop growth (phytotoxicity) (Figure 5) and to compare herbicide sorption (K_d) characteristics. The three soils were from Kingaroy (clay loam), Applethorpe (sandy loam) and Wellcamp (clay). Each soil had different characteristics (pH, organic carbon and clay content) influencing the capacity for herbicides to bind and therefore their availability to plants. By measuring plant damage and by extracting and quantifying herbicide residues from the soil, we were able to validate predictions in bioavailability.

Table 1. Physicochemical properties and sorption coefficients (K_d) for imazapic and diuron for four contrasting soils. Where OC = Organic carbon and CEC = Cation exchange capacity. Soils with a higher clay fraction tend to have a higher CEC.

Soil	**OC (%)**	**pH**	**CEC (cmol$^+$/g)**	**Clay (%)**	**Imazapic K_d**	**Diuron K_d**
Sand	0.01	6.6	0.5	0.5	0.01	1.5
Applethorpe	0.59	6.1	4.1	5	0.17	3.3
Wellcamp	1.5	7.8	72	39	0.50	20.7
Kingaroy	1.8	5.1	18	20	2.19	18.0

Relationship between sorption and phytotoxicity

The sorption of imazapic and diuron differed between each other and between different soil types (Table 1). For imazapic, the K_d values were generally <1 indicating a high proportion of imazapic will reside in the soil solution in most soil types (i.e. available for plant uptake), rather than being bound to soil particles. Sorption of imidazolinone herbicide is known to be highly influenced by soil pH (and hence label plant backs increase in acidic soils). This was confirmed in this study where imazapic sorption was greater in the highly acidic soil from Kingaroy. The K_d values for diuron are much higher than for imazapic. This demonstrates that diuron is bound to soil to a greater extent than imazapic and is therefore generally less mobile and less available for plant uptake, especially in soils with higher organic carbon.

The relationship between sorption and phytotoxicity was determined by plotting ED$_{20}$ and ED$_{50}$ values against the K_d values determined for each herbicide and for each of the four soil types outlined in Table 1 (Figure 6).

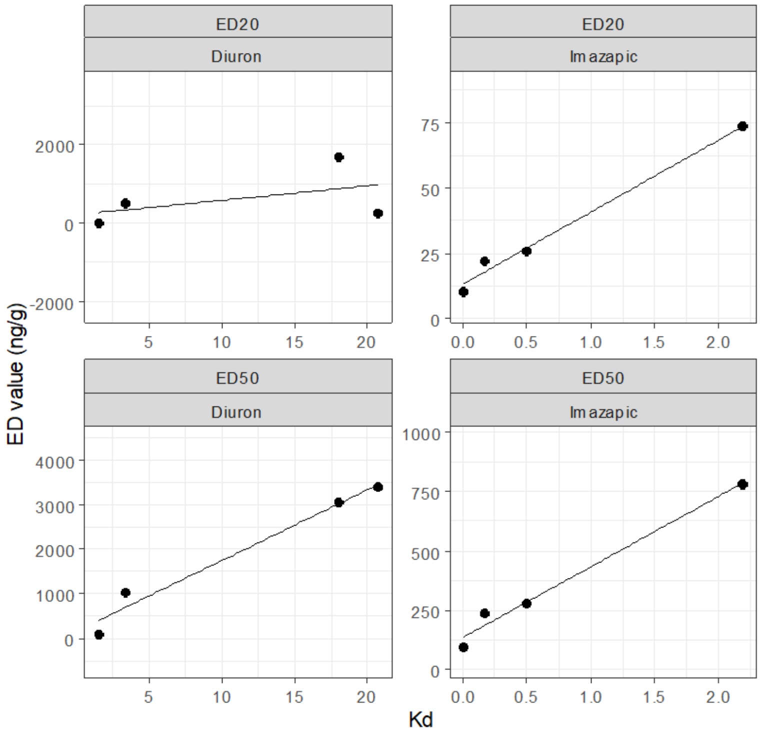


Figure 6. Relationship between K_d and toxicity threshold values (ED_{20} and ED_{50}) to wheat for diuron (left) and imazapic (right) for four different soil types. The individual points on each graph represent the four soils (K_d x ED) and the line represents the fit. The closer the points are to the line, the better the fit and model.

