

Herbicide degradation on Queensland cropping soils and crop residue

Half-lives measured in a controlled environment

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Abbreviations

AMPA	– α -Amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid, glyphosate degradation product
DAFF	– Queensland Department of Agriculture, Fisheries and Forestry
DNPH	– 2,4-Dinitrophenylhydrazine, Brady's reagent
DNRM	– Queensland Department of Natural Resources and Mines
Ea	– Activation energy
EC	– Electrical conductivity
GBR	– Great Barrier Reef
Koc	– soil organic carbon partition coefficient
LCMS	– liquid chromatography – mass spectrometry
LOD	– limit of detection
NATA	– National Association of Testing Authorities Australia
PPDB	– Pesticide Properties Database, University of Hertfordshire
PSII	– photosystem two
pKa	– dissociation constant
QC	– quality control
TOC	– Total organic carbon
UPLC MSMS	– Ultra performance liquid chromatography – tandem mass spectrometry
UV	– ultra violet radiation

Definitions

Dissipation - The overall process leading to the eventual disappearance of substances from the site of its application or an environmental compartment, without implying any particular mechanism or process. Dissipation comprises two main types of processes; transport processes, such as volatilization, leaching, plant uptake, runoff or erosion that transfer substances to different environmental compartments; and transformation processes such as microbial degradation, hydrolysis and/or phototransformation that produce transformation products.

Half life – Calculation of a half-life assumes first order degradation kinetics. In this case, the reaction rate is proportional to the reactant concentration and constant over time. The time required for the concentration of a pesticide to be reduced (i.e., degrade, metabolize or otherwise dissipate) to one-half.

50% dissipation time (DT₅₀) - No assumptions are made about the kinetics of the degradation process. When the reaction follows first-order degradation kinetics, the half-life will be equivalent to the 50% dissipation time.

Executive Summary

Herbicides applied in the cropping industries in Queensland are regularly detected in waters flowing to the Great Barrier Reef (GBR) and Reef Plan (Anon, 2013) sets targets for the reduction in loads of 'priority' herbicides by 2018. Progress towards these targets is assessed through the Paddock to Reef Integrated Monitoring, Modelling and Reporting Program (P2R) which includes modelling from farm scale to end of system loads. The ability to accurately predict the fate of herbicides is an important aspect to assessing the environmental risks of application and making informed land management decisions, however, there are currently limited data available to inform prediction of the fate of herbicides in a tropical environment. The objective of this study was to provide measured half-lives for herbicides on Queensland cropping soils and crop residue to improve modelling of herbicide fate in the GBR catchment.

Half-lives of commonly applied herbicides in cane, grains and grazing industries in Queensland have been compared in a controlled environment on common cropping soils. Cropping soils were collected from the tilled layer (0-0.1 m) from nine sites in Queensland to represent a range in textural properties and pH. Cane crop residues (trash) were also collected. Soils were kept moist using capillary rise from a hanging water column and were placed in a temperature controlled glasshouse. Following herbicide application, surface samples were collected over a period of 100 days to track dissipation of the herbicides. Half-lives have been calculated for fourteen herbicides including those considered to be high 'priority' under Reef Plan (Anon, 2013) (atrazine, ametryn, diuron, hexazinone and tebuthiuron) and alternative residual products which are being used with increasing frequency in Queensland (isoxaflutole, imazapic, pendimethalin, trifloxysulfuron, S-metolachlor, metribuzin). Three commonly applied knockdown herbicides, 2,4-D, glyphosate and paraquat, were also included in the study. Preliminary results from this study are reported here.

Half-lives were found to range from 12 days for atrazine on the Ferrosol (WAK) to >744 days for paraquat on a heavy Vertosol (MAK). The half-life values were comparable to international database and literature values from tropical field studies for well-studied herbicides including atrazine and ametryn. However, half-lives for several herbicides that have not previously been reported under local conditions (imazapic, pendimethalin, trifloxysulfuron) were on average 2.5-6 fold faster than international database values (PPDB, University of Hertfordshire). For example, the mean half-life of imazapic was 37 days (ranging from 20-81) which is approximately 6 fold shorter than reported in the PPDB. In contrast, the degradation rate of isoxaflutole was >10 fold slower than PPDB values. Half-lives for all herbicides on cane residues were slower than has been previously reported, which may be due to the effects of herbicide washoff in field studies and to limited photodegradation in the current study.

Half-lives varied by less than a factor of 2 between soils for the herbicides atrazine, 2,4-D and isoxaflutole whereas half-lives for diuron varied by a factor of 14. Total organic carbon was found to be a significant explanatory variable for predicting degradation rates for many of the herbicides in this study. Further analysis of the data is required to investigate the relationship between measured half-lives and soil properties to extend prediction of spatial variability in herbicide degradation for all soils in the GBR catchment.

Half-lives of herbicides in the controlled environment were compared to dissipation measured on several of these same soils in field trials. The lack of consistent trends between herbicide degradation rates observed in the field and those observed in the controlled glasshouse environment highlights the difficulty in isolating factors contributing to dissipation in a field scenario. Values derived in the current study can be considered to provide conservative

estimates for the tested soil temperature and moisture conditions since loss processes including leaching, runoff, plant uptake and to some degree photodegradation have been excluded. Further, the half-lives derived in this study relate to the surface 2.5 cm of soil which is the depth relevant to extraction of herbicides into runoff. These values are more appropriate for use in agricultural soil water balance models where losses due to degradation are considered as a separate process to loss through runoff/leaching/plant uptake. Adoption of the half-life values from this study in the paddock to reef modelling program will improve prediction of herbicide losses under various management scenarios and therefore improve the prediction of loads of herbicides entering the GBR lagoon.

Introduction

Herbicides represent an important tool in weed control for cropping industries. The promotion of conservation and no-till farming methods in Australia to reduce soil disturbance and erosion has increased the reliance on herbicides as weeds are no longer controlled through tillage operations in these farming systems. However, herbicides can be transported off site and have potential to cause detrimental impacts for downstream aquatic ecosystems. The persistence of herbicides in soil and on crop residues following application is important in determining the potential for offsite transport.

Under best management practice guidelines in Queensland, Australia, reduced reliance on the use of 'residual' herbicides in favour of 'knockdown' herbicides is considered an improved farming practice. Residual herbicides are applied pre-emergence to prevent seeds germinating and/or emerging, and as such are required to persist for a period of time after application. Knockdown herbicides are used to kill emerged weeds and therefore generally have shorter half-lives than residual herbicides. Residual herbicides are also reasonably soluble as they are required to be absorbed from the soil into plant roots whereas this is not necessarily the case for knockdown herbicides which may be more strongly sorbed to the soil. Commonly applied residual herbicides are the photosystem II (PSII) inhibiting compounds; atrazine, diuron, ametryn, hexazinone and tebuthiuron. The focus on reducing the use of these PSII herbicides has anecdotally led to increasing use of alternative residual herbicides, from here on referred to as 'non-regulated' herbicides.

In the Great Barrier Reef (GBR) catchment, residual herbicides applied to cropping lands are regularly detected in waterways that flow to the world heritage protected reef lagoon (Lewis et al., 2009, Packett et al., 2009, Smith et al., 2012) and have been shown to be present through the wet and dry seasons at nearshore reefs (Shaw et al., 2010; Kennedy et al., 2012). To address the issue of diffuse agricultural pollution entering the GBR, Reef Plan (Anon 2009, 2013) has set a target of a 50% and 60% reduction in the loads of 'priority' herbicides by 2018 and 2020 respectively. Under this initiative, the Paddock to Reef Monitoring, Modelling and Reporting Program has been implemented to report on progress towards reducing loads of herbicides and other pollutants (Carroll et al., 2012). The paddock modelling component of this program represents improvements made to land management at a farm scale so that the impacts on end of catchment loads of pollutants can be predicted. Sensitivity analysis of the agricultural water balance model used for predicting the impacts of herbicide management options on offsite transport, HowLeaky, showed that half-life was the most important parameter for predicting herbicide fate (Shaw et al., 2011). This highlights the importance of deriving relevant herbicide degradation rates from experimental data for Queensland soils.

There is currently limited data available to inform prediction of the fate of herbicides in tropical environments. The majority of available half-life data have been derived in temperate environments (Sanchez-Bayo and Hyne, 2011). Reviews of available fate data for tropical environments indicate that herbicides will generally dissipate more quickly due to higher temperatures and wetter conditions (Racke et al., 1997; Sanchez-Bayo and Hyne, 2011). When considering field derived dissipation data, it is difficult to separate losses due to processes such as runoff, leaching or plant uptake from transformation of the parent compound. This is particularly the case in tropical environments where high annual rainfall with high rainfall intensity events leads to relatively high losses of herbicides in runoff. Also, where crop residues such as cane trash are retained, herbicides on the crop residue can wash onto the soil via rainfall and result in increasing herbicide concentrations in soil for some weeks after application which further complicates derivation of half-lives.

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The degradation of herbicides in a field situation is influenced by many environmental factors which include temperature, soil moisture, soil properties and microbial activity. Temperature has a large impact on the derived herbicide half-lives from both field and laboratory studies. It is generally accepted that the temperature dependency may be described using the Arrhenius equation which gives the degradation rate coefficient as a function of the temperature and the activation energy, E_a (J mole⁻¹) (EFSA, 2007; Wu and Nofziger, 1999). Use of the underlying Arrhenius equation in this approach is appropriate for temperatures between 0 and 30 °C. Similarly, soil moisture content has been shown to influence pesticide degradation with slower degradation observed on drier soil (Walker, 1976). An approach for incorporating soil moisture in the prediction of pesticide degradation has also been proposed (Walker, 1976; Wauchope et al., 2004). Soil properties have also been shown to influence herbicide degradation. It has been noted from field trials that persistence of herbicides was greater in clay soils followed by sandy loams, loamy sands and sandy soils (Mansingh et al 2003). The pH of a soil will also have an effect with acidic pesticides noted as persisting for longer on soils with a low pH (Sanchez-Bayo and Hyne, 2011) and triazines (e.g. atrazine) noted as degrading at a faster rate in soils with a low pH (Walker and Blacklow 1994). However, while the impacts of temperature and moisture may be accounted for in modelling herbicide degradation, there is no widely accepted approach to account for the effects of soil properties.

The ability to accurately predict the fate of herbicides is an important aspect to assessing the environmental risks of application and making informed land management decisions. The objective of this study was to provide measured half-lives for priority and non-regulated herbicides on Queensland cropping soils and crop residue. The study was conducted using a range of soils in a glasshouse that controlled temperature and soil moisture. The study was designed to provide half-life values appropriate for use in modelling herbicide fate in Queensland. Since agricultural water balance models represent losses due to runoff, leaching, plant uptake or washoff separately to herbicide degradation, field derived half-lives are not well suited to application in a modelling context. Importantly, this study provides data to relate half-life to soil properties and, therefore, to improve spatial extrapolation of half-lives as required in the GBR wide modelling program. Half-lives of herbicides in the controlled environment were compared to dissipation measured on several of these same soils in field trials. The results of this study improve the data available to predict the fate of herbicides in the GBR catchment, including many herbicides which have been poorly studied to date but which are being used more frequently. This report presents preliminary results from the controlled environment degradation experiment and selected field studies.

Methods

Soil and Cane Trash

Nine soils and one crop residue (cane trash) were collected across five regions of the GBR catchment (Bundaberg, Mackay-Whitsunday, Fitzroy, Burdekin and Wet Tropics) (Table 1). Soils were selected to represent a range of textural properties with varying pH (see Results and Discussion, Figure 8). A photograph of each of the soils included in the study is provided in Figure 1. Soils were selected from sites where the history of herbicide applications was known and where herbicides had been applied on a regular basis for several seasons prior to the commencement of this experiment. Priority was given to sites where field dissipation data would also be available for some of the tested herbicides. Approximately 400-500 kg of top soil (0-0.1 m) was obtained from each field site for use in the controlled environment study. Soil was air dried and coarsely sieved using 0.5 inch mesh to remove rocks and plant matter while maintaining soil aggregate structure.

Table 1. Description of soils

Soil ID	Australian Soil Classification	Global Range of Soils ^a	Site Name, GBR Region, Site History	pH ^b	EC	TOC ^c	Clay:Silt: Sand
WAK	Red Ferrosol	Clay	Walkamin, Wet Tropics, Research Station	6.4	0.05	1.91	52:15:33
BUN	Brown Chromosol	Sandy loam to fine sandy loam	Bundaberg, Burnett Mary, Demo cane farm	6.1	0.03	1.8	8:16:77
MAK	Black Vertosol	Clay loam/clay	Victoria Plains, Mackay Whitsundays, Demo cane farm	6.3	0.08	2.4	56:32:12
MT1	Brown Chromosol	Silt loam	Marion, Mackay Whitsundays, Demo cane farm	6.8	0.04	1.07	16:19:65
MT3	Brown Chromosol	Clay loam	Marion, Mackay Whitsundays, Demo cane farm	7.1	0.12	2.22	24:24:53
TUL	Brown Kandosol	Loam	Tully, Wet Tropics, Demo cane farm	5	0.03	2.51	22:13:65
MGO	Black Vertosol	Clay loam/clay	Moonggoo, Fitzroy, Demo grains farm	7.6	0.04	1.07	64:12:24
BRG	Duplex	Clay loam	Brigalow catchments, Fitzroy, Demo grains farm	6.9	0.04	1.46	25:10:65
BUR	Brown Dermosol	Loam/loamy sand	Burdekin, Demo cane farm	7.8	0.03	0.8	14:9:77

Soil ID	Australian Soil Classification	Global Range of Soils ^a	Site Name, GBR Region, Site History	pH ^b	EC	TOC ^c	Clay:Silt:Sand
TRH	Cane Trash	-	Bundaberg, Burnett Mary, Demo cane farm	-	-	-	-

^a Wauchope et al., 2004

^b pH method - EC Aqueous (1:5)

^c TOC method - wet oxidation (Heanes)

Soil microbial activity has been shown to influence the dissipation of herbicides. Air dried soil can be biologically inactive. However, microbial activity should be restarted by rewetting for a period (Dr. John Thompson, DAFF, pers comms, 2012). Soil microbial activity following air drying and subsequent re-wetting over a seven day period was compared to 'fresh' field soil (for selected field sites included in this study). Two methods of assessing microbial activity, ecoplates and fluorescein diacetate assays, were applied to four of the study soils (MAK, MT1, MT3, TUL). Analysis was conducted by the University of Queensland. Microbial activity in the dried-re-wet soil was not significantly different to that in fresh field soils ($p > 0.05$) (see Appendix I). On that basis, it was judged that the air dried soils were appropriate to use in the trial following re-wetting over a 2 week period. Additional 'fresh' soil was collected from each site in the 2 weeks prior to commencement of the experiments and mixed with the dried-rewet soil to ensure that there were active microbial communities present as the air dried soil was re-wet.

Soil was placed into alfoil lined styrofoam boxes 448 mm x 290 mm and 140 mm in depth. Soil was filled to a depth of 130 mm with a surface area of 0.125 m². In an initial pilot study, soils were watered prior to herbicide application and allowed to dry over the period of the experiment. In the current study a hanging water column was created to maintain soil moisture throughout the experiment. Toweling lined the floor of the box and hung through an opening into rainwater storage below. Soils were prepared two weeks prior to spraying to allow sufficient time for the soils to re-wet and microbial communities to become active. Trash was placed on top of the Ferrosol soil from Walkamin, weighed to 1.8 kg/m² or 0.23 kg/replicate, which corresponded to the trash expected from a cane yield of 85 tonnes/ha which was typical for the Mackay Whitsunday region in Australia (Steve Attard, CSIRO, pers comms, 2011). Soil moisture was maintained through the hanging water column throughout the experiment with the rainwater source monitored and topped up at least twice a week. Rainwater was also misted onto the soil surface three times a week (Mon, Wed and Fri) starting at day 12 of the experiment, if drying was observed; the quantity of water added was recorded. Rain water was also misted on to the trash three times per week although it was not possible to keep the trash continuously moist. The bulk density of each replicate was determined by weighing soil removed from a known sample volume to two decimal places.



1. WAK



2. MGO



3. MT3



4. MT1



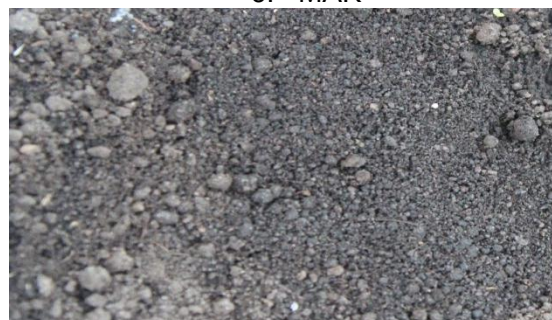
5. BRG



6. MAK



7. BUR



8. TUL



9. BUN



10. TRH

Figure 1. Photograph of soils and crop residue

Controlled Environment

Air temperature was controlled through air-conditioning/heating within a glasshouse in Toowoomba, Australia (Figure 4, Figure 5). Air temperature in the glasshouse was logged at 3 min intervals using two calibrated Tinytag data loggers (TGU-4500, Gemini) suspended at approx. 2 m above the ground. Technical difficulties retrieving data meant that temperature was not measured for 48 hrs within the experimental period. The air-conditioning did not maintain a constant temperature but rather controlled the range of variations so that there was diurnal fluctuation. The average air temperature was 24.5 °C (± 3.4 °C SD) and ranged from 19 °C to 41 °C (Figure 2). Soil and trash temperatures were logged at 1 cm depth using Tinytag loggers fitted with an external probe and ranged from 11 °C to 47 °C throughout the experimental period. Examples of the measured soil temperatures are shown in Figure 3.

The glasshouse was fitted with window glass which absorbs a considerable amount of light in the UV-B range (280–320 nm) (Katagi, 2004). This spectrum overlaps with the UV absorption profile of many herbicides (Katagi, 2004) and since direct photolysis requires adsorption of sunlight by the chemical of interest, will reduce the role of photodegradation processes in the current study. Available information on the maximum adsorption spectra of herbicides included in this study is summarised in Table 3.

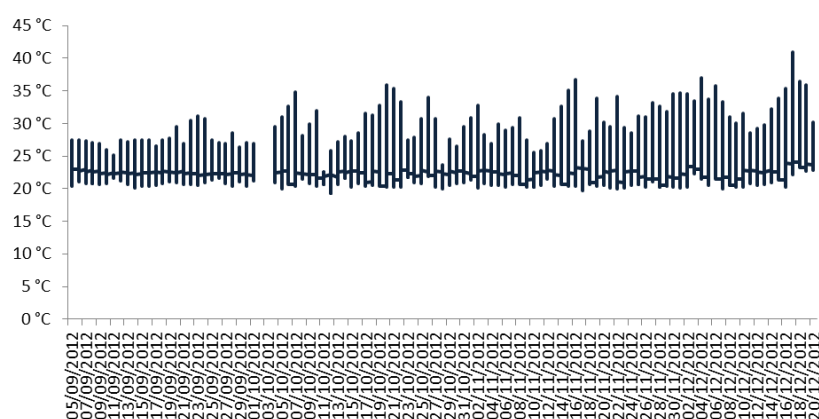


Figure 2. Measured glasshouse air temperature reported at 3 min intervals

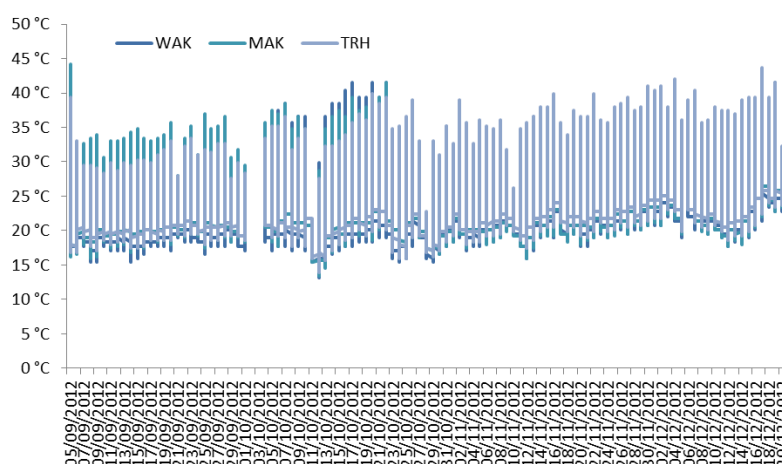


Figure 3. Measured soil temperature in selected soils reported at 3 min intervals



Figure 4. Glasshouse in Toowoomba



Figure 5. Inside the glasshouse in Toowoomba

Sampling

Samples were collected from the surface 2.5 cm as this depth is relevant for herbicide extraction into runoff. A pilot study showed that judgement of depth could vary between operators and could contribute to variability in the results as the applied herbicides were not evenly distributed through the surface 2.5 cm but rather concentrated towards the soil surface. Therefore, sampling guides (1 cm² gridded stainless steel mesh, visible in Figure 6) were placed at 2.5 cm depth as the boxes were prepared to prevent sampling beyond the specified depth. As the soils were placed into the boxes dry and subsequently allowed to become moist through the hanging water column, the distance from the surface to the mesh was increased as some soils swelled. The depth of each sample was therefore measured after each sampling event to allow for correction due to sample depth/volume. The mean sample depth was 2.51 cm with a range from 1.5 cm to 3.45 cm. Acetone washed aluminum strips were used to delineate the boundary of a sample and to maintain the integrity of the adjacent soil surface during sample removal.

Samples from a randomly selected location within each replicate were collected as soon as practicable following herbicide application (T0), after 12 hrs (T0.5), 24 hrs (T1), 48 hrs (T2), 5 days (T5), 8 days (T8), 12 days (T12), 20 days (T20), 36 days (T36), 48 days (T48), 61 days (T61), 76 days (T76) and 99 days (T99). Only selected time points were submitted for analysis. These included T0, T1, T5, T12, T36, T60 and T99.

Samples were placed in zip lock bags lined with solvent washed aluminum foil pockets. Samples were placed on ice immediately, and then transported on ice to -20 °C storage as soon as practicable following collection. Prior to submission to the laboratory, samples were defrosted and homogenized using stainless steel, acetone washed spatulas to ensure a representative sub-sample. Subsamples for moisture content were also taken. Samples were re-frozen at -20 °C before being shipped on ice overnight to the laboratory.



Figure 6. Soil trays at ~ middle of experiment with the stainless steel mesh indicating the location of previous sub-sampling.

Sample Analysis

Herbicide analysis was conducted by ACS Laboratories Australia in Melbourne. ACS is undertaking NATA accreditation to the ISO 170225 standard and was identified as the most suitable laboratory in Australia to provide testing for novel or 'emerging' herbicides within the study timeframes. Analyses were also provided for the degradation products of some herbicides; atrazine (desethyl atrazine, desisopropyl atrazine), diuron (DCPU and DCPMU), glyphosate (AMPA) and isoxaflutole (diketonitrile).

Soil samples were accurately weighed to 5.00 g and recorded to 2 decimal points. Samples for all herbicides other than paraquat and glyphosate/AMPA were extracted in acidified methanol and sonicated for 30 mins. The extracts were then filtered through a 0.45 µm Teflon membrane filter to remove sediment. The filtered extract was pH and volume adjusted then analysed by UPLC MSMS in negative and positive mode, using selected ion monitoring.

Soil samples for paraquat were extracted with 35% sulphuric acid in water under reflux at 60 °C for three hours, to digest the active sites on the soil and release the bound paraquat. The extract was decanted and an accurate portion of the liquid was pH and volume adjusted before being diluted in water. The adjusted extract was cleaned up using a silica cartridge and made up to volume in water. The filtered extract was then analysed by LCMS in positive mode, using selected ion monitoring.

Soil samples for glyphosate and APMA analysis were extracted with buffered aqueous solvent and sonicated for 30 mins. The filtered extract was pH adjusted before being derivatized with DNPH and analysed by UPLC MSMS in negative mode, using selected ion monitoring.