Imazapic thresholds for 20% and 50% shoot biomass reductions (i.e. ED_{20} and ED_{50}) were both significantly correlated with the soil K_d value. In contrast, for diuron, the ED_{50} but not the ED_{20} was significantly correlated to the K_d.

Relationships between K_d and crop tolerance have potential to allow for estimation of phytotoxicity thresholds in different soil types, if the K_d and tolerance to the specific crop are known. Evaluation of more soils will strengthen the model. Based on our work, prediction of K_d values through either wet chemistry determination or MIR should allow a reasonable estimation of soil specific toxicity thresholds.

Conclusion

Through this proof-of-concept research we have developed a framework to derive crop toxicity thresholds and predict K_d values, and therefore herbicide availability. The information produced can be used in decision making to minimise crop loss. Potentially a traffic light tool (safe - green, caution – yellow, high risk - red) could be developed from the data to indicate safety for recropping, where soil K_d and residual herbicide remaining are available.

The framework for predicting herbicide plant-back damage is outlined in Figure 7. In this framework, a soil sample is analysed using either wet chemistry or MIR and this identifies the total herbicide concentration and also information required to identify K_d using the sorption model (Figure 3). A calculation of K_d, the bioavailability model (Figure 6) and dose response curves (Figure 5) can be used to identify a soil specific toxicity threshold (eg ED_{20}). This ED value can then be compared with the measured soil herbicide concentration and risk for crop damage predicted.

While imazapic and diuron were used in this pilot study, baseline dose response curves (e.g. ED_{20} values in sand for each crop type) would need to be established for any other herbicide x crop combination.

Herbicides with low K_d values have the potential for increased mobility in the soil. This may require soil samples for residue determination to be collected from varying soil depths.

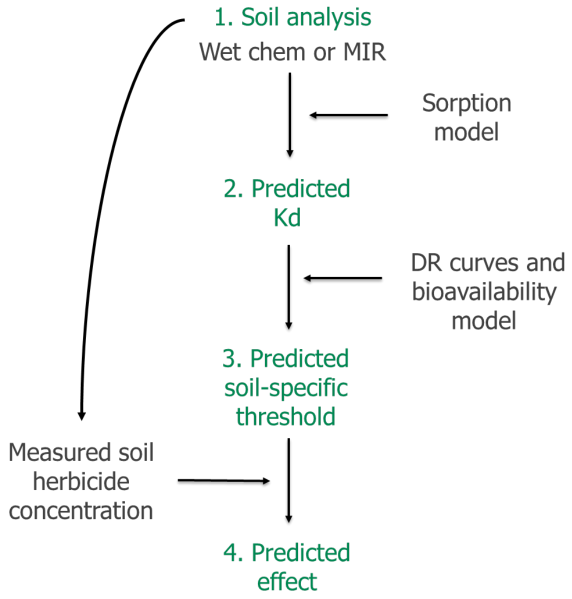


Figure 7. Framework for predicting herbicide plant-back damage potential. DR = Dose response.

The framework is adaptable to other pre-emergence herbicides and other herbicide-crop combinations, provided the baseline crop x herbicide tolerance data is generated. To make the predictions of risk more reliable, additional laboratory evaluation across a wider range of soil types is recommeded. Additional information from field trials would also provide insight into whether the damage measured in the laboratory results in yield loss.

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Contact details

Michael Widderick (Principal Research Scientist)
Queensland Department of Agriculture and Fisheries
Leslie Research Facility, Toowoomba
Ph: 07 4529 1325
Email: Michael.widderick@daf.qld.gov.au

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