Samples were quantitated against standardised calibration curves using freshly and accurately prepared standards. As well as freshly prepared standards, stock standards from a second source were also analysed to provide added confidence. Blanks, spikes and duplicates analysis was conducted as in accordance with ACS QC policy for herbicide and herbicide residues so that each batch of samples included 5% blank analysis, 10% duplicate analysis and 10% high/low spikes.

Soil moisture was determined through weighing before and after 48 hrs drying at 105 °C. Weight was determined using a calibrated balance to two decimal places (0.00 g). All results are presented on a dry weight basis. Soil properties were determined by the Chemistry Centre in the Queensland Department of Science, Information Technology, Innovation and the Arts, Brisbane.

Data Analysis

Half-life values were calculated from soil concentration reported on a dry weight basis following correction for the depth of the sample. Samples found to be below the limit of detection (LOD) were assigned half the LOD concentration in all half-life calculations. A half-life was calculated for each of the three replicates in each treatment and the means of those values are presented here. The half-life was calculated using a first-order or exponential kinetic decay function to describe pesticide dissipation (Wauchope et al. 1992):

$$C = C_0 e^{-kt} \quad (1)$$

In this equation, C is the concentration of the herbicide at time t , C_0 is the initial concentration applied to the soil, k is the rate constant for disappearance, and t is time (days). The time taken to reach 50% of the initial concentration was then derived from:

$$\text{Half-life} = \ln 0.5 / k \quad (2)$$

where k was derived from the slope of the linear fit through log transformed soil concentrations. Multiple linear regression was conducted for each herbicide against soil properties using Excel 2010, as was two-way analysis of variance. Data were log transformed prior to analysis to satisfy the assumption of normality and significant differences were assigned at $p < 0.05$.

Field Dissipation Studies

Pesticide dissipation was also measured at three field sites in Queensland on an opportunistic basis (Table 2). Samples were collected from the top 2.5 cm of soil with three subsamples within a treatment bulked and homogenized to form a single sample. Laboratory and data analyses were performed as outlined for the controlled environment study. The exception to this was laboratory analysis of samples collected from the Herbert and Silkwood study sites which was conducted by the Queensland Health Forensic and Scientific Services NATA accredited laboratory in Brisbane.

In addition to the field dissipation samples described here, the Paddock to Reef Integrated Monitoring Modelling and Reporting Program collected dissipation data for a range of herbicides on several of the soils included in the controlled environment study for direct comparison; MAK (Rohde et al., 2011), BUN (Nachimuthu et al., 2012), TUL (Armour et al., 2011) and also cane trash at these sites.

Table 2. Description of field dissipation study sites

Site	Lat Long ^a	Soil Type	Clay:Silt:Sand	Date of pesticide application	Sampled timepoints
Silkwood	-17.745, 146.018 ^b	NA ^c	NA	23 Sept 2011	1,4,14,35
Herbert	-18.47475, 145.90094	Dermosol, clay loam	22:21:62	9 Sept 2011	0,4,35
Burdekin	-19.59885, 147.300	Dermosol, clay loam	32:24:44	5 Sept 2012	1,2,6,15,35,59

^aGDA 94 Zone 55

^bApproximate only

^cNA-Data currently not available

Herbicides

Fourteen herbicide active ingredients commonly applied for weed management in sugarcane, grains and grazing operations in Queensland were included in the study (Table 3). The active ingredients included the five herbicides considered priority pollutants under Reef Plan; atrazine, ametryn, diuron, hexazinone and tebuthiuron. Herbicides were applied as 3 mixes since it was not practically feasible to apply each separately. Herbicides are commonly applied as mixtures in farm situations, although it is recognised that the mixtures applied here do not represent commonly applied mixtures. Previously reported decreases in microbial biomass and activity following the application of some pesticide products, generally

insecticides or fungicides (e.g. Munoz-Leoz et al., 2011), suggested that there was potential for the composition of the mixtures of herbicides applied in the current study to influence microbial degradation. An assessment of the relative impact of each of the three herbicides mixes was conducted using assays of microbial activity prior to commencing the experiment (see Appendix I). Significant differences were detected between Mix 1 and Mix 3 for two of the soils tested in the fluorescein diacetate assay (MT1 and MT3, $p < 0.05$ using Tukey's HSD following two way ANOVA). Therefore, it is acknowledged that the composition of the herbicide mixtures may influence the rate of degradation as they impact the microbial communities present.

Herbicides were applied at label rates (Table 3) with the highest permitted rates applied for herbicides such as imazapic where the predicted concentration in soil was close to the laboratory detection limit. Herbicides were applied in commonly available product formulations sourced from commercial suppliers. Tebuthiuron was applied as a wettable powder, Spike, which is not commercially available in Australia. This product was supplied by DowAgrosciences since the pellet form of tebuthiuron (Graslan) registered in Australia was not suitable for application in this study. Application of pellets would result in concentration gradients around each pellet which would make it difficult to collect representative samples.

Herbicides were applied in a custom built spray cabinet at the Queensland Government Leslie Research Centre in Toowoomba (Figure 7). The canister containing the herbicide mixture was agitated between sprays. Each replicate was sprayed individually to ensure that placement of the soil relative to the nozzles was consistent between replicates.



Figure 7. Spray cabinet in which herbicides were applied to soil and crop residue

Table 3. Physical chemical properties of herbicides

Active Ingredient	Product Name (A.I. g/L)	Application Rate (L or kg/ha)	Solubility in water ^a (mg/l)	Soil organic carbon partitioning factor ^a (Linear Koc, ml/g)	Dissociation constant ^a (pKa at 25°C)	Volatility ^a (Vapour pressure at 25°C, mPa)	Maximum UV-vis absorption ^{ab} (L mol ⁻¹ cm ⁻¹)	Mode of Action ^a
Mix 1								
Atrazine	Gesapax Combi (500)	6	35	100	Very weak base 1.7	Non-volatile 0.039	NR	Inhibitor of photosynthesis at PSII
Ametryn	Gesapax Combi (500)	6	200	316	Very weak acid 10.07	Non-volatile 0.365	NR	Inhibitor of photosynthesis at PSII
S-metolachlor	Dual Gold (960)	1.1	480	226.1 ^c	No dissociation	Volatile 3.7	266nm = 534; 274nm = 443; ≥290nm = 10	Inhibitor of cell division
Glyphosate	Agrochem Growler (450)	3	10500	21699	Strong acid 2.34	Non-volatile 0.0131	NR	Inhibition of lycopene cyclase.
Mix 2								
Metribuzin	Soccer (700)	2	1165	38 ^c	Strong acid 0.99	Non-volatile 0.121	294nm = 8175	Inhibitor of photosynthesis at PSII
Imazapic	Flame (240)	0.4	2230	137	Strong acid 2.0	Non-volatile 0.01	NR	Inhibits the production of amino acids necessary for cell division and growth

Active Ingredient	Product Name (A.I. g/L)	Application Rate (L or kg/ha)	Solubility in water ^a (mg/l)	Soil organic carbon partitioning factor ^a (Linear Koc, ml/g)	Dissociation constant ^a (pKa at 25°C)	Volatility ^a (Vapour pressure at 25°C, mPa)	Maximum UV-vis absorption ^{ab} (L mol ⁻¹ cm ⁻¹)	Mode of Action ^a
Isoxaflutole	Balance (750)	0.2	6.2	145	No dissociation	Non-volatile 1.00 X 10 ⁻⁰³	In neutral solution: Maxima at 204nm and 269nm, No absorption <290nm	Acts by indirect carotenoid biosynthesis inhibition.
Ametryn	Krismat (731.5)	2	200	316	Very weak acid 10.07	Non-volatile 0.365	NR	Inhibitor of photosynthesis at PSII
Trifloxysulfuron sodium	Krismat (18.5)	2	25700	306	Weak acid 4.76	Non-volatile 0.001	NR	Inhibitor of acetoacetate synthase
Mix 3								
Diuron	Barrage (468)	3	36	1067	No dissociation	Non-volatile 1.15 X 10 ⁻⁰³	Max 250.2nm; tail 290nm	Inhibitor of photosynthesis at PSII
Hexazinone	Barrage (132)	3	33000	54	Weak base 2.2	Non-volatile 0.03	NR	Inhibitor of photosynthesis at PSII
Pendimethalin	Stomp Xtra (455)	2.2	0.33	15744	Strong acid 2.8	Volatile 1.94	238nm = 28775, 425nm = 5490	Inhibitors of microtubule assembly
Paraquat dichloride	Gramoxone (250)	1.2	620000	100000	No dissociation	Non-volatile 0.01	290nm	Photosystem I (electron transport) inhibitor

Active Ingredient	Product Name (A.I. g/L)	Application Rate (L or kg/ha)	Solubility in water ^a (mg/l)	Soil organic carbon partitioning factor ^a (Linear Koc, ml/g)	Dissociation constant ^a (pKa at 25°C)	Volatility ^a (Vapour pressure at 25°C, mPa)	Maximum UV-vis absorption ^{ab} (L mol ⁻¹ cm ⁻¹)	Mode of Action ^a
2,4-D	2,4-D Amine (625)	0.75	23180	88.4	Strong acid 2.87	Non-volatile 0.0187	290nm = 164.97	Increases biosynthesis and production of ethylene causing uncontrolled cell division and so damages vascular tissue.
Tebuthiuron	Spike (80%)	1g/m2	2500	80	NR	Non-volatile 0.27	NR	Inhibitor of photosynthesis at PSII

^a Pesticides Properties Database (PPDB), University of Hertfordshire

^b The ultraviolet-visible (UV-vis) absorption spectrum is a quantitative measure of the ability of a substance to absorb radiation between 290 and 600 nm. Gives some indication of the wavelengths at which a chemical may be susceptible to direct photodegradation. Photodegradation of a chemical depends upon the total energy absorbed in the specific wavelength regions.

^c Freundlich Koc, rather than linear

Results and Discussion

Soils

Selected soil properties are provided in Table 1. Particle size analysis showed a large variation in the texture of soils selected for inclusion in this study. The clay fraction ($< 2 \mu\text{m}$) ranged from 7.4% (BUN) to 55.1% (MGO). Sand (coarse + fine) versus clay present for each of the soils is shown in Figure 8. The pH of the soils measured at the start of the experiment is also shown. Samples collected at day 70 showed that the pH had decreased in most soils following the addition of rainwater through the hanging water column or misting onto the surface (mean decrease of 0.3). Two replicates in the BUN soil and one replicate each of MGO and MT1 recorded an increase in pH of 0.7, 0.8, 0.2 and 0.2 respectively from the background level at day 70.

Soil moisture was measured in each of the time points submitted for herbicide analysis (Figure 9). There was variation in the measured moisture levels. This was expected as the samples were not removed at exactly the same time each day and soils were observed to dry out during the hotter period of the day when surface moisture evaporated at a faster rate than it was replaced through the hanging water column. Variation was also expected due to the periodic misting of water onto the soil surface which was done three times a week. Importantly, Figure 9 shows that the soils maintained moisture throughout the study rather than gradually drying. Moisture content varied between soils and would be expected to relate to soil matric potential (the capillary and absorptive forces within the soil matrix).

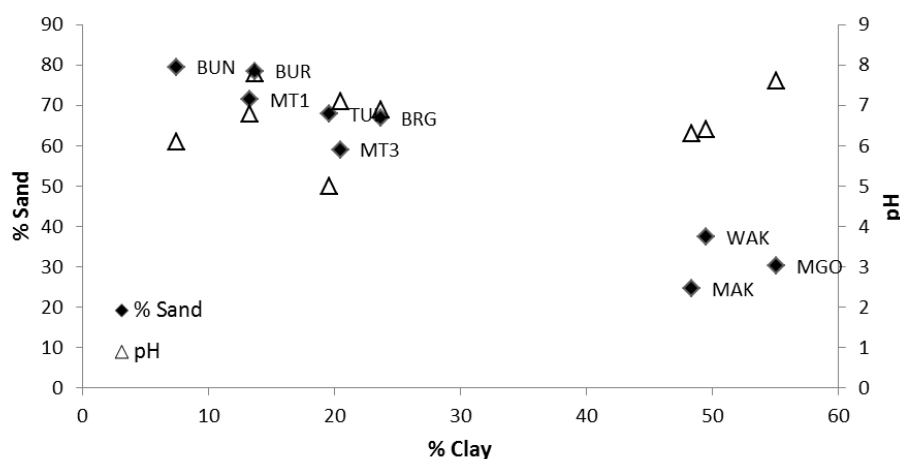


Figure 8. Sand, clay and pH values of soils

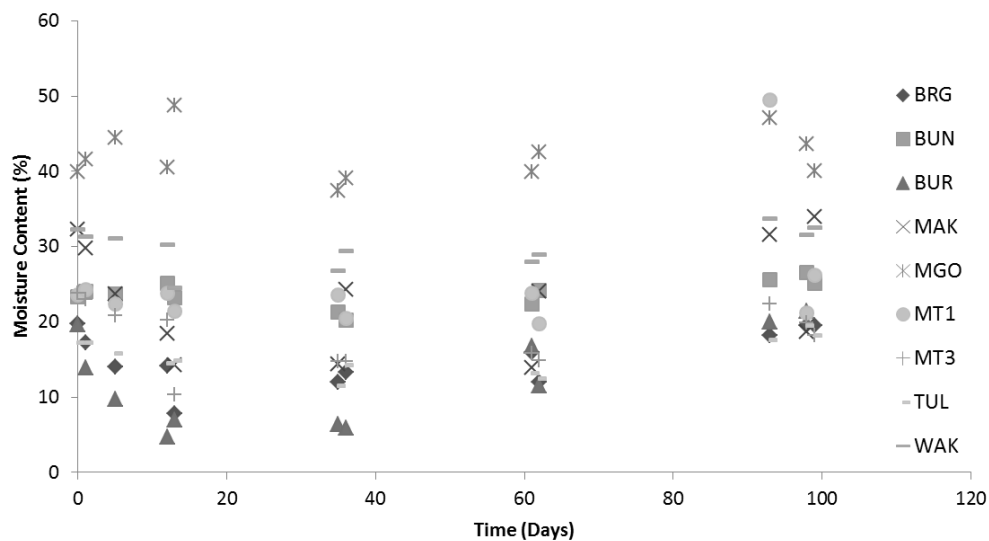


Figure 9. Per cent moisture (gravimetric) in soil at selected time points. Results represent the mean of all replicates for each soil.

Pesticide Degradation

In an initial pilot study, herbicides applied onto soil without a hanging water column were found to display non-detectable or limited degradation following 36 days of exposure in the glasshouse (e.g. Figure 10). These results are consistent with first principles that chemical and biological processes are less active at very low soil moisture and concur with the findings from previous studies (e.g. Walker, 1976; Wauchope et al., 2004). From a practical perspective, the results of the pilot study suggest that herbicides applied to dry soil (or soil which dries rapidly) will persist for some time and will be available to control weeds when rainfall occurs.

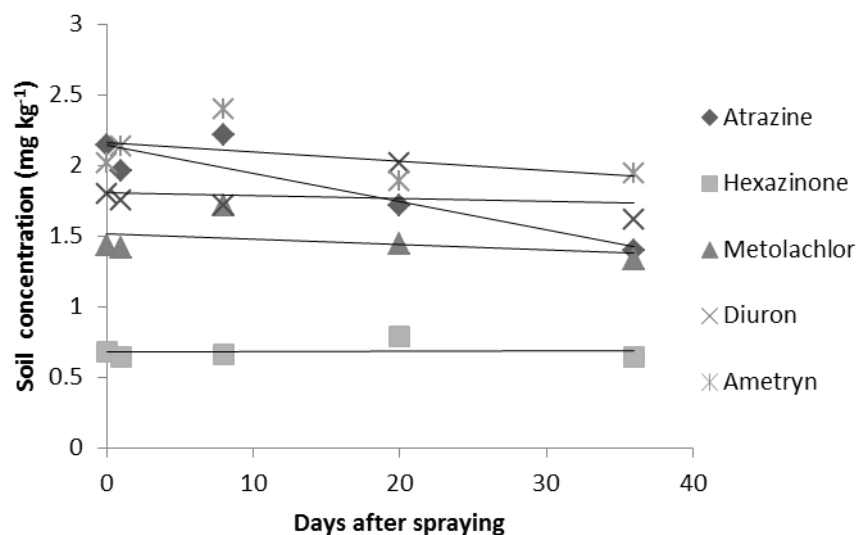


Figure 10. Herbicide concentration in the BRG soil in a pilot study without a hanging water column to maintain soil moisture. Values represent a pooled analysis of 5 individual replicates and a linear fit is shown.

By comparison, in this study where soils were kept moist measureable rates of degradation were observed for all herbicides applied to each soil. The decrease in herbicide

concentrations in the soil generally followed first order kinetics, meaning that the rate of degradation followed a constant exponential decay rate from the day of application till the end of the experiment. Exceptions to this were observed in early timepoints and were attributed to sampling and analytical variation. Figure 11 provides an example of atrazine degradation observed in the current study on the same soil as presented in Figure 10. Degradation was also observed for herbicides applied to cane trash with the exception of diuron and tebuthiuron, where no measureable degradation occurred within the 100 day experimental timeframe. Plots of the measured concentration over time for each herbicide on all of the soils and on cane trash are provided in Appendix II.

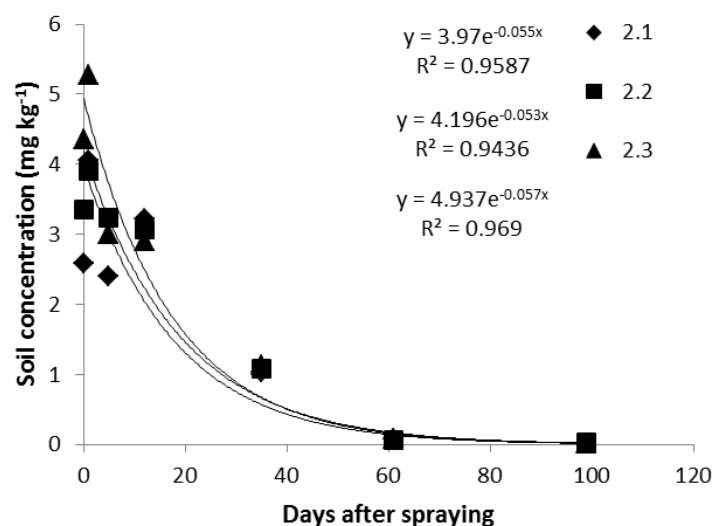


Figure 11. Atrazine concentrations in the BRG soil in the current study where a hanging water column maintained soil moisture. Results from three replicates are shown with the fit for an exponential decay.

Table 4 shows the half-life and associated coefficients of variation calculated for all herbicide and soil combinations. Both soil type and herbicide active ingredient had a significant impact on half-life ($p = 2.4E^{-49}$ and $p = 6.6E^{-85}$ respectively). The half-lives ranged from 12 days for atrazine on the Ferrosol (WAK) to >744 days for paraquat on a heavy Vertosol (MAK). The calculated half-life could vary considerably between the three replicates with coefficients of variation ranging from 4 - 322%. The highest coefficients of variation were observed for the herbicide paraquat. It is likely this can be attributed to reproducibility of the laboratory process for extracting this tightly bound herbicide from soil for analysis.

The degradation rate measured in the current study is relevant for relatively high temperatures (11 °C to 47 °C) and soil moisture content and has been measured only in the shallow surface layer which is exposed to climatic extremes. The half-lives presented here are therefore expected to be shorter than many available literature values.

While the degradation half-lives derived were comparable to literature values for some herbicides, such as atrazine, others produced results that were considerably different (Table 5). For example, the mean half-life for imazapic was 37 days (ranging from 20-81) which is approximately 6 fold faster than reported in the pesticides properties database (PPDB, University of Hertfordshire) which largely draws on data from temperate regions (Table 5). This study, along with a field study on the MAK soil with trash covered soil (Rohde et al., 2011, Table 6), represent the first estimates of the half-life of imazapic and other 'non-regulated' herbicides in a tropical environment. Half-lives of trifloxysulfuron sodium and pendimethalin were also faster than PPDB estimates, by a factor of 2-2.5 on average. In contrast, the half-life measured for the emerging herbicide isoxaflutole was more than 10 times slower than the PPDB value for each of the soils tested. These values are more consistent with anecdotal evidence from Queensland growers that isoxaflutole provides

effective weed control for extended periods. Importantly, it should be noted that it is the diketonitrile derivative of isoxaflutole that is herbicidally active and is formed rapidly in plants following root and shoot uptake as well as in the soil (Pallett et al., 2001). A study conducted in Minnesota, USA, on three soil types recorded half-lives of isoxaflutole plus the diketonitrile metabolite as 8-18 days (Papiernik et al., 2007)¹ while the half-life of only the parent compound was found to be 14-22 days on Queensland soils. Comparison of PPDB values to the half-lives determined for Queensland cropping soils highlights the importance of locally relevant data for realistic prediction of herbicide fate.

Table 4. Measured half-lives (days) for each herbicide and soil. The mean is presented (n=3) with coefficients of variation (%) in parentheses.

Herbicide	WAK	BUN	MAK	MT1	MT3	TUL	MGO	BRG	BUR	TRH
Diuron	55 (84)	56 (21)	200 (55)	50 (15)	134 (36)	64 (28)	14 (19)	49 (55)	26 (12)	>100
Hexazinone	43 (30)	38 (9)	97 (42)	43 (22)	75 (51)	49 (35)	33 (42)	48 (34)	28 (54)	97 (3)
Pendimethalin	41 (26)	33 (24)	56 (28)	35 (10)	60 (16)	40 (10)	29 (10)	30 (30)	32 (8)	19 (4)
Tebuthiuron	87 (44)	120 (62)	260 (186)	190 (71)	178 (51)	70 (33)	90 (43)	120 (107)	162 (133)	>100
2,4-D	18 (6)	19 (13)	15 (12)	16 (34)	17 (6)	22 (10)	21 (4)	16 (13)	14 (10)	32 (7)
Atrazine	12 (8)	17 (25)	19 (4)	21 (9)	22 (8)	19 (12)	13 (25)	13 (4)	16 (8)	44 (38)
Ametryn (gesapax)	17 (7)	19 (6)	41 (7)	21 (10)	27 (13)	39 (24)	13 (32)	19 (8)	25 (10)	37 (32)
Ametryn (krismat)	20 (7)	18 (8)	40 (12)	22 (8)	46 (30)	61 (31)	13 (4)	17 (6)	23 (4)	45 (67)
S-Metolachlor	20 (7)	17 (5)	50 (2)	26 (7)	40 (13)	23 (20)	20 (43)	36 (10)	28 (16)	74 (66)
Glyphosate	20 (6)	18 (3)	34 (9)	20 (23)	25 (13)	42 (20)	31 (12)	20 (10)	19 (18)	59 (31)
Imazapic	50 (8)	81 (10)	42 (27)	20 (13)	38 (36)	31 (19)	26 (27)	26 (5)	20 (6)	117 (117)
Isoxaflutole	18 (8)	18 (3)	14 (12)	17 (10)	21 (5)	14 (3)	22 (13)	18 (3)	21 (9)	45 (56)
Metribuzin	25 (11)	16 (5)	44 (41)	21 (19)	62 (51)	24 (41)	19 (5)	28 (9)	18 (3)	84 (94)
Trifloxysulfuron	28 (10)	37 (9)	21 (4)	31 (19)	33 (14)	20 (7)	21 (6)	17 (12)	25 (5)	93 (118)
Paraquat	528 (71)	462 (45)	744 (202)	67 (322)	326 (44)	247 (69)	253 (39)	176 (23)	244 (53)	41 (61)

Atrazine is one of the most commonly applied herbicides used to control broadleaf weeds in Queensland cropping (Rayment and Simpson, 1993; Simpson et al., 2001a). It is applied pre-emergence in expectation of providing season long residual weed control. However, the half-lives determined in this study (12-21 days) were comparable or shorter than those observed for knockdown herbicides such as 2,4-D or glyphosate. The half-lives determined

¹ The diketonitrile product was also measured in the current study, however, results are not yet available.

in this study were similar to those derived in a field study on a black Vertosol in Queensland (16-20 days) (Ratray et al., 2007) and were not much faster than reported in the PPDB (29 days). The repeated use of atrazine at a site has been shown to reduce the half-life in that location as microbial populations adapt to rapidly mineralise the herbicide (Krutz et al., 2010). These findings suggest that the effectiveness of atrazine for weed control can reduce over time. Importantly, it also has implications for modelling of the fate of atrazine. Accurate prediction of half-life of atrazine may need to take into account the history of atrazine applications at a given location. By comparison, a study of the degradation of six insecticides in tropical conditions showed no accelerated degradation after several repeat application experiments (Ciglasch et al., 2006), suggesting that this phenomena is likely to be compound specific. Given that each of the soils included in the current study was from a cropped site with a history of herbicide applications which likely included atrazine², it is expected that the short half-life values observed were representative of results for cropped soils where atrazine has previously been applied. However, in situations where atrazine is applied each season to the same site, half-life values may be shorter than reported here.

Tebuthiuron is applied to control woody weeds in grazing situations in Queensland and has been reported to provide weed control for many years following application (Graham Fossett, DowAgrosciences, pers comms, 2013). The degradation rate reported under laboratory conditions in the PPDB was 360 days while a field half-life as long as 1062 days has been reported (USEPA, 1994). The half-life on all soils in the current study was shorter than 260 days and was as low as 70 days on the sandy TUL soil. Tebuthiuron was applied as Spike, a wettable powder, when only the pellet formulation is currently registered in Australia. The wettable powder was used in this study since it would not have been possible to collect representative soil samples from a box surface if the pellet form had been applied. However, it is possible that there are differences in the fate of these formulations. Furthermore, the majority of tebuthiuron usage is in the dry tropics region of the GBR catchment which experiences relatively low annual average rainfall. Therefore, the soil moisture levels maintained in the controlled environment experiment may exceed field moisture levels for many tebuthiuron application scenarios. Tebuthiuron has been noted to take longer to break down in areas that have less rainfall. It has also been noted that the half-life for tebuthiuron is greater in high organic soils, regardless of rainfall (WSSA, 1989), although this was not found to be a significant explanatory variable in the current study.

Effect of soil properties on herbicide degradation

The half-lives for some of the herbicide products were very similar across all of the soil types. For example, the mean half-life of atrazine, 2,4-D and isoxaflutole varied less than 2 fold (1.8, 1.6 and 1.5 respectively) across the tested soils. By comparison, the mean half-life of diuron varied 14 fold, which makes prediction of the appropriate degradation rate for a given environmental situation challenging. Multiple linear regression suggested that pH and total organic carbon (TOC) were important factors for predicting the diuron half-life where as other factors considered (clay content, electrical conductivity (EC) and average moisture at sampling timepoints) were not found to be significant explanatory variables. TOC was a significant explanatory variable in the observed degradation rates for many of the herbicides. Previous studies have also noted slower herbicide degradation rates on soils with higher organic matter content (e.g. Ismail et al., 2012, Walker and Blacklow, 1994). However, soil organic carbon in tropical regions is generally much lower than in temperate environments (Sanchez-Bayo and Hyne, 2011).

TOC was not found to be a significant explanatory variable for degradation rates of paraquat, tebuthiuron, 2,4-D, glyphosate or isoxaflutole. There were no significant correlations with any

² The herbicide application history for each soil is being compiled.

of the examined soil properties for the herbicides tebuthiuron or paraquat. Both of these herbicides showed slow degradation rates as well as high variability in results.

An earlier study on Queensland soils found that degradation of diuron was much slower on Ferrosols (half-life >150->250 days) compared to a Kandosol or Chromosol (half-life 6-15 days). This was attributed to the binding capacity of the Ferrosol soil, which had high clay%, protecting the compound from microbial and chemical degradation processes (Simpson et al., 2001b). Other field trials have similarly noted that persistence of herbicides was greater in clay soils followed by sandy loam, loamy sand and sandy soils (e.g. Masingh et al 2003). However, the Ferrosol soil included in this study (WAK, 55 days) did not show slower rates of diuron degradation. Furthermore, the soils with highest clay content exhibited both the slowest (MAK, 200 days) and fastest (MGO, 14) degradation (Figure 12).

Table 5. Mean and range of measured half-life (days) compared to selected database and literature review values

Herbicide	Glasshouse half-life ^a	PPDB Field half-life ^b	PPDB Lab half-life ^b (20°C)	Typical tropical half-life ^c
Diuron	72, 14-200	89	75.5	16, 15–31
Hexazinone	51, 33-97	105	90	21, 20–21
Pendimethalin	40, 29-60	90	123	32, 13–1396
Tebuthiuron	142, 70-260	400	360	NR ^d
2,4-D	18, 14-22	10	14	1, 0.5–1.3
Atrazine	17, 12-22	29	66	13, 5–41
Ametryn	25, 13-41	37	60	25, 17–33
S-Metolachlor	29, 17-50	21	14.5	33, 14–47
Glyphosate	25, 18-42	12	49	31, 9–50
Imazapic	37, 20-81	232	120 ^e	NR ^d
Isoxaflutole	18, 14-22	1.3	2.3	NR ^d
Metribuzin	28, 16-62	19	11.5	NR ^d
Trifloxysulfuron	26, 17-37	63.5	70	NR ^d
Paraquat	339, 67-744	365	365	41, 36-46

^a Current Study

^b Pesticide Properties Database (PPDB), University of Hertfordshire

^c Sanchez Bayo and Hyne, 2011

^d NR=Not reported

^e 'Typical' value, lab data not available

The PSII inhibiting herbicide ametryn was included in the current study in two different product formulations; as Gesapax which includes atrazine and as Krismat which includes trifloxysulfuron. The mean calculated half-life values for ametryn applied in each formulation were similar with values within a factor 0.92 - 1.5. In a study comparing ametryn degradation on pH adjusted soils, pH was found to contribute significantly to observed degradation rates (Andrade et al., 2010). In the current study, pH was a significant explanatory variable for the

degradation of ametryn applied as Krismat while not significant for ametryn applied as Gesapax. TOC and the average soil moisture were found to contribute significantly to degradation of ametryn in both formulations.

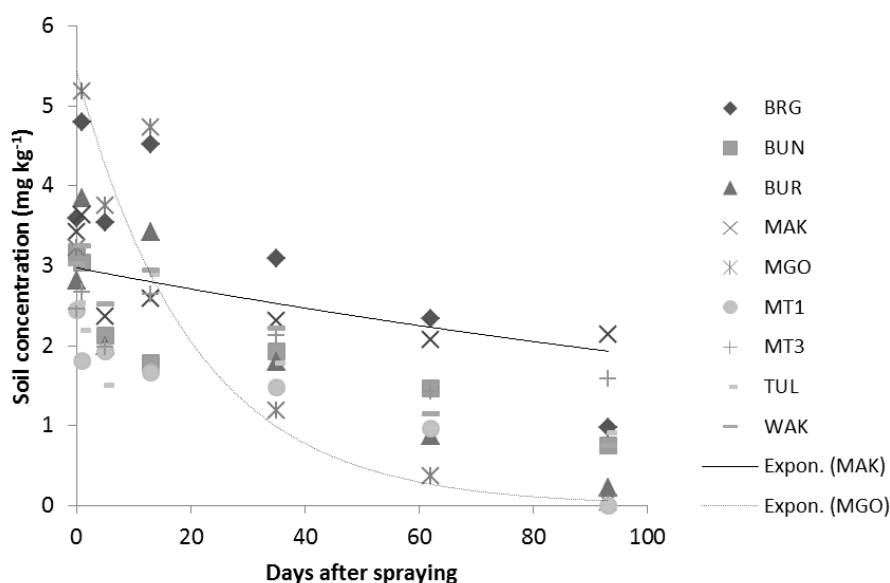


Figure 12. Diuron concentration in each soil (mean, n=3). A trendline is shown for the soil with the shortest (MGO) and longest (MAK) half-life.

Comparison to field derived half-lives

Degradation in a controlled environment such as the glasshouse was not subject to losses via offsite transport processes such as runoff or leaching. Degradation measured in the glasshouse was compared to the dissipation of herbicides observed at the field sites from which the soils were collected for use in the glasshouse and at other sites within the GBR catchment (Table 6). The half-lives determined in the controlled condition were consistent with estimates from the field sites in many instances. For example, the half-lives for diuron in the MAK soil and pendimethalin in the TUL soil were similar to the field derived values. On the sandy soil from a cane demonstration farm in Bundaberg (BUN), the glasshouse value was the same as the upper estimate from the field for atrazine (17 days). However, the glasshouse derived value for this same herbicide was 1.7 times faster than the field derived value in the Wet Tropics. In contrast, degradation of hexazinone on a heavy Vertosol in the Mackay region was slower in the glasshouse than observed in the field.

The lack of consistent trends between herbicide degradation rates observed in the field and those observed in the controlled glasshouse environment highlights the difficulty in isolating factors contributing to dissipation in a field scenario. In field scenarios, studies have shown that significant losses occur through leaching, runoff and plant uptake (e.g. >15% of the applied isoxaflutole can be lost through leaching in 25 days (Papiernik et al., 2007)). This would mean that the glasshouse degradation rates, which exclude losses due to runoff/leaching/plant uptake, are more appropriate for use in predicting herbicide fate in agricultural soil water balance models where losses due to degradation are considered as a separate process to loss through runoff/leaching/plant uptake. However, it needs to be considered that for herbicides where photodegradation is an important loss pathway the glasshouse will underestimate loss.

In certain instances, the degradation rates measured in the glasshouse were faster than observed in Queensland field situations. It is hypothesized that this is due to the maintenance of relatively high soil moisture levels in the glasshouse through the use of a hanging water column whereas in a field situation soil will dry out between rainfall events.

This is consistent with the findings of the pilot glasshouse study which found limited to no degradation in soils which were allowed to dry out over time.

Table 6. Measured half-life (days) in the controlled environment compared to field dissipation rates derived for the same or similar soils in Queensland

Soil	Herbicide	Glasshouse half-life	Field half-life	Reference
BUN	Atrazine	17	10, 17, 8	Nachimuthu et al., 2012
	Pendimethalin	33	18	
	S-Metolachlor	17	34,17	
	Paraquat	426	260	
	Metribuzin	16	5,3	
MAK	Diuron	200	199	Rohde et al., 2011
	Hexazinone	97	53	
	Imazapic	42	118	
TUL	Diuron	64	38	Armour et al., 2011
	Atrazine	19	33	
	Hexazinone	49	19	
	Pendimethalin	40	37	
WAK				
TRH	Hexazinone	97	119	Rohde et al., 2011
	Imazapic	117	13	Rohde et al., 2011
	Atrazine	44	3.7	Nachimuthu et al., 2012
	S-Metolachlor	74	6.1	Nachimuthu et al., 2012
Brown Dermosol	2,4-D	14 ^a	13.9	Davis et al., 2012
	Glyphosate	19 ^a	21.4	
Black Vertosol	2,4-D	15, 21 ^b	11.7, 27.6	Davis et al., 2012
	Glyphosate	34, 31 ^b	42.1	
Red Dermosol-Herbert	Ametryn		231	Bare soil at P2R rainfall simulation study site, (Cowie et al., 2013). See Appendix III.
	Atrazine		15.5	
	Diuron		77	
	Hexazinone		173	
	S-Metolachlor		69.3	
Silkwood	Diuron		23	See Appendix III.
	Hexazinone		7	
	Metribuzin		7	
Burdekin	2,4-D		9.4	See Appendix III.
	Glyphosate		7.8	
	Fluroxypyr		14.1	
	Diuron		69.3	
	Atrazine		12, 25	
	Ametryn		14.7, 20	
	S-metolachlor		13.6	
	Metribuzin		16.9	
	Pendimethalin		23.1	
	Isoxaflutole		2.3	
	Imazapic		15.8	

^a BUR – values from the glasshouse trial soil considered most similar to the field site

^b MAK/MGO – values from the glasshouse trial soils considered most similar to the field site

Pesticide residues are generally thought to degrade more quickly on plant surfaces and on crop residues than in soil. In the SWAT pesticide model, half-lives for pesticides on crop residues are assumed to be less than the soil half-life by a factor of 0.5 to 0.25 depending on

vapour pressure and sensitivity to photodegradation and are capped at a maximum of 30 days (Neitsch et al 2004). Degradation rates on cane trash in the current study were found to range from 19 to 117 days, with no detectable degradation observed for diuron or tebuthiuron, which is considerably slower than reported from relevant field studies. It is expected that dissipation due to wash off is a significant loss pathway from crop residues in the field (Dang et al., 2012). However, photodegradation is also likely to contribute to herbicide losses from cane trash more than from soil where the penetration depth of light is known to be limited to approximately 0.5 cm (Katagi, 2004). Degradation rates on trash from the current experiment can be considered conservative estimates for application in modelling.

Conclusions

Degradation rates have been measured for 14 herbicides on nine common cropping soils and on crop residues under controlled temperature and soil moisture conditions. In addition, field studies have provided comparison of dissipation under field situations. Half-lives were found to range from 12 days for atrazine on the Ferrosol (WAK) to >744 days for paraquat on a heavy Vertosol (MAK). The half-life values were comparable to international database and literature values from tropical field studies for well-studied herbicides including atrazine and ametryn. However, half-lives for several herbicides that have not previously been reported under tropical conditions (imazapic, pendimethalin, trifloxysulfuron) were on average 2.5-6 fold faster than PPDB values. In contrast, the degradation rate of isoxaflutole was >10 fold slower than PPDB values. Half-lives for all herbicides on cane residues were slower than has been previously reported, which may be due to the effects of herbicide washoff in field studies and to limited photodegradation in the current study.

Half-lives varied by less than a factor of 2 between soils for the herbicides atrazine, 2,4-D and isoxaflutole whereas half-lives for diuron varied by a factor of 14. Total organic carbon was found to be a significant explanatory variable for predicting degradation rates for many of the herbicides in this study. Further analysis of the data is required to investigate relationships between soil properties and herbicide half-lives, which may allow estimation of half-lives for all soils in the GBR catchment.

The results presented here highlight the importance of locally derived half-life data for use in prediction of herbicide fate. Values derived in the current study can be considered to provide conservative estimates for the tested soil temperature and moisture conditions since loss processes including leaching, runoff, plant uptake and to some degree photodegradation have been excluded. The half-lives derived in this study relate to the surface 2.5 cm of soil which is the depth relevant to extraction of herbicides into runoff. Adoption of the half-life values from this study in the paddock to reef modelling program will improve prediction of herbicide losses under various management scenarios and will therefore improve prediction of loads of herbicides entering the Great Barrier Reef lagoon.



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Appendix I

Microbiology Assay Results

Ecoplate Assay

The Ecoplate assay provides a comparison of carbon sources that are able to be utilised and provides an overall measure activity for culturable microorganisms.

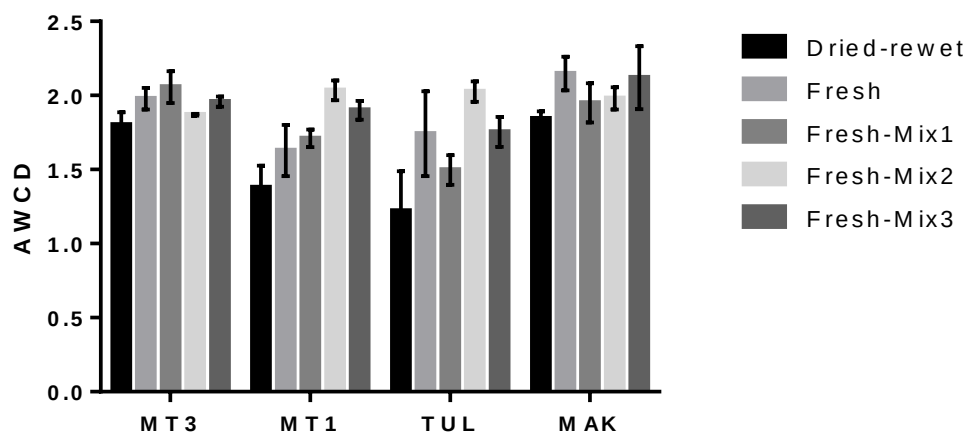


Figure 13. Mean well colour development (AWCD) indicating microbial activity in the Ecoplate assay following seven days exposure to dried-rewet and fresh field soils from four sites. Microbial response to the fresh soil after application of the three mixtures of herbicides used in the glasshouse trial is also shown. Error bars show ± 1 standard deviation, (n=3).

Fluorescein Diacetate Assay

The fluorescein diacetate assay (FDA) provides a measure of hydrolysis of FDA by microbes in soil. Lipase, protease and esterase enzymes are involved in this process and therefore a broad spectrum of microbiological 'activity' is detected.

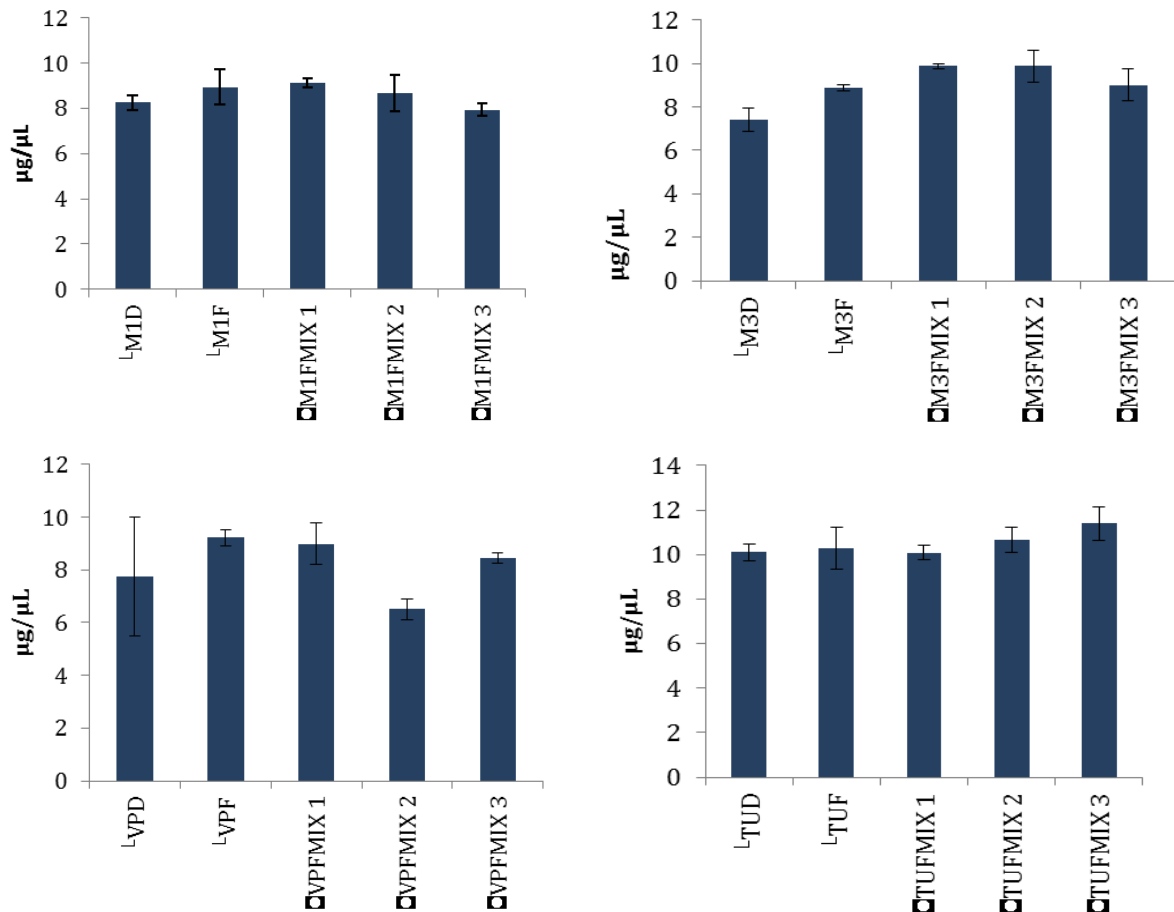


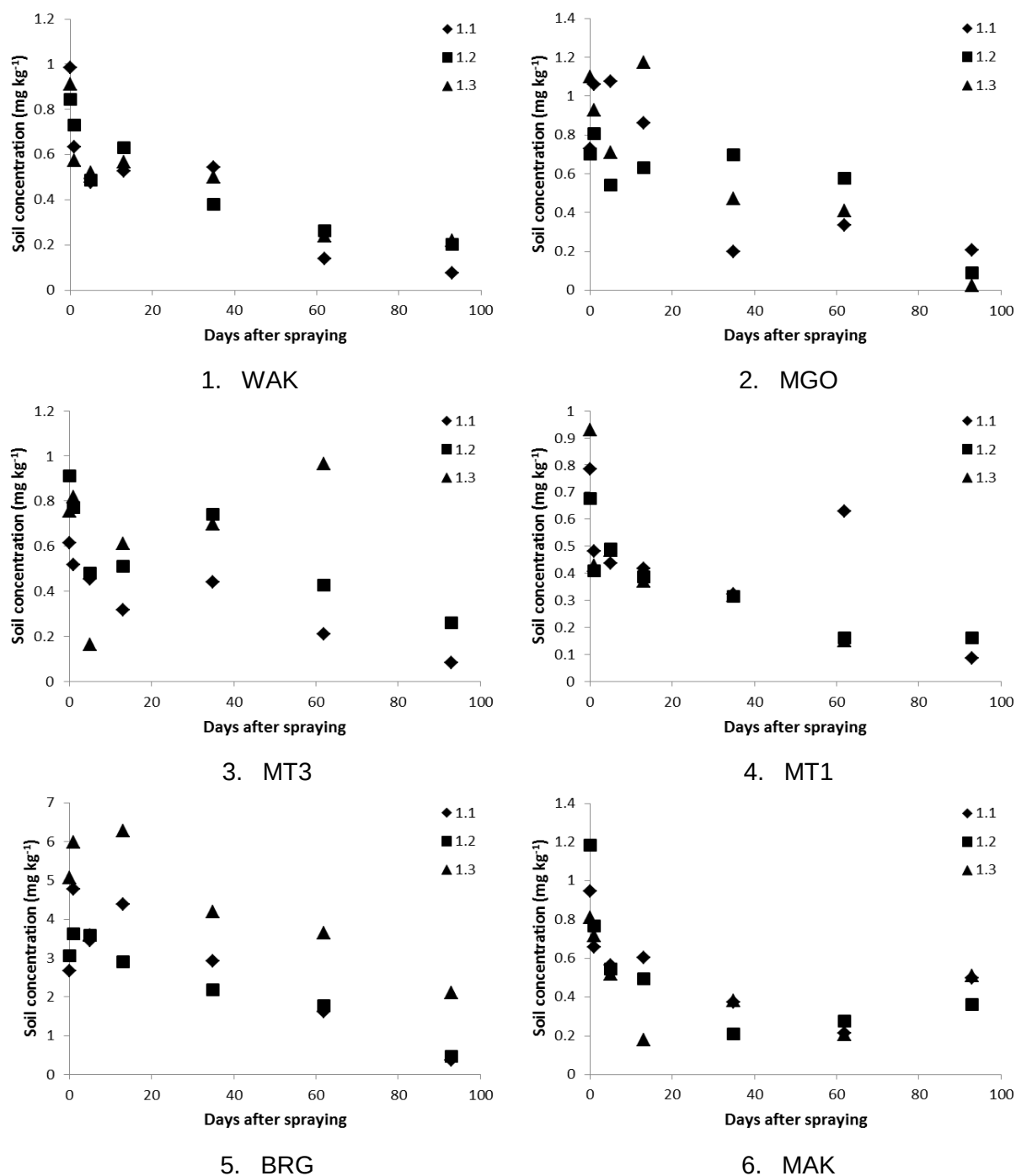
Figure 14. Mean fluorescein production (µg/µL) indicating microbial activity in the FDA assay following seven days exposure to dried-rewet (D) and fresh (F) field soils from four sites (M1=MT1, M3=MT3, VP=MAK, TU=TUL). Microbial response to the fresh soil after application of the three mixtures of herbicides used in the glasshouse trial is also shown. Error bars show ± 1 standard deviation, (n=3).

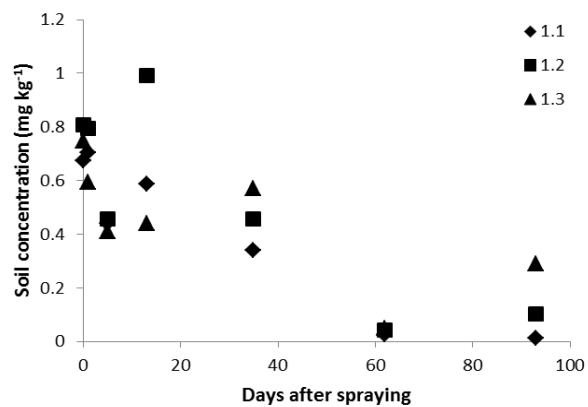
Appendix II

Plots of herbicide concentration in soil

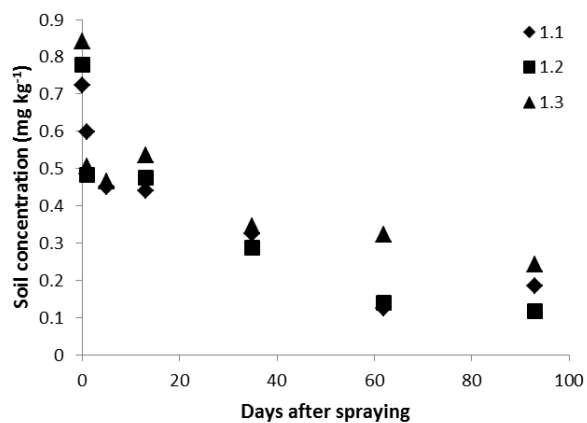
Measured concentrations of herbicides in soil and cane trash are shown below for each replicate at each sampling timepoint. Replicate numbers (1.1, 2.1, 3.1 etc) indicate the mix in which each herbicide was applied.

Diuron

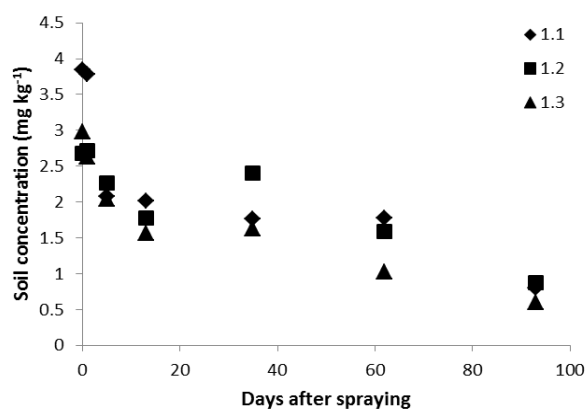




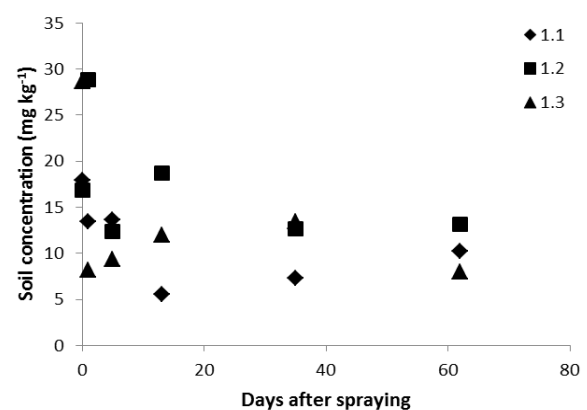
7. BUR



8. TUL

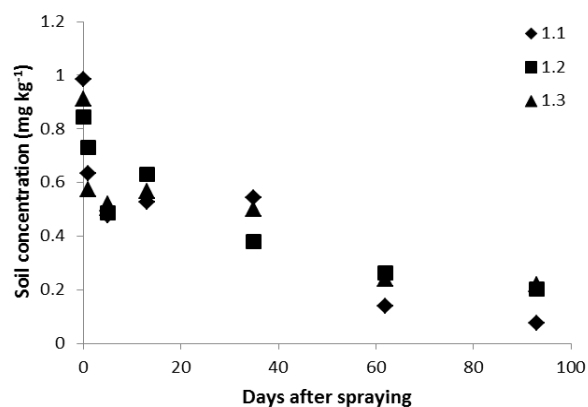


9. BUN

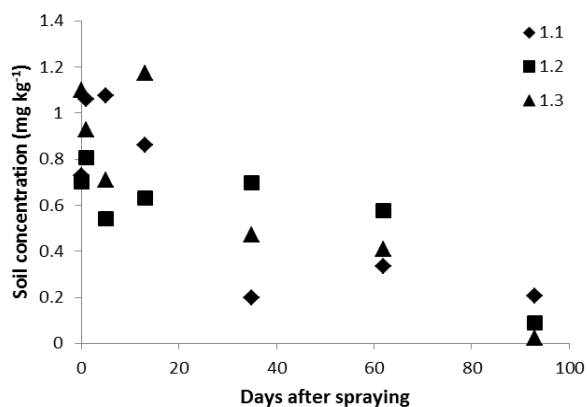


10 TRH

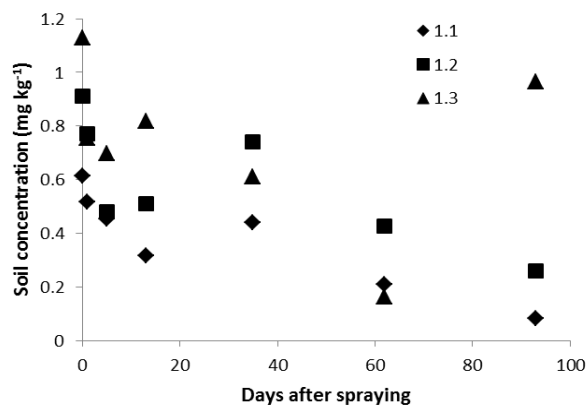
Hexazinone



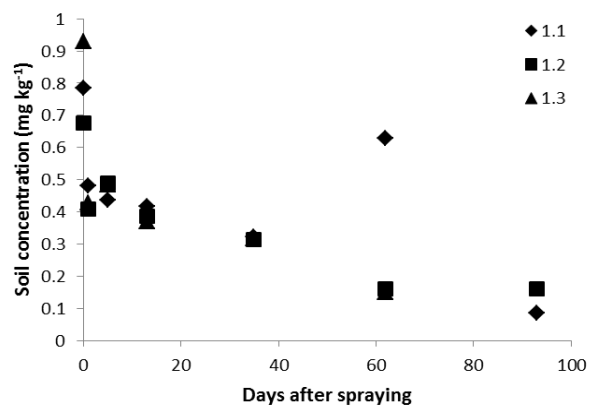
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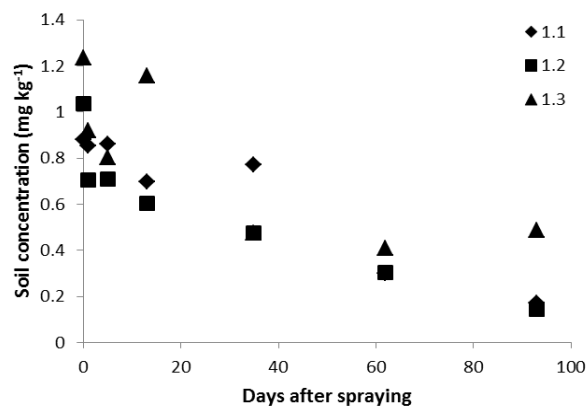
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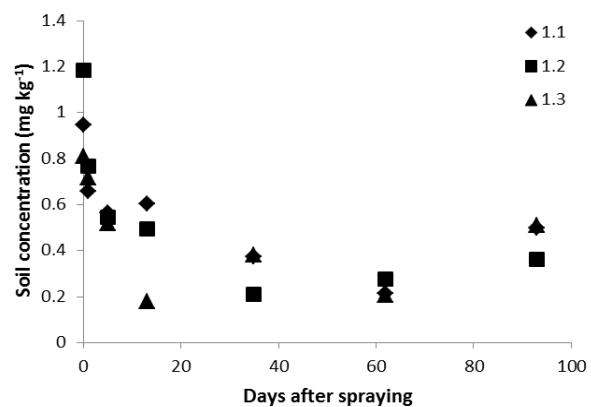
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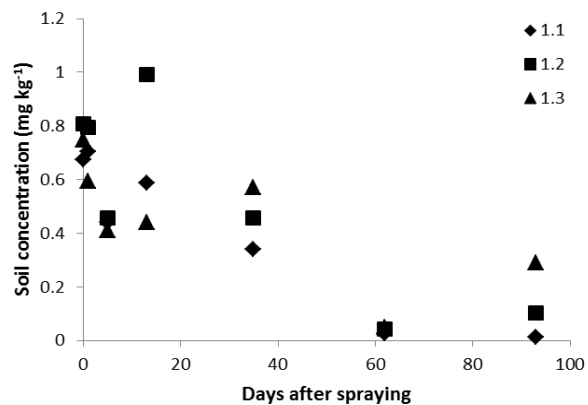
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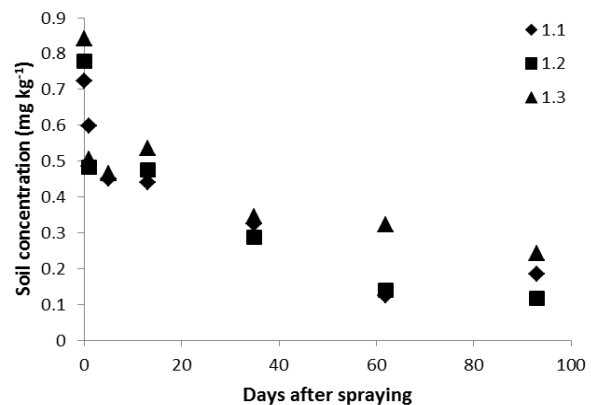
5. BRG



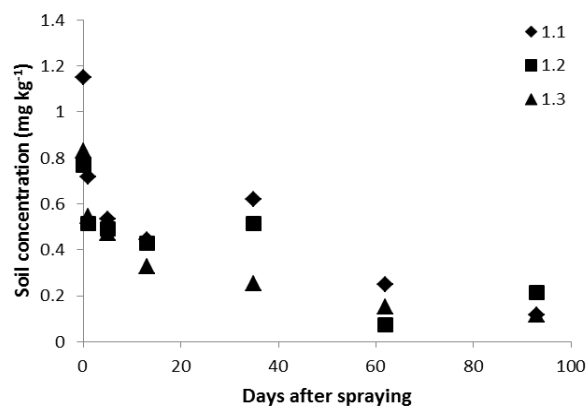
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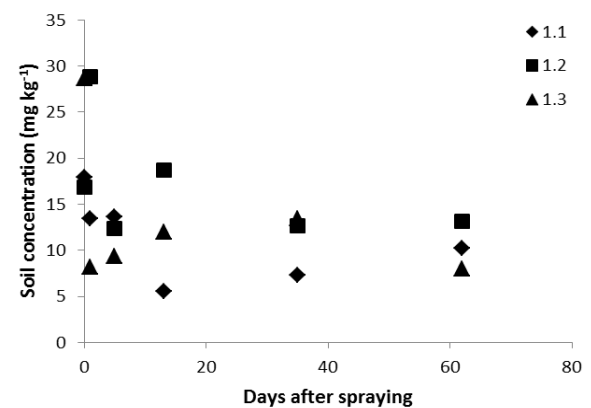
7. BUR



8. TUL

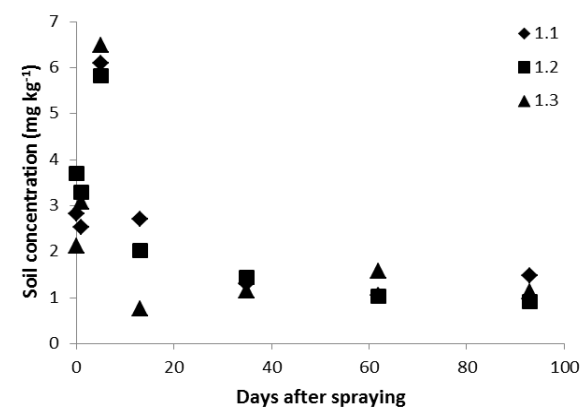
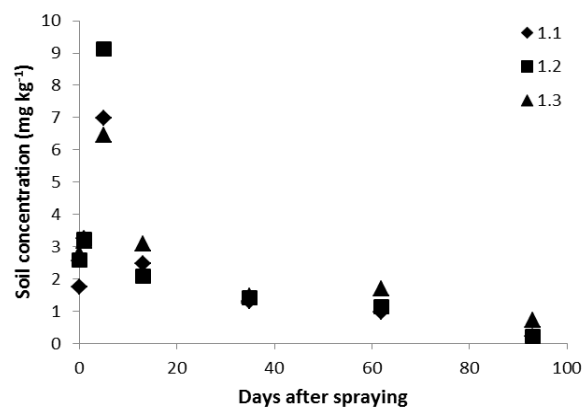
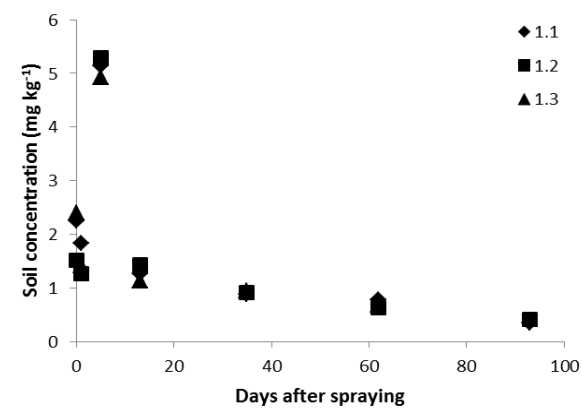
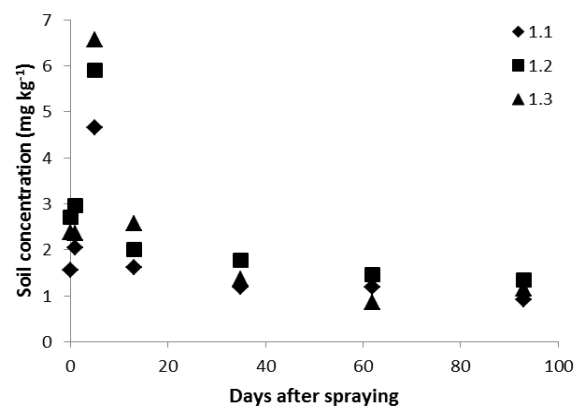
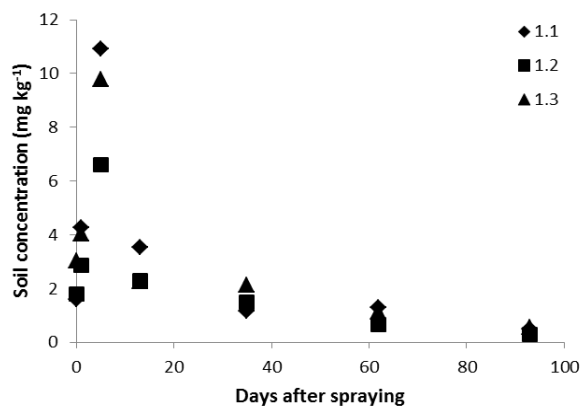
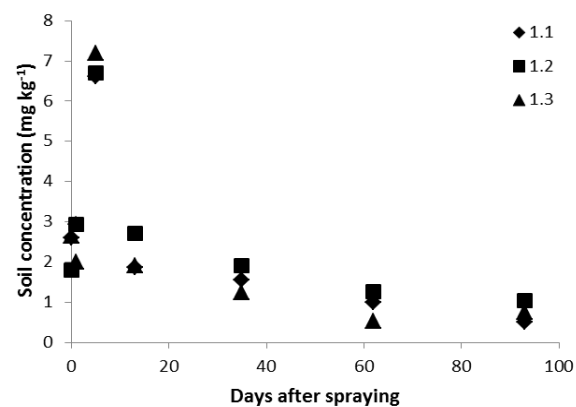


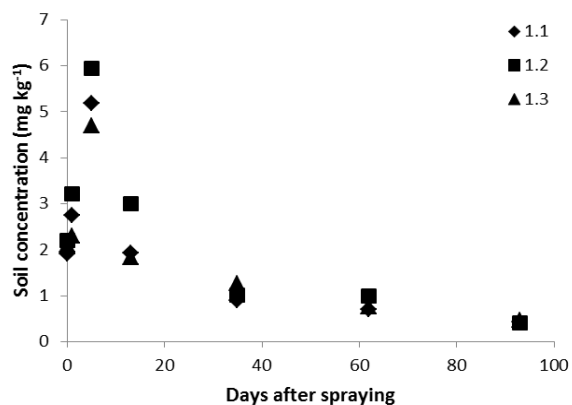
9. BUN



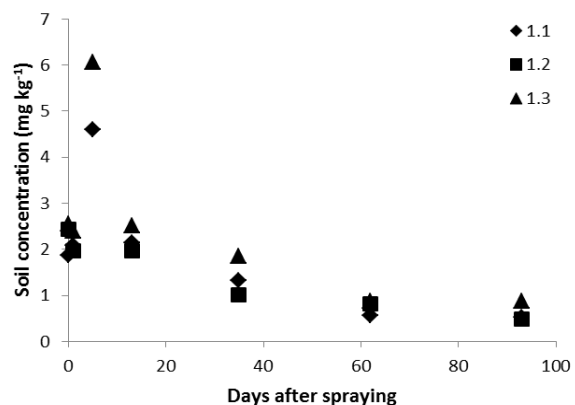
10. TRH

Pendimethalin

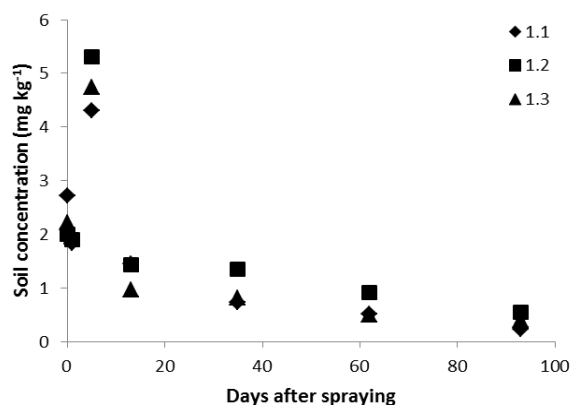




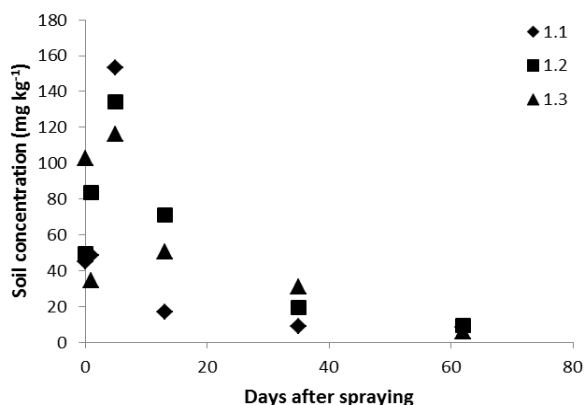
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8. TUL

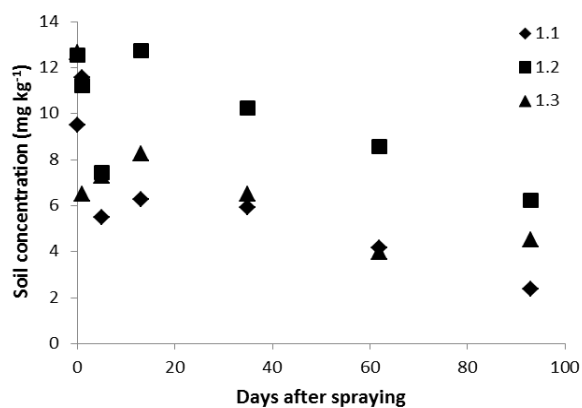


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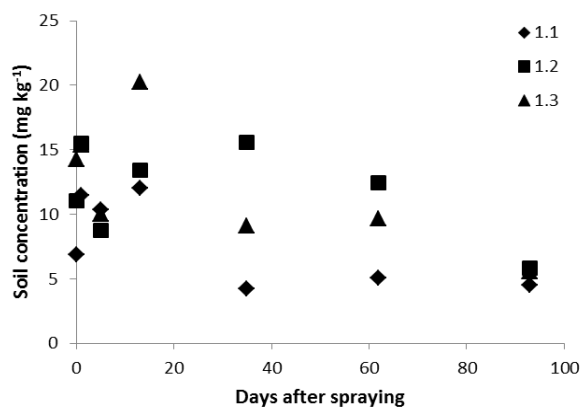


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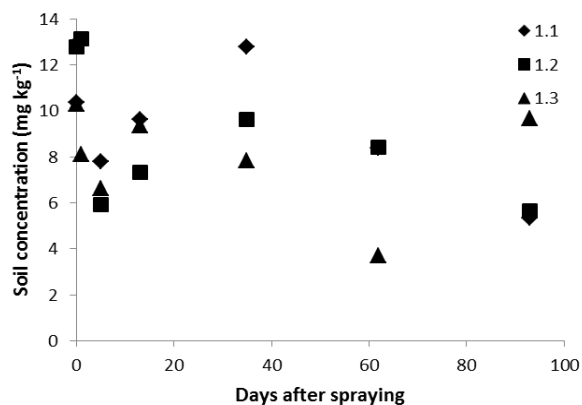
Tebuthiuron



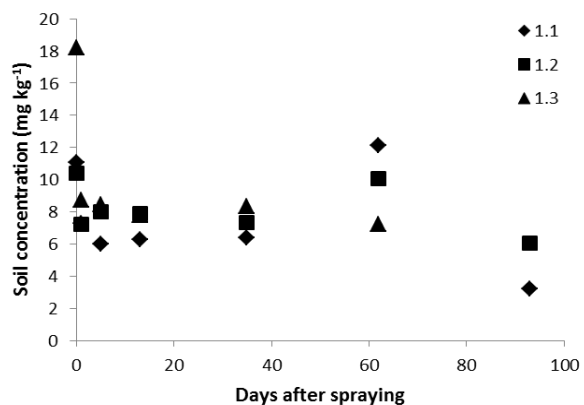
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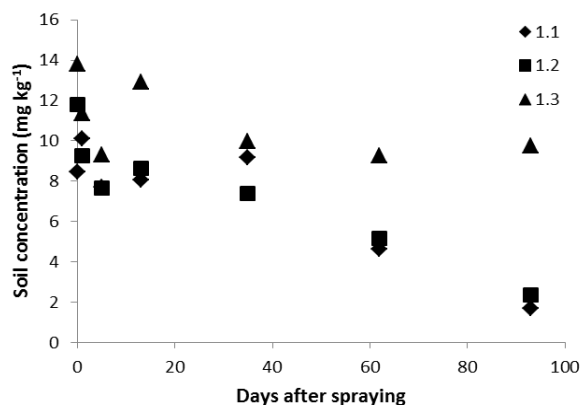
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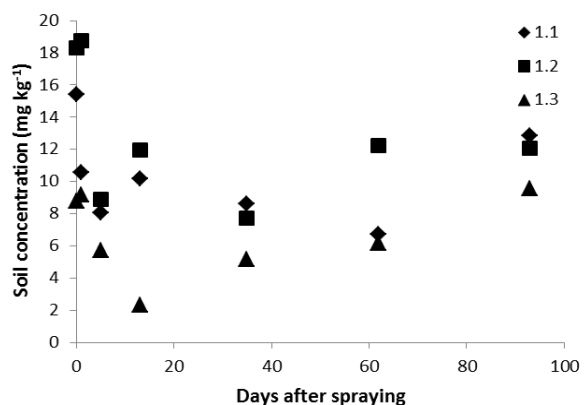
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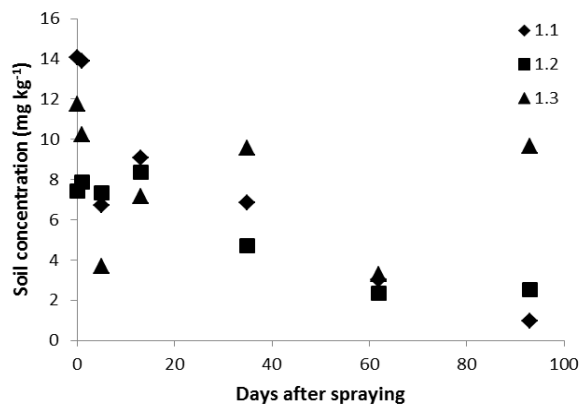
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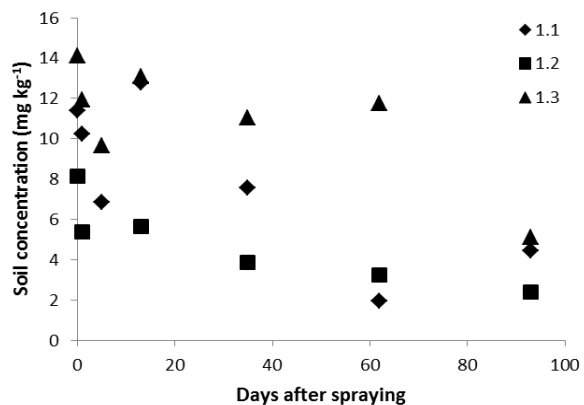
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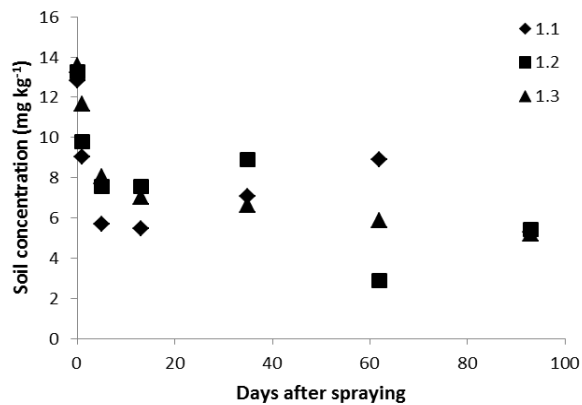
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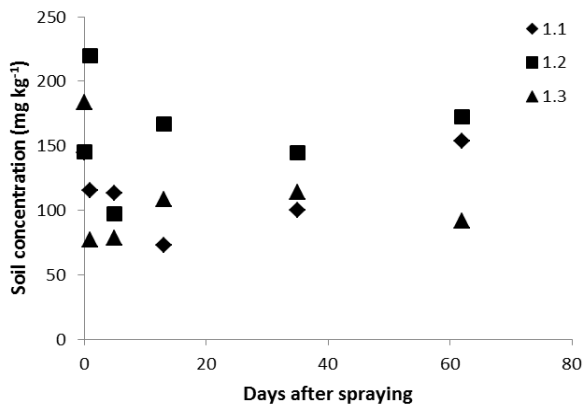
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8. TUL

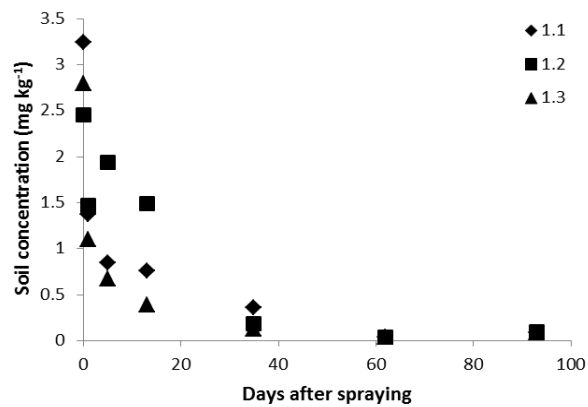


9. BUN

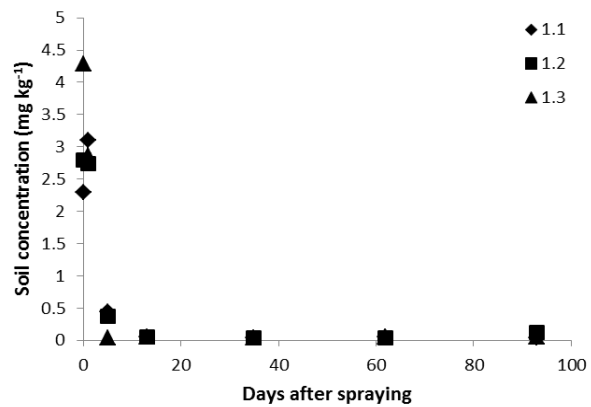


10. TRH

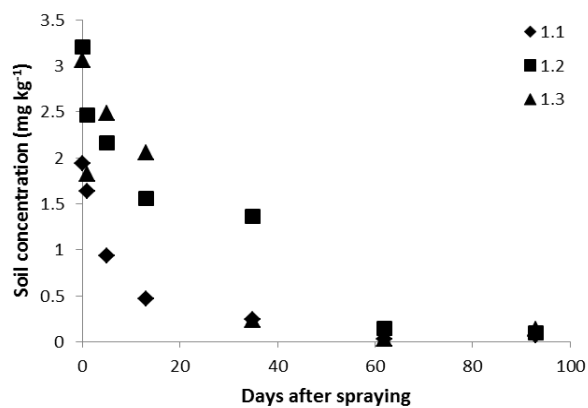
2,4-D



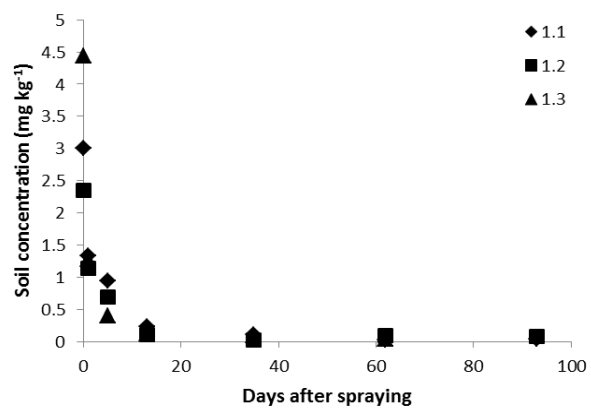
11. WAK



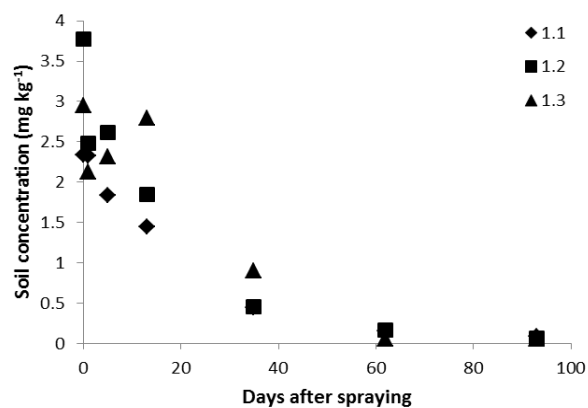
12. MGO



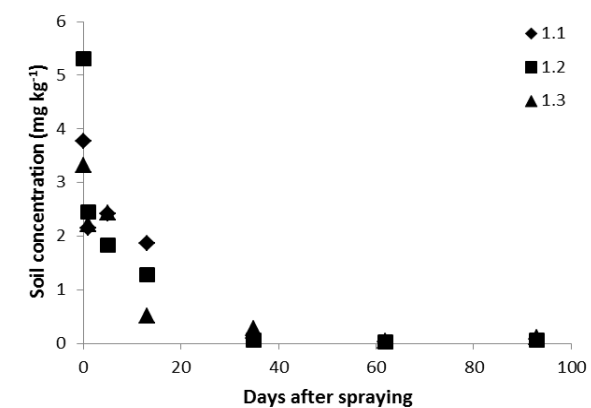
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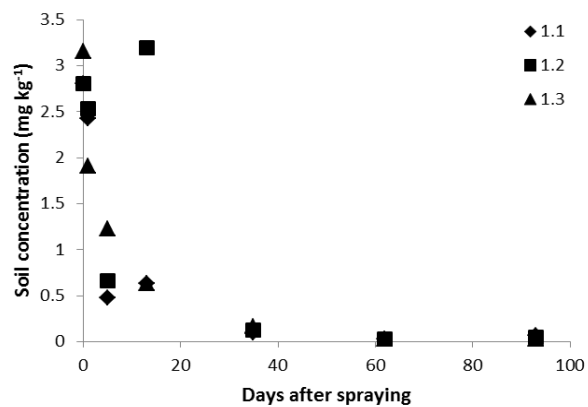
14. MT1



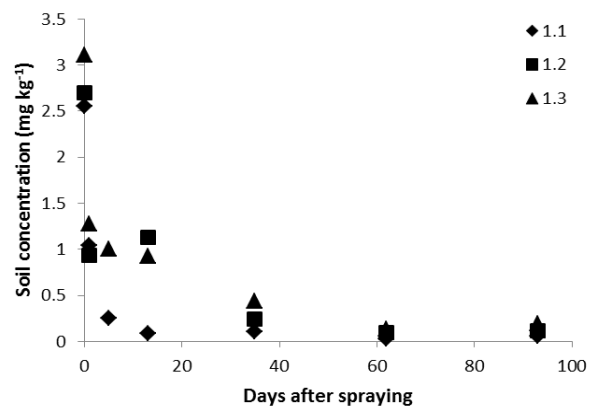
15. BRG



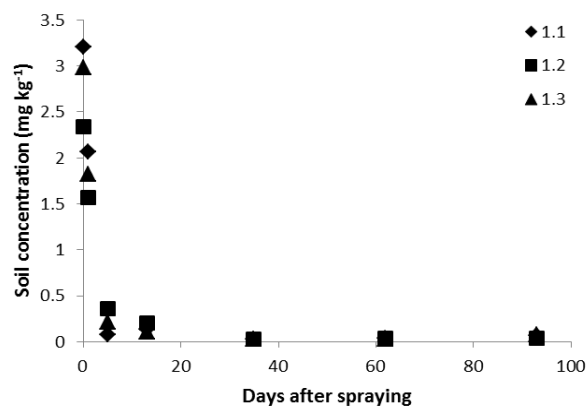
16. MAK



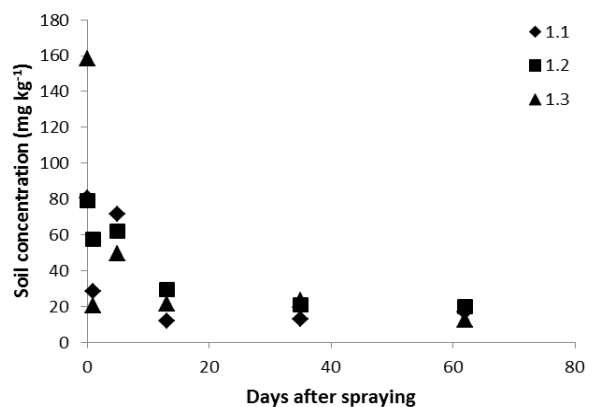
17. BUR



18. TUL

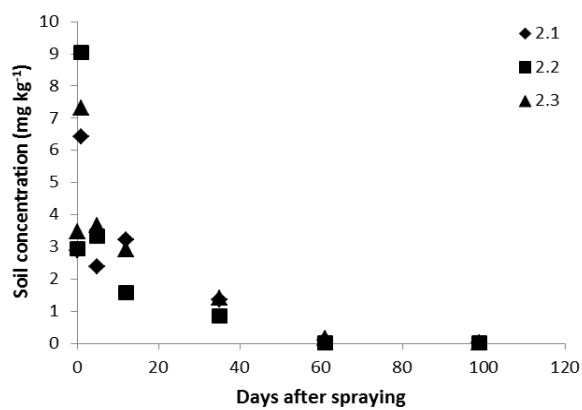


19. BUN

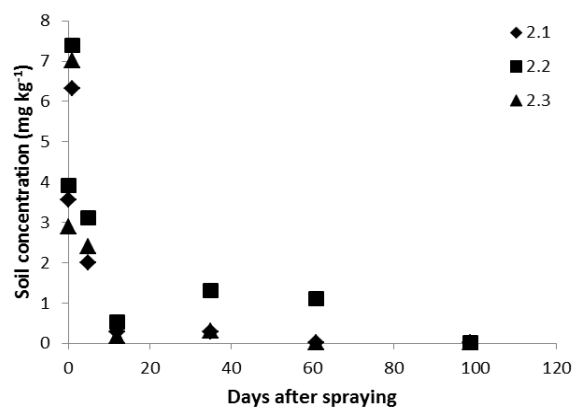


20. TRH

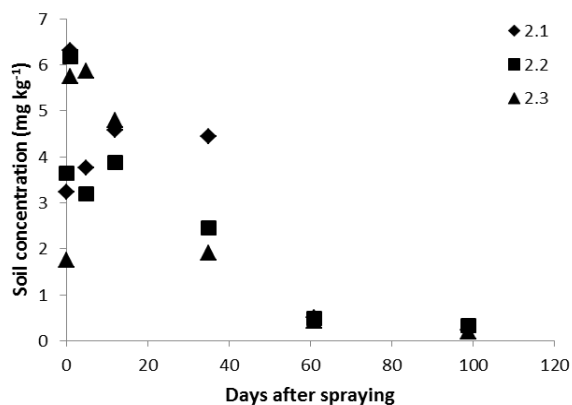
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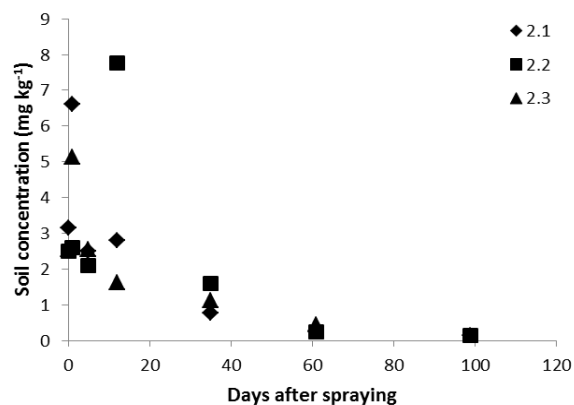
1. WAK



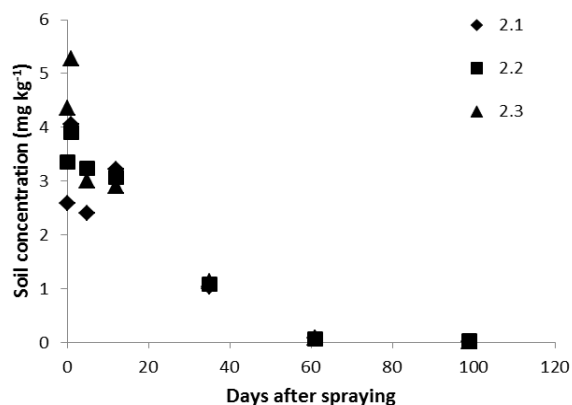
2. MGO



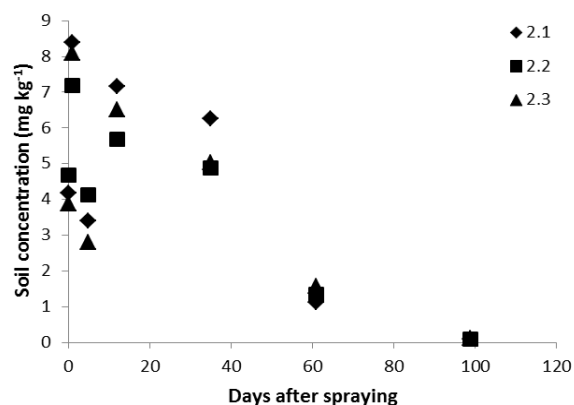
3. MT3



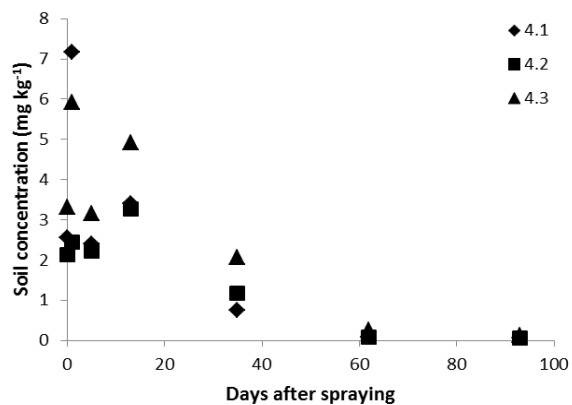
4. MT1



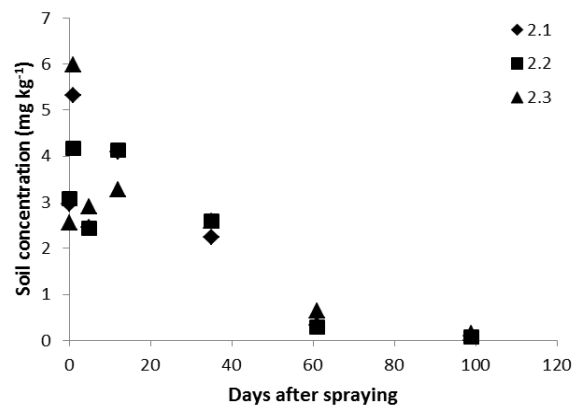
5. BRG



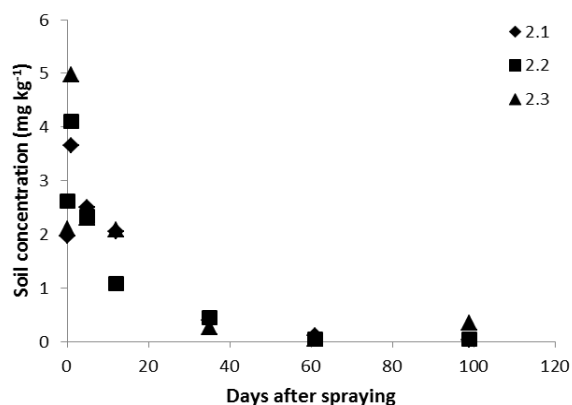
6. MAK



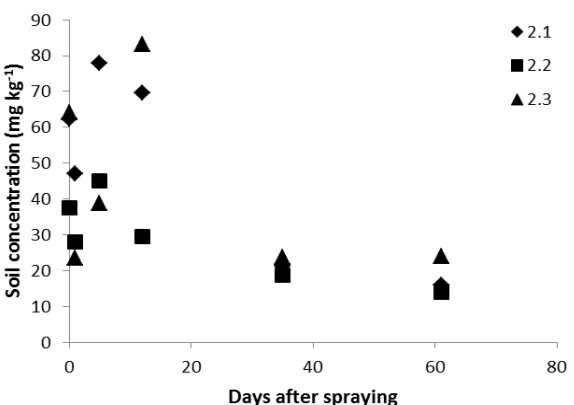
7. BUR



8. TUL

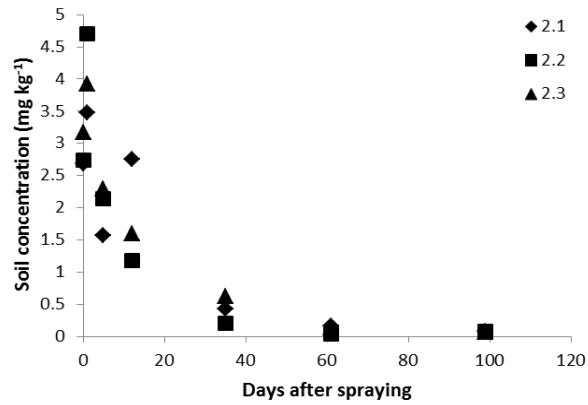


9. BUN

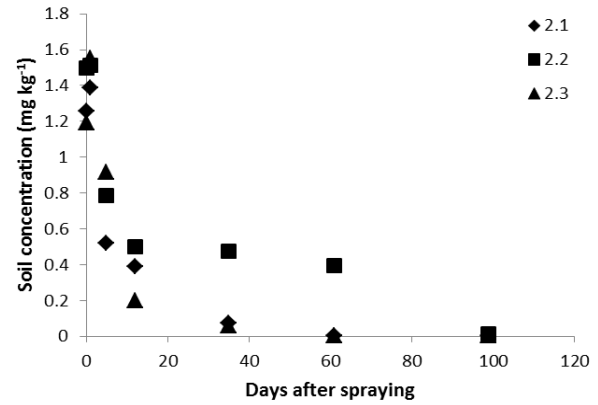


10. TRH

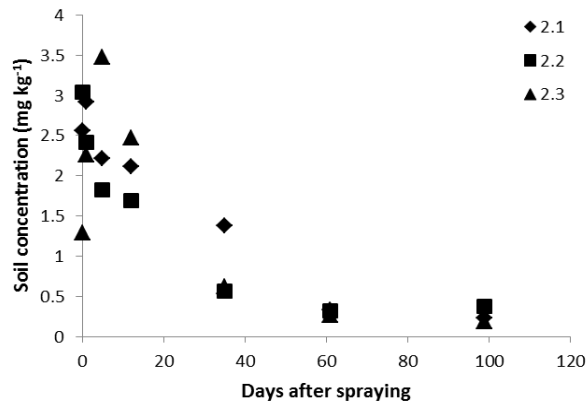
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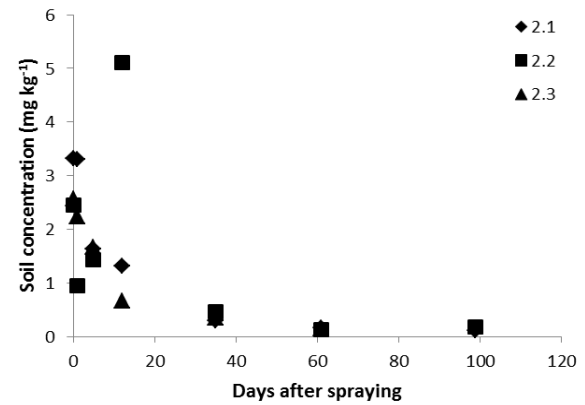
1. WAK



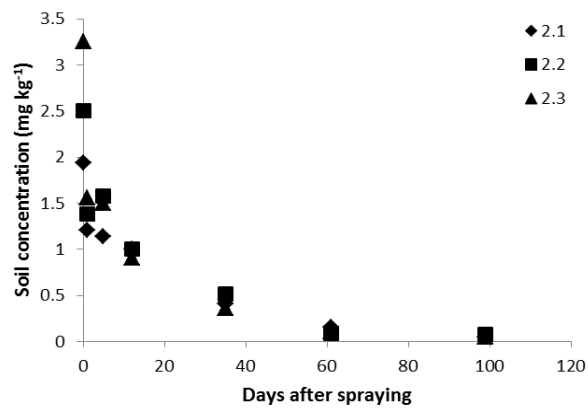
2. MGO



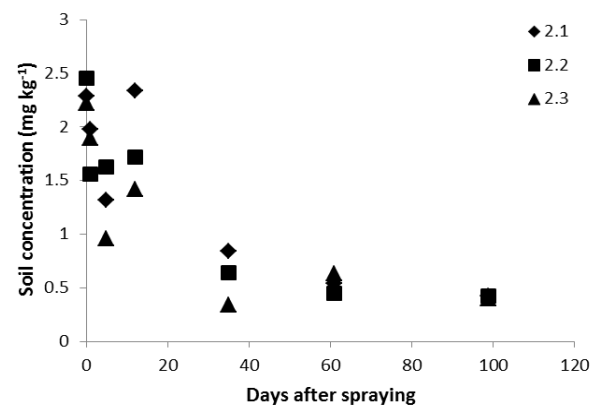
3. MT3



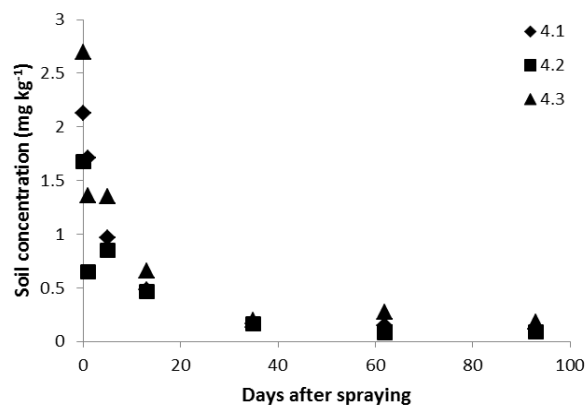
4. MT1



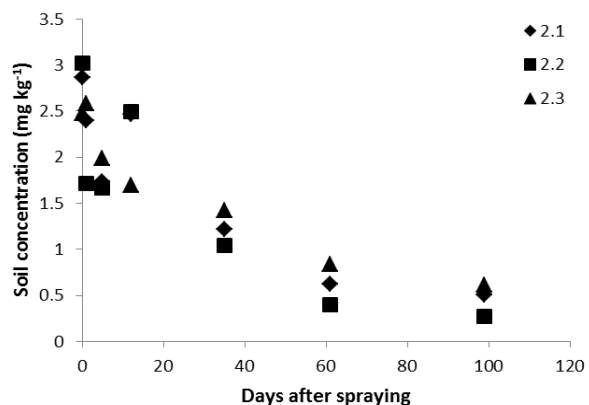
5. BRG



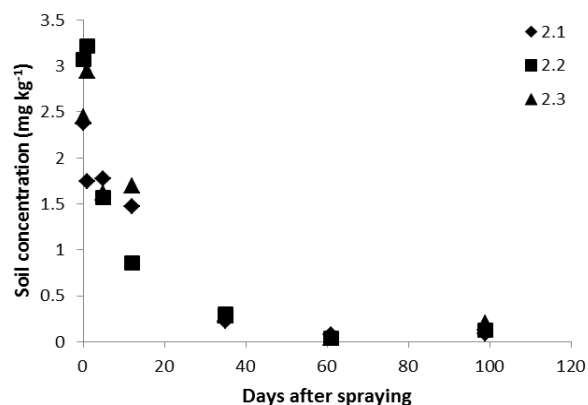
6. MAK



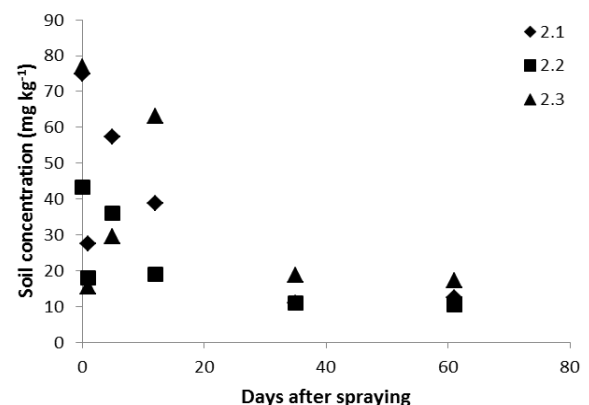
7. BUR



8. TUL

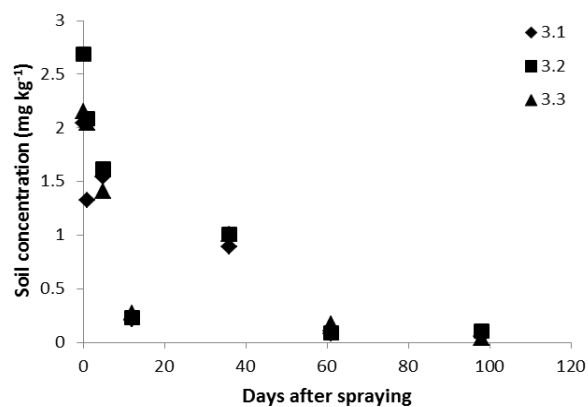


9. BUN

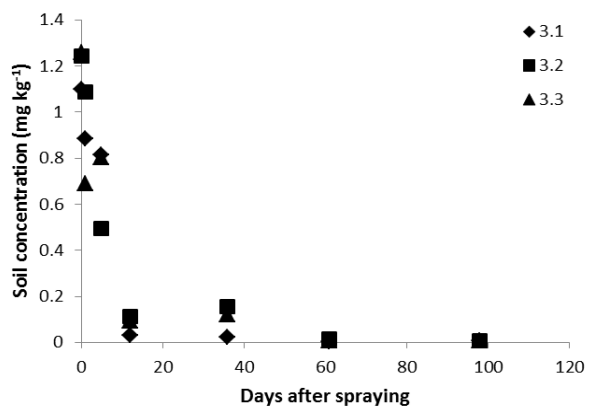


10. TRH

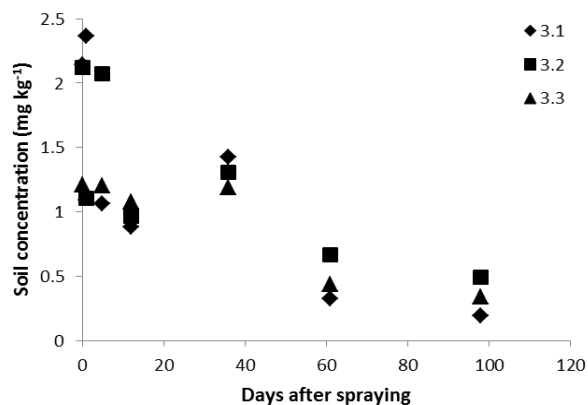
Ametryn (krismat)



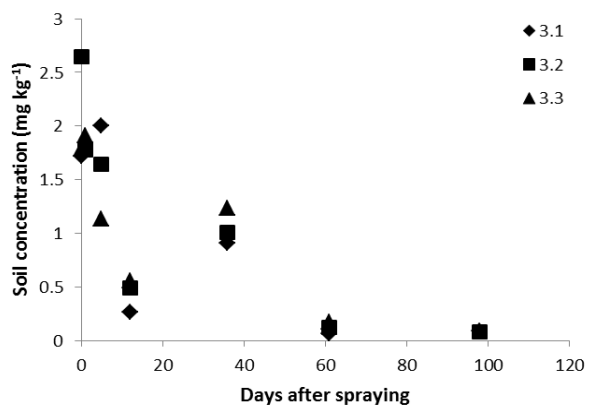
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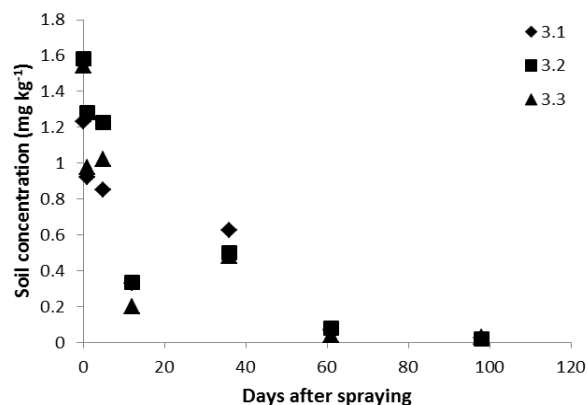
2. MGO



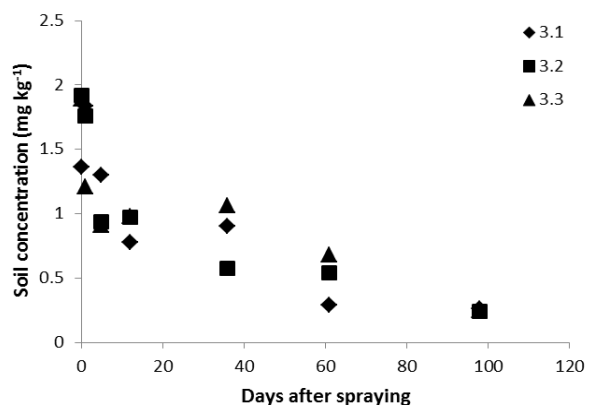
3. MT3



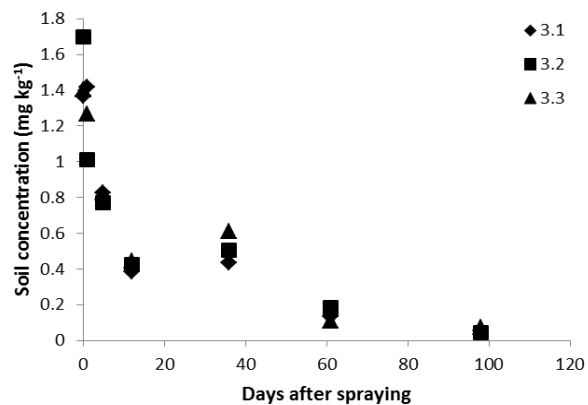
4. MT1



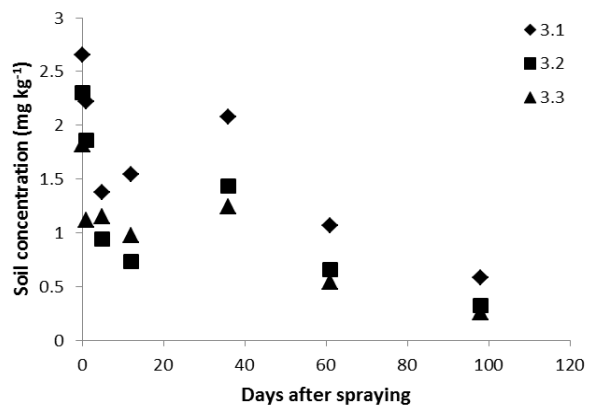
5. BRG



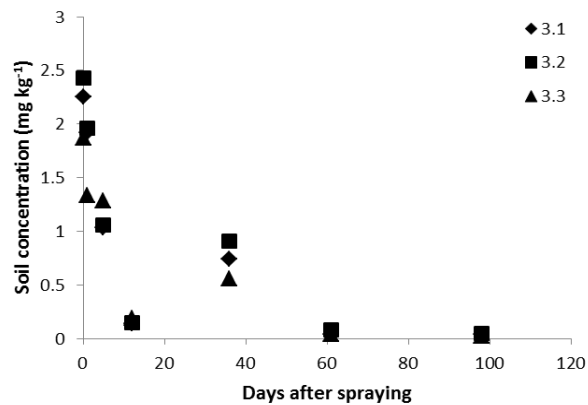
6. MAK



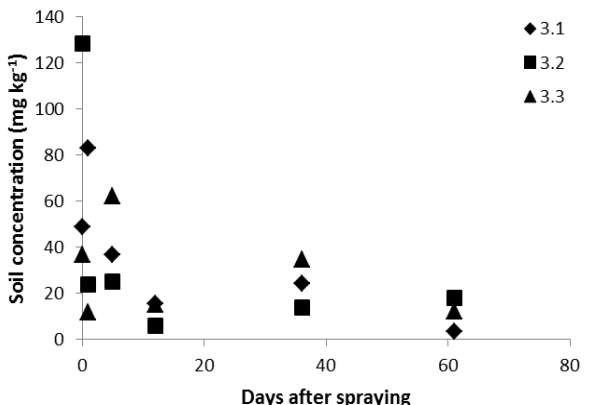
7. BUR



8. TUL

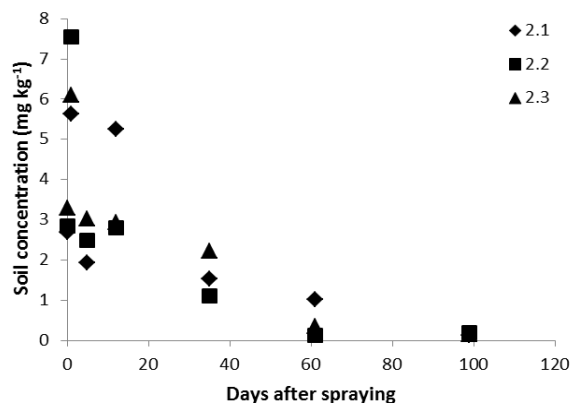


9. BUN

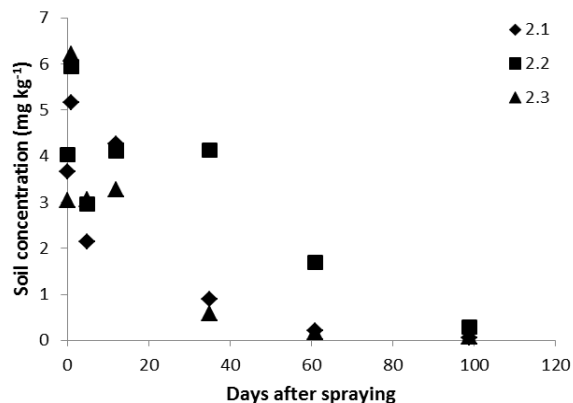


10. TRH

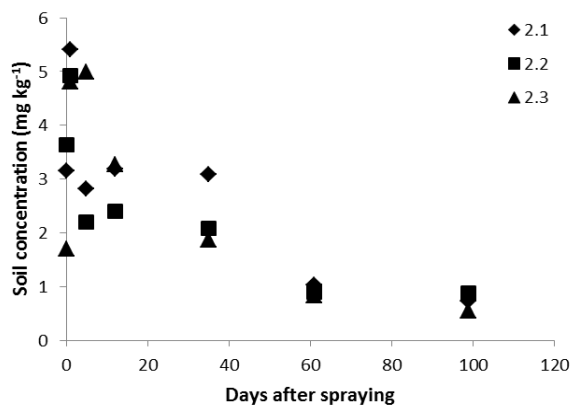
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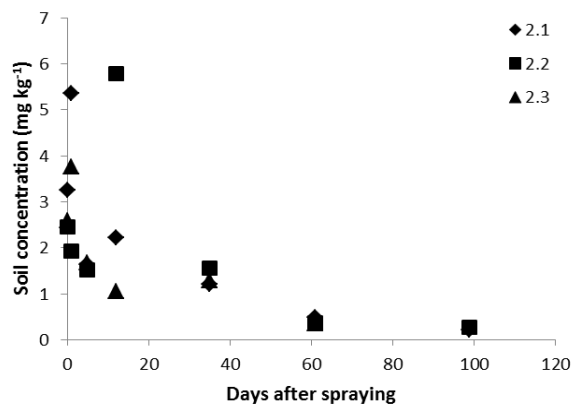
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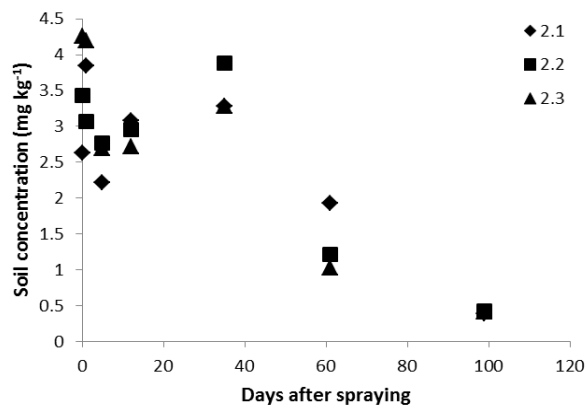
2. MGO



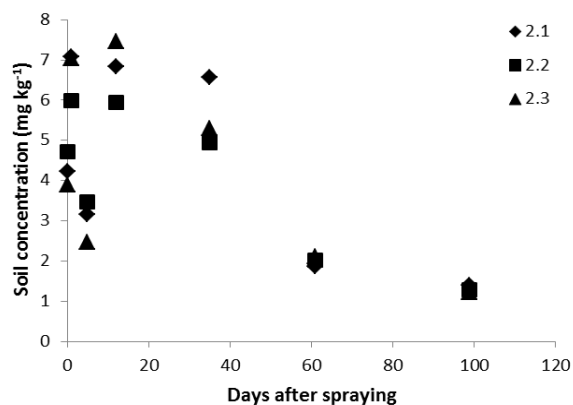
3. MT3



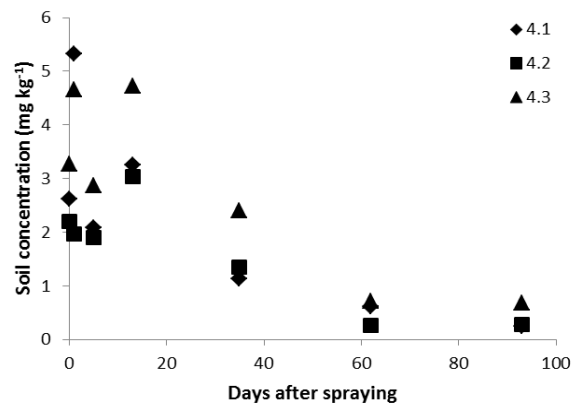
4. MT1



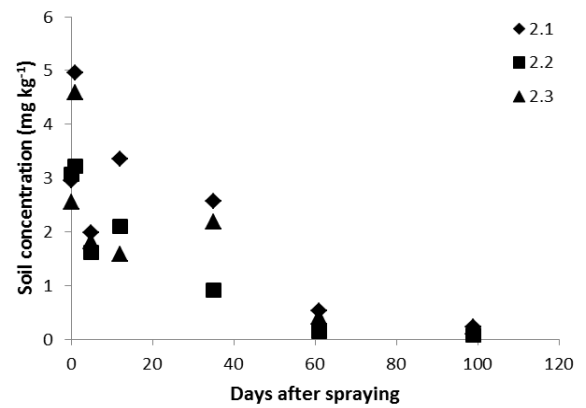
5. BRG



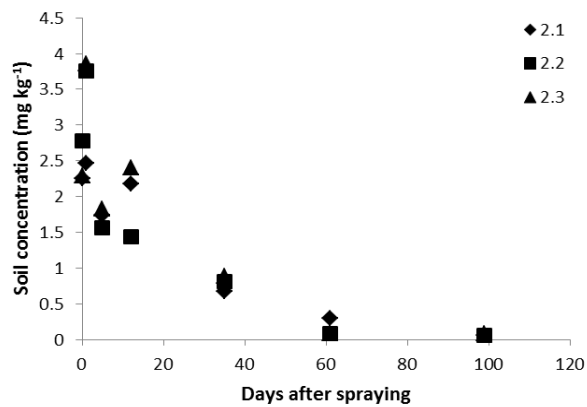
6. MAK



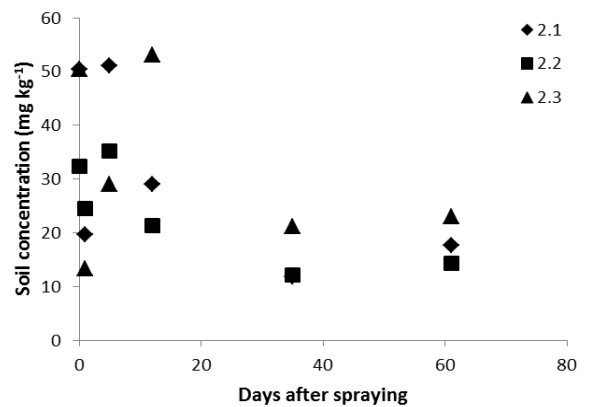
7. BUR



8. TUL

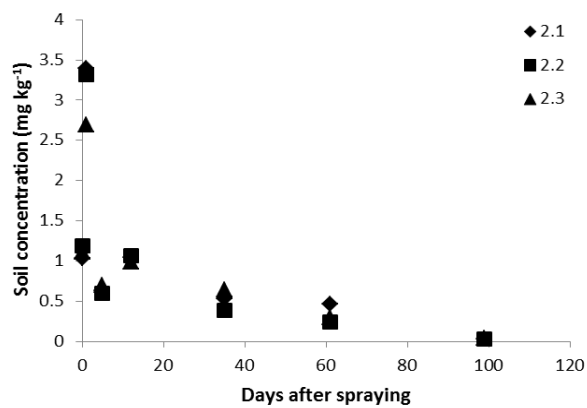


9. BUN

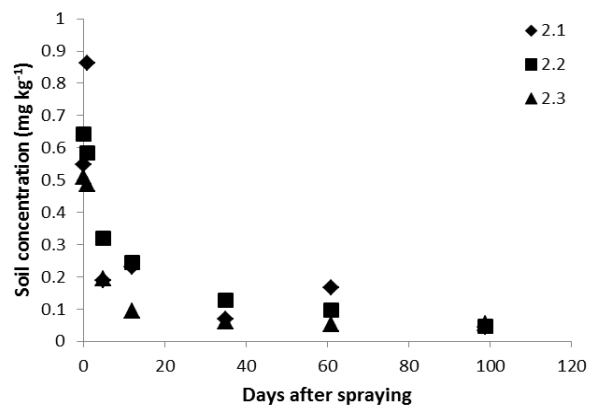


10. TRH

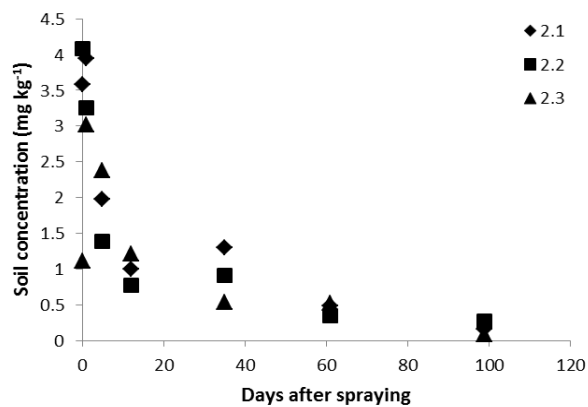
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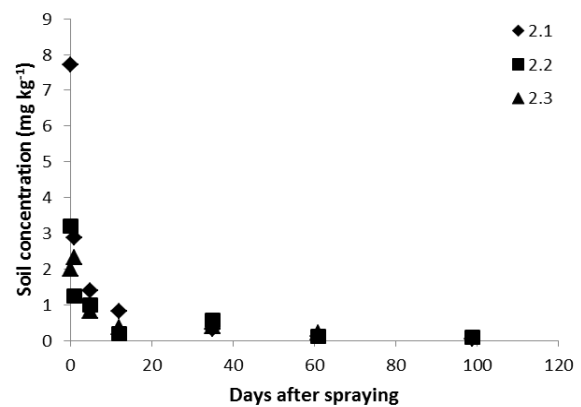
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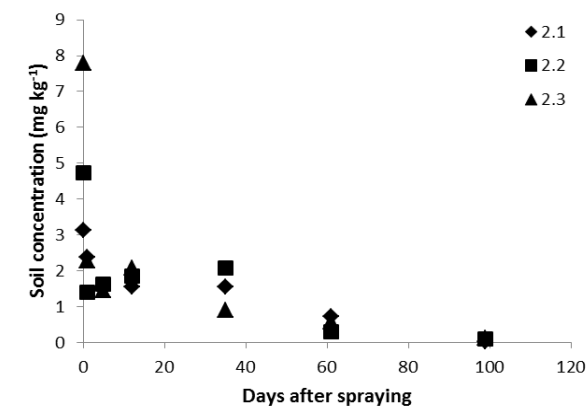
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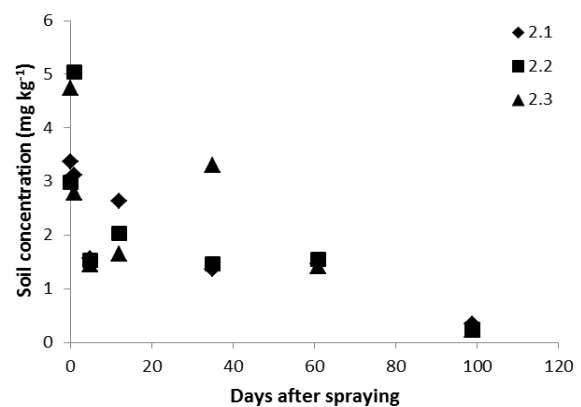
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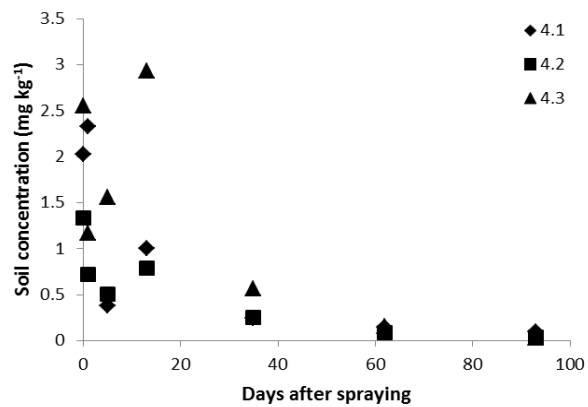
4. MT1



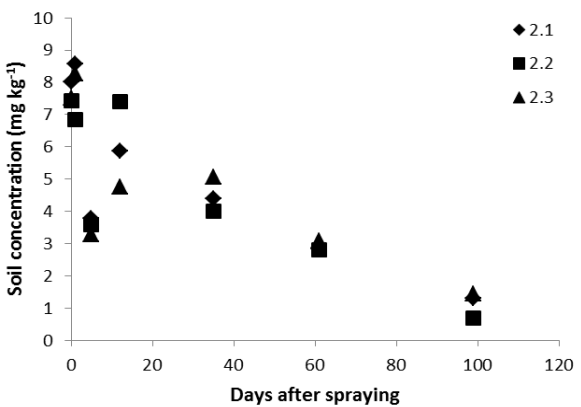
5. BRG



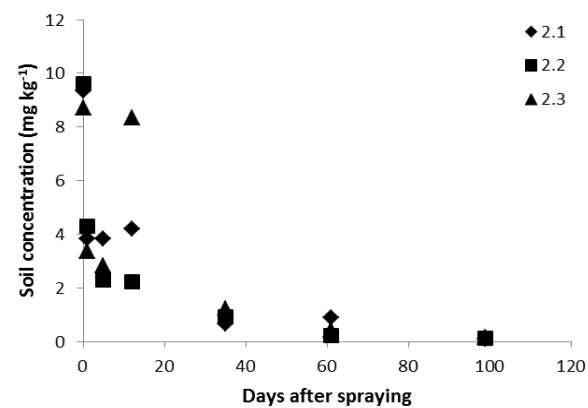
6. MAK



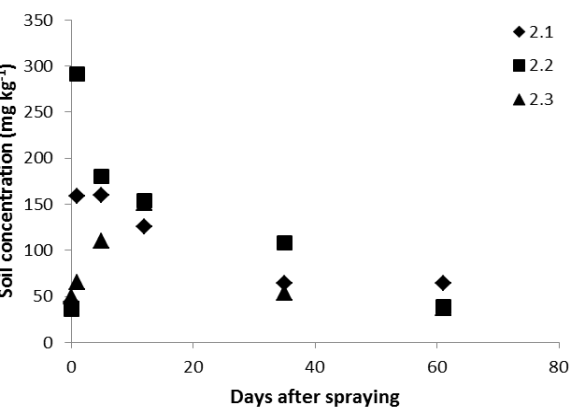
7. BUR



8. TUL

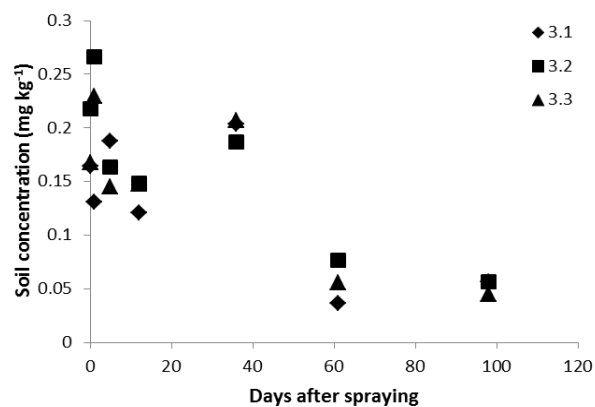


9. BUN

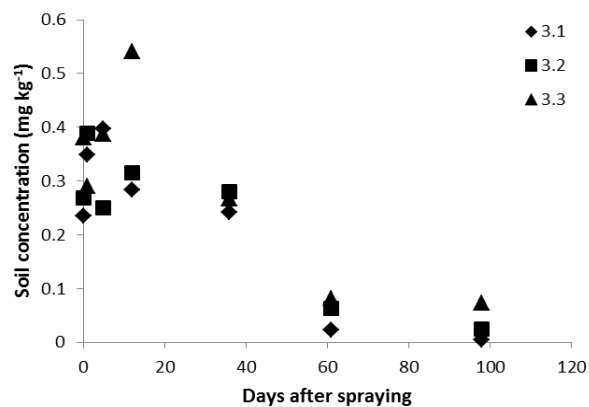


10. TRH

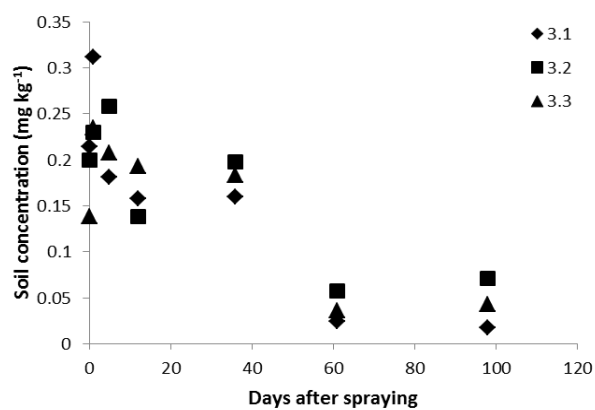
Imazapic



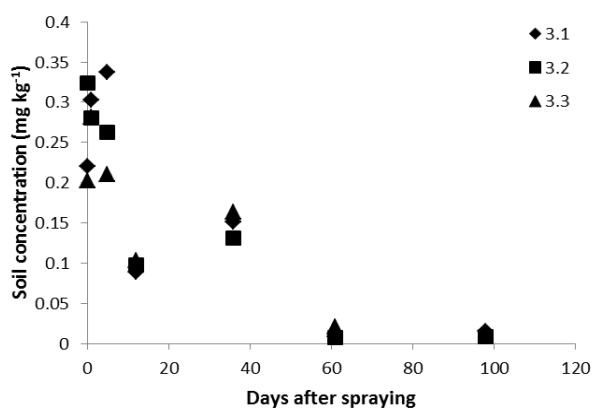
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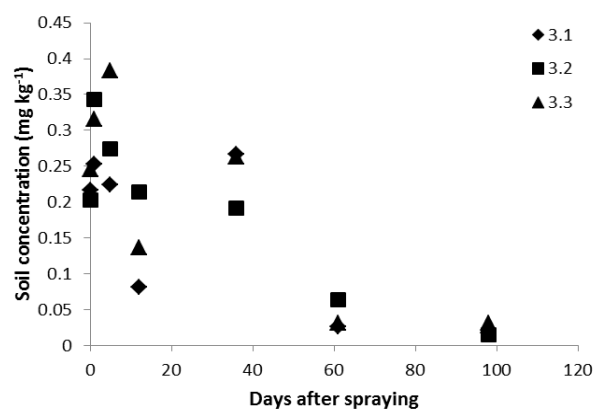
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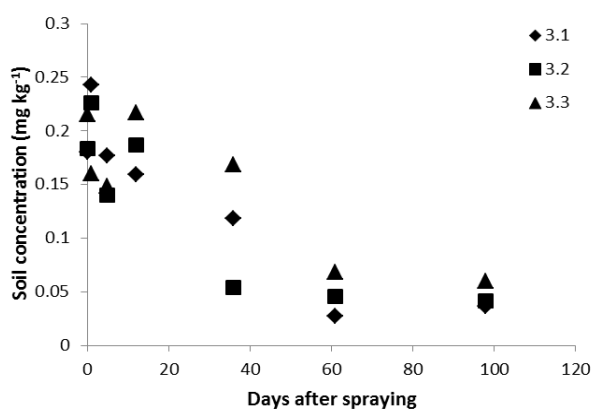
3. MT3



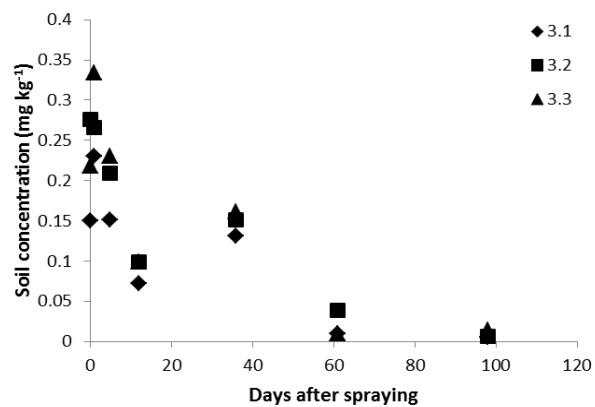
4. MT1



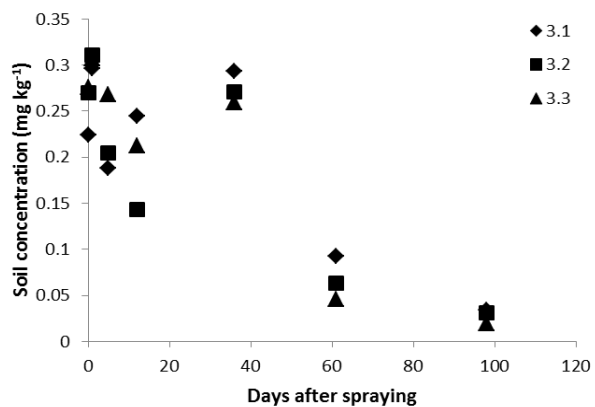
5. BRG



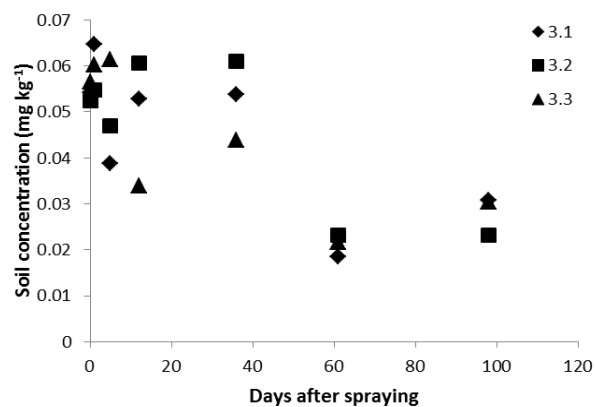
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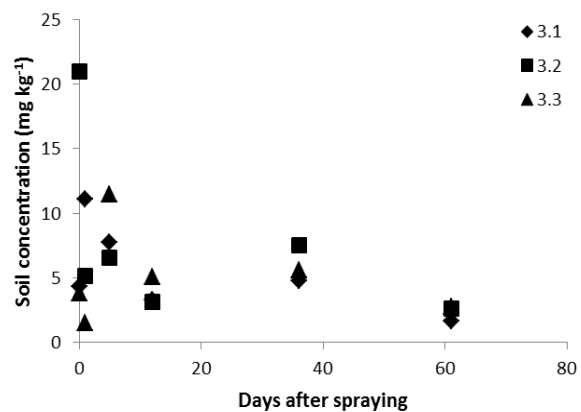
7. BUR



8. TUL

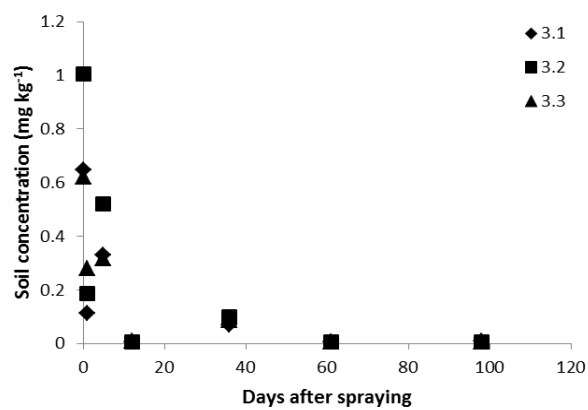


9. BUN

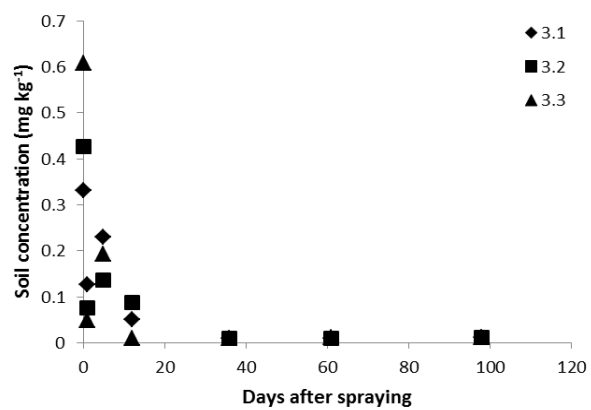


10. TRH

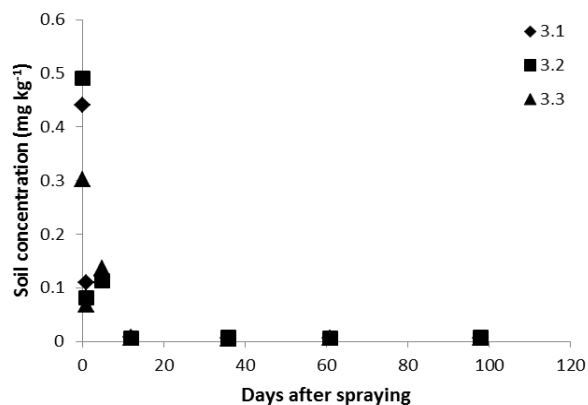
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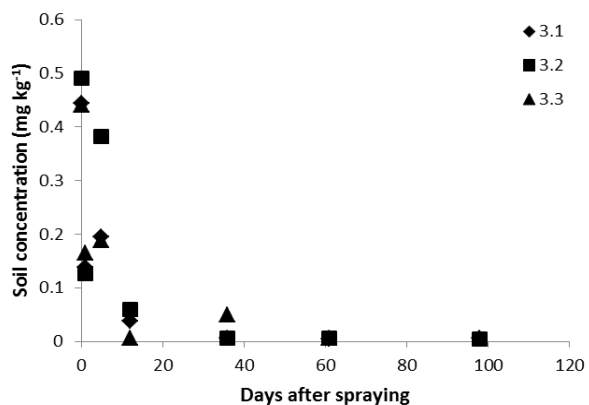
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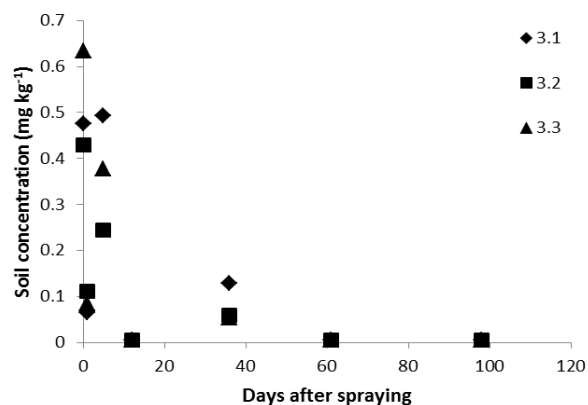
2. MGO



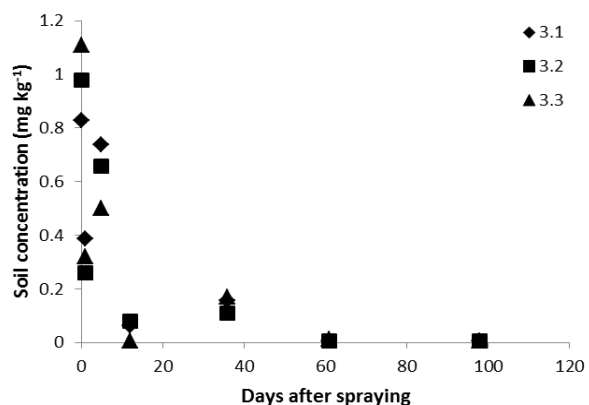
3. MT3



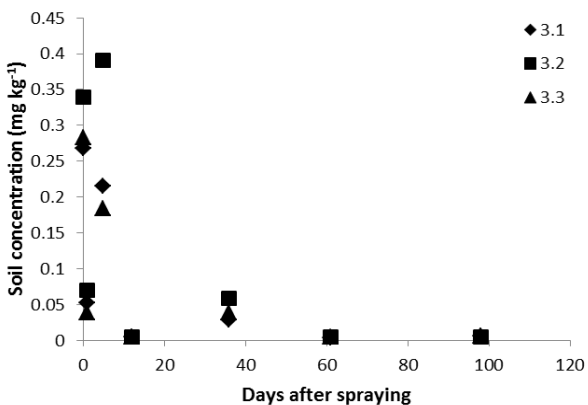
4. MT1



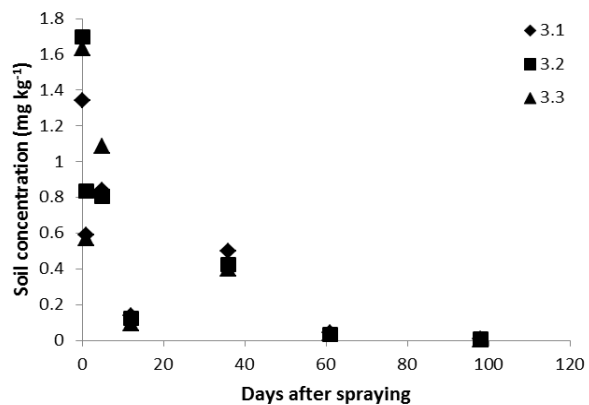
5. BRG



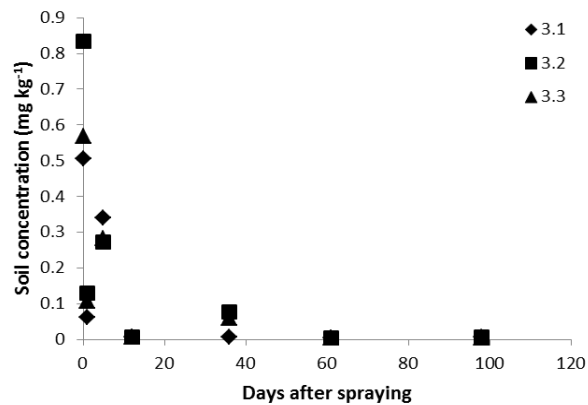
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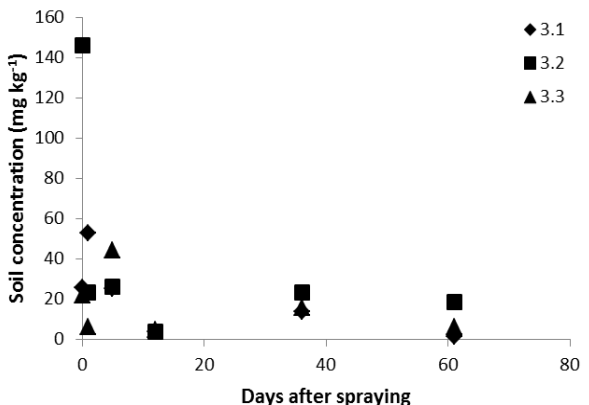
7. BUR



8. TUL

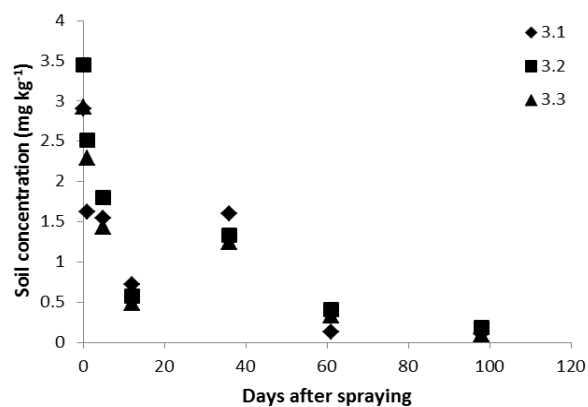


9. BUN

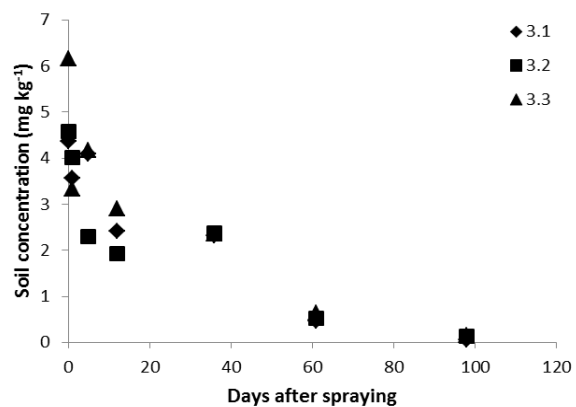


10. TRH

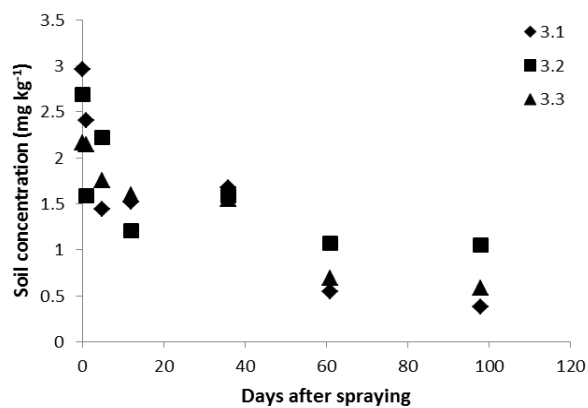
Metribuzin



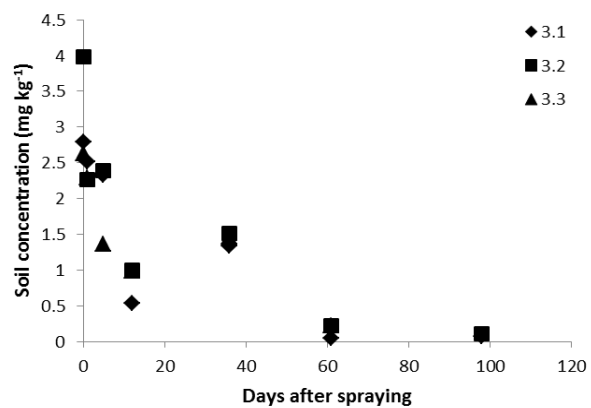
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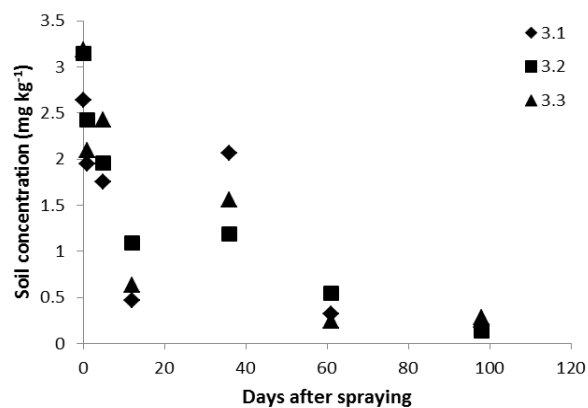
2. MGO



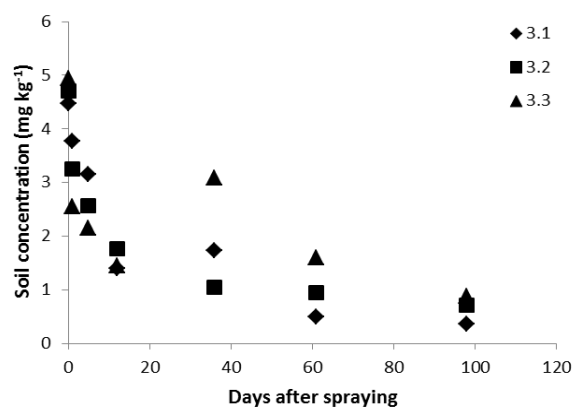
3. MT3



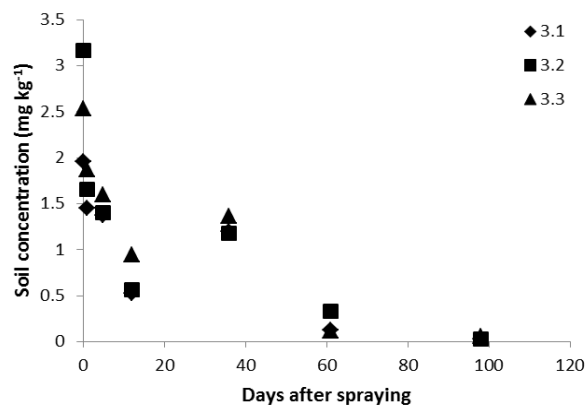
4. MT1



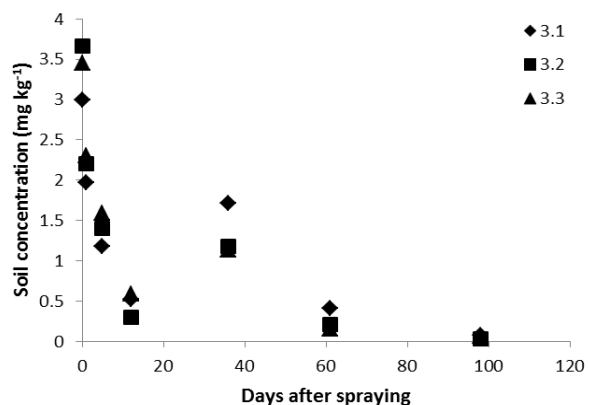
5. BRG



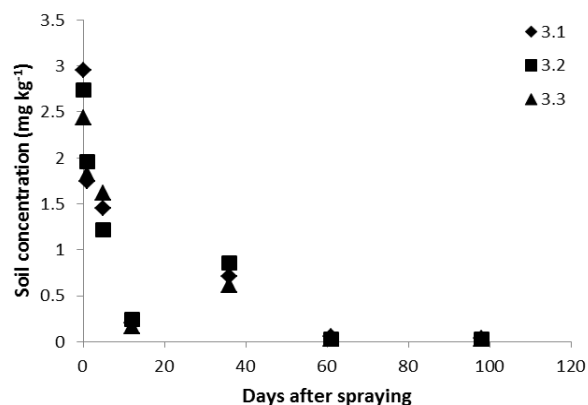
6. MAK



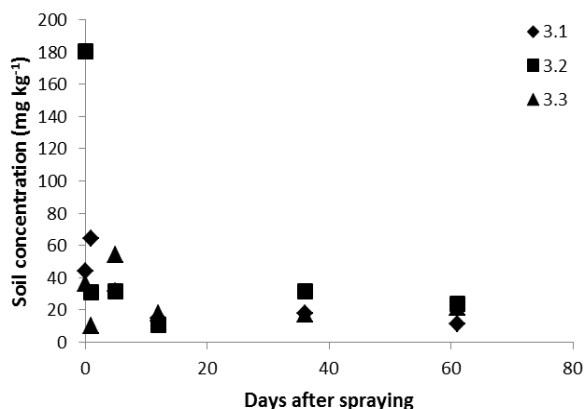
7. BUR



8. TUL

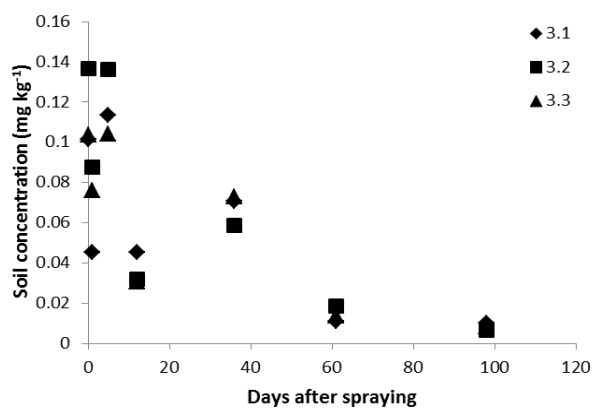


9. BUN

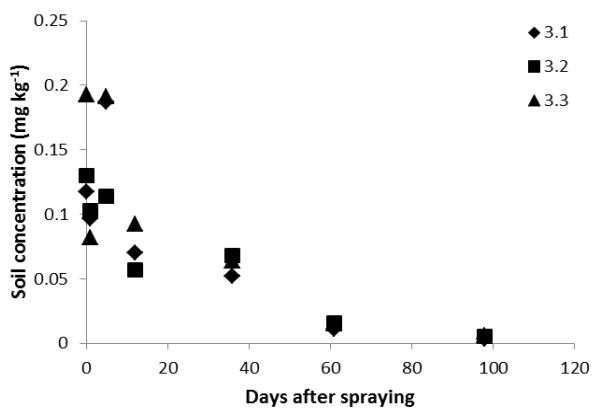


10. TRH

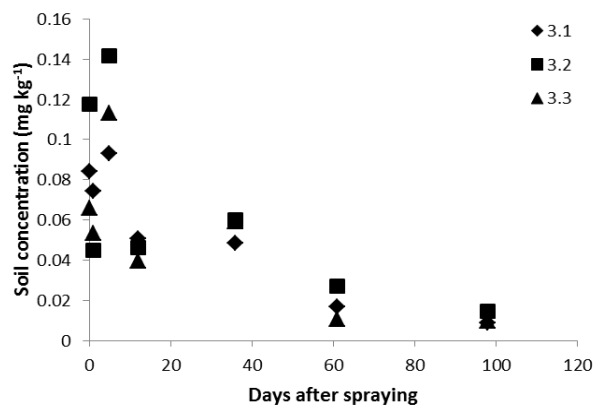
Trifloxysulfuron



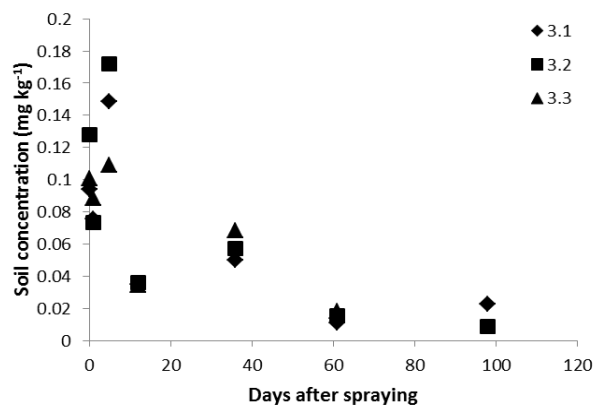
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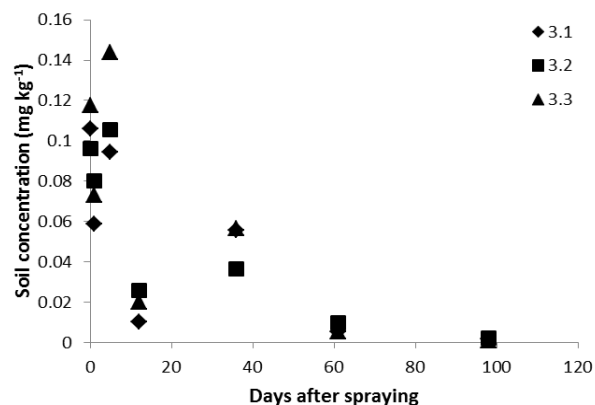
2. MGO



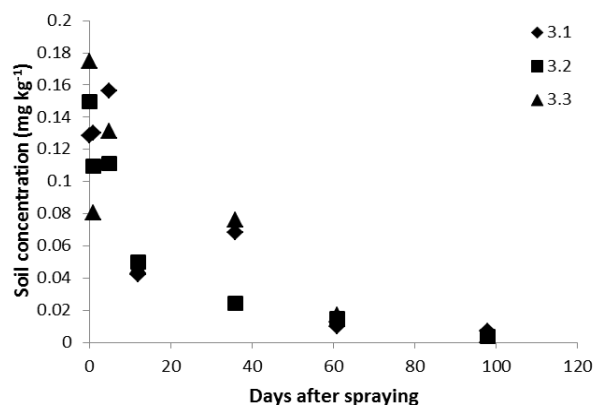
3. MT3



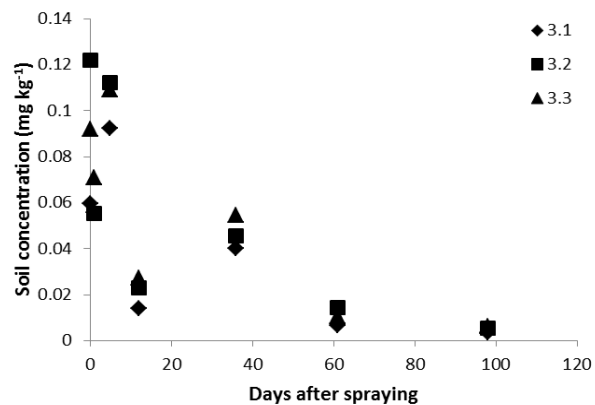
4. MT1



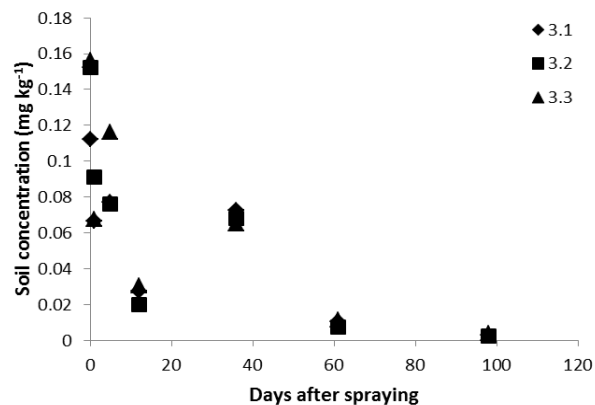
5. BRG



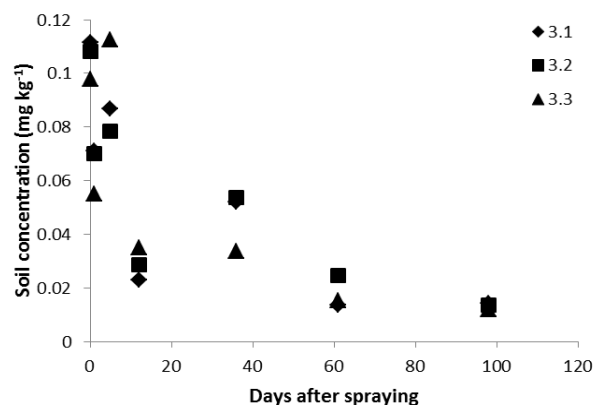
6. MAK



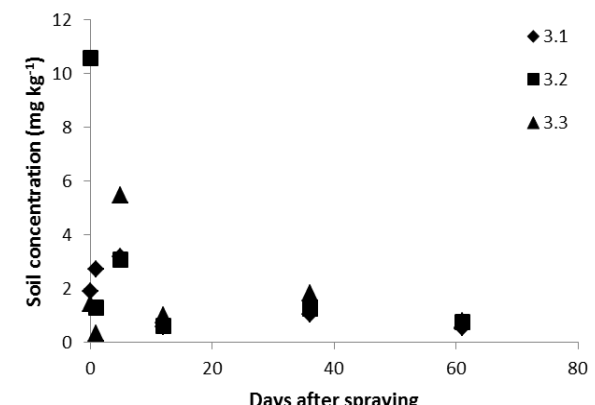
7. BUR



8. TUL

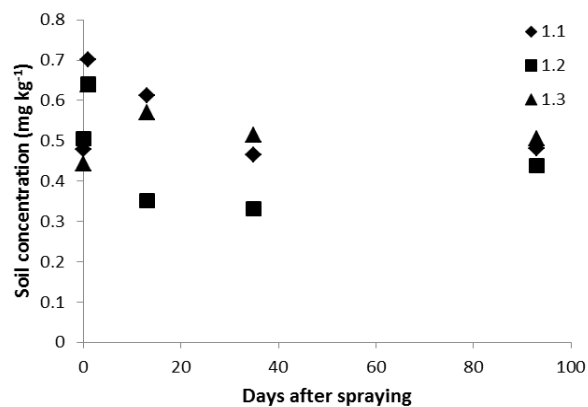


9. BUN

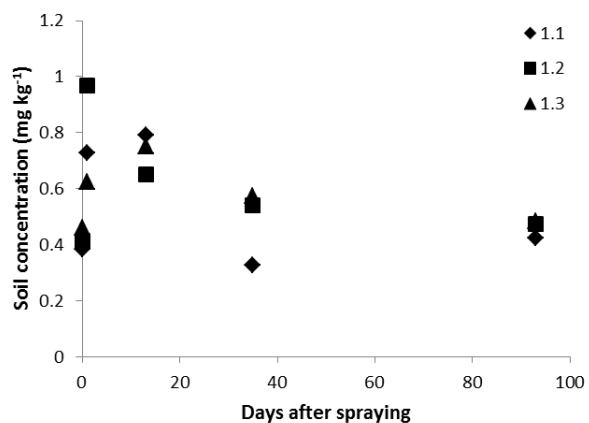


10. TRH

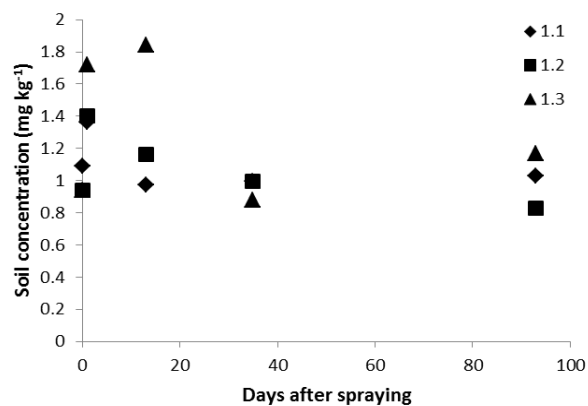
Paraquat



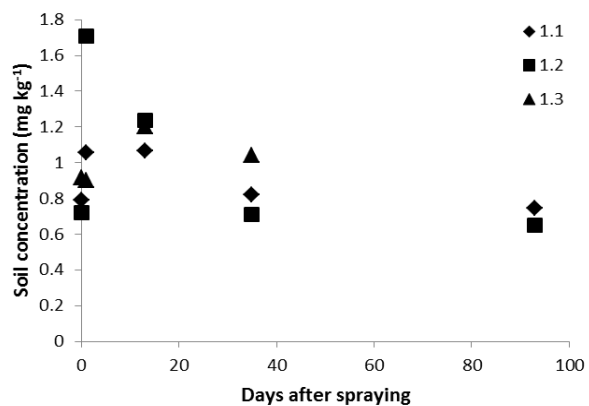
1. WAK



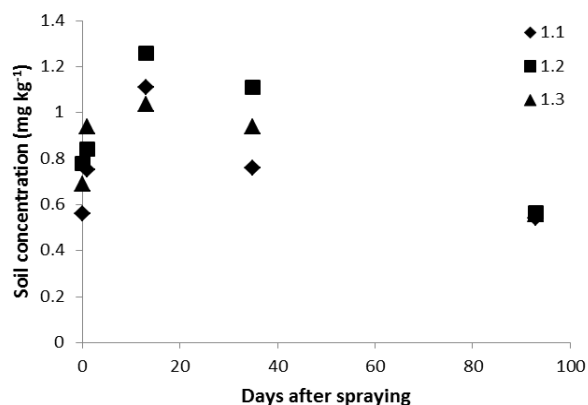
2. MGO



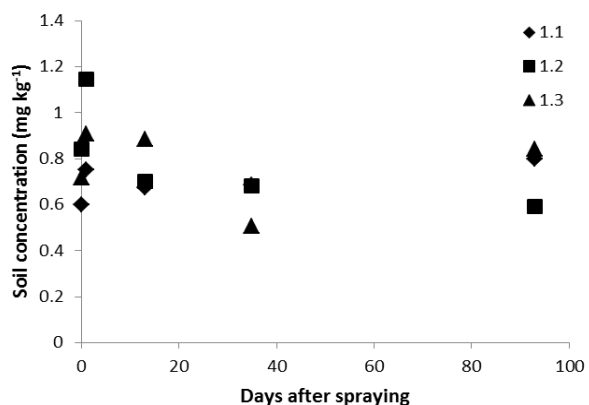
3. MT3



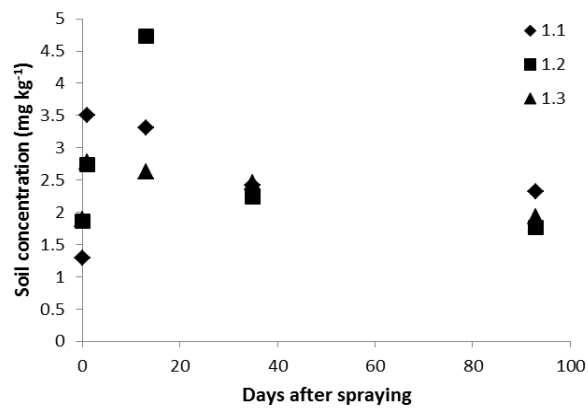
4. MT1



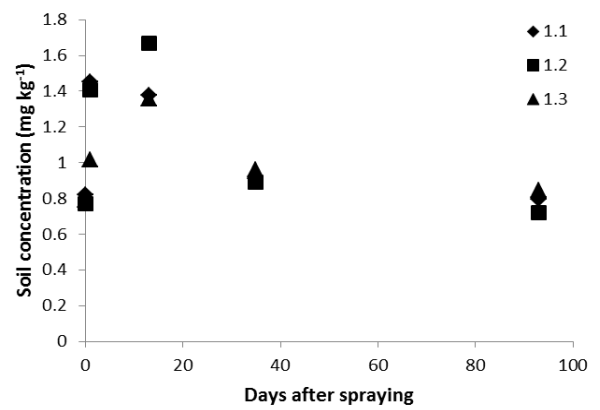
5. BRG



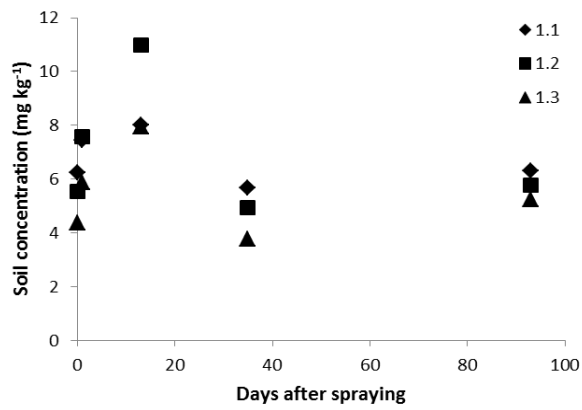
6. MAK



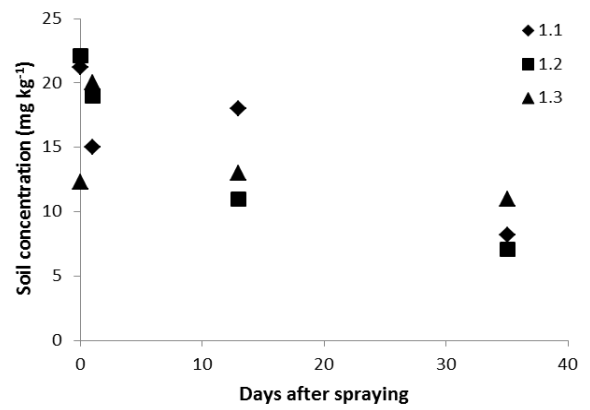
7. BUR



8. TUL



9. BUN



10. TRH

Appendix III

Field Dissipation Data

Silkwood

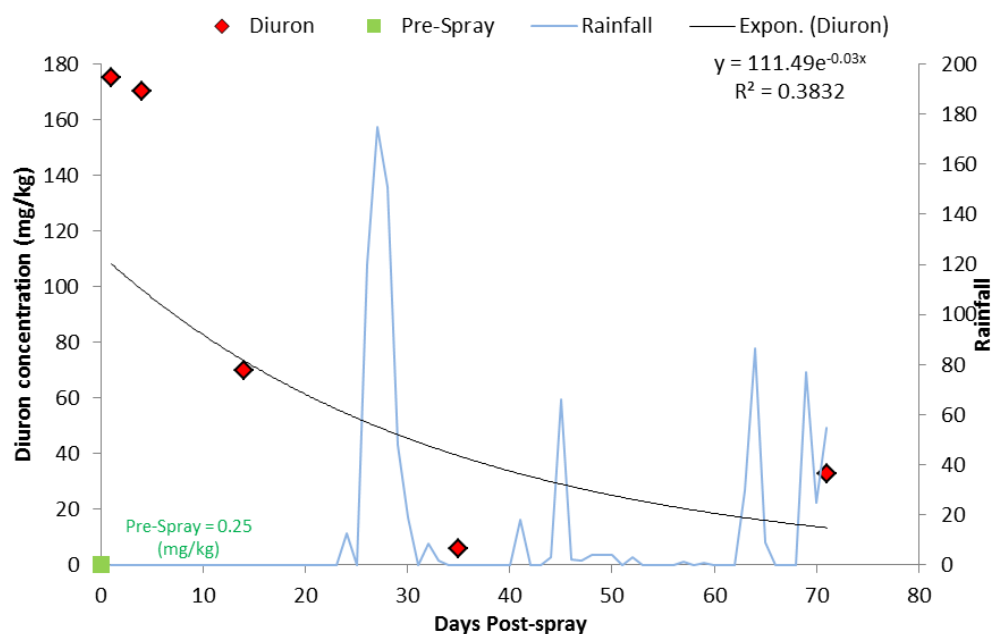


Figure 15. Concentration of diuron in soil after time of application from a Silkwood cane farm. Values represent the analysis of a bulked, homogenised sample from multiple sample points within the experimental plot. The fit for an exponential curve is shown.

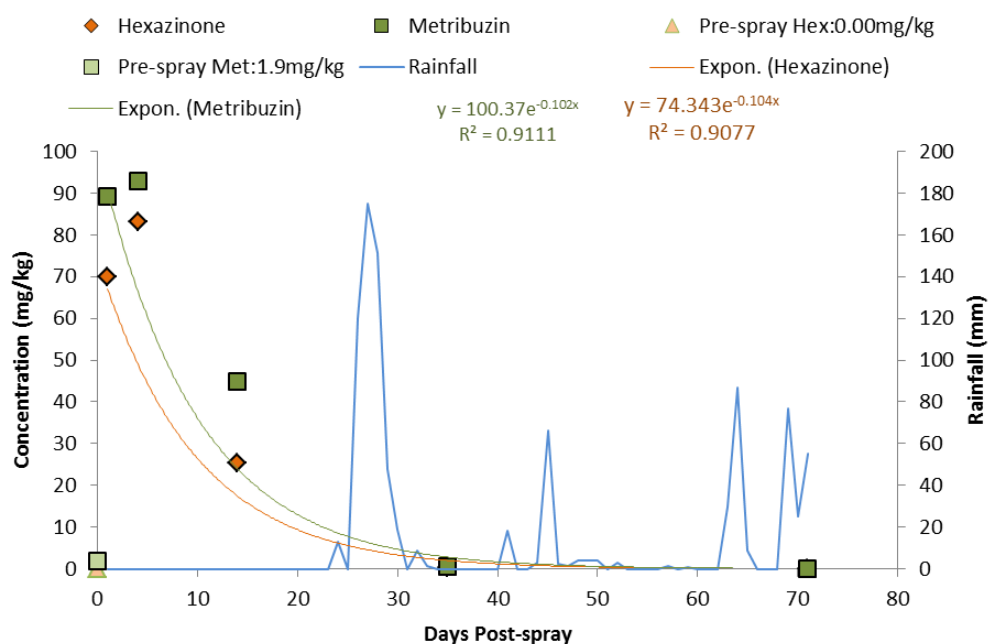


Figure 16. Concentration of hexazinone and metribuzin in soil after time of application from a Silkwood cane farm. Values represent the analysis of a bulked, homogenised sample from multiple sample points within the experimental plot. Lines show the exponential fit for each herbicide.

Herbert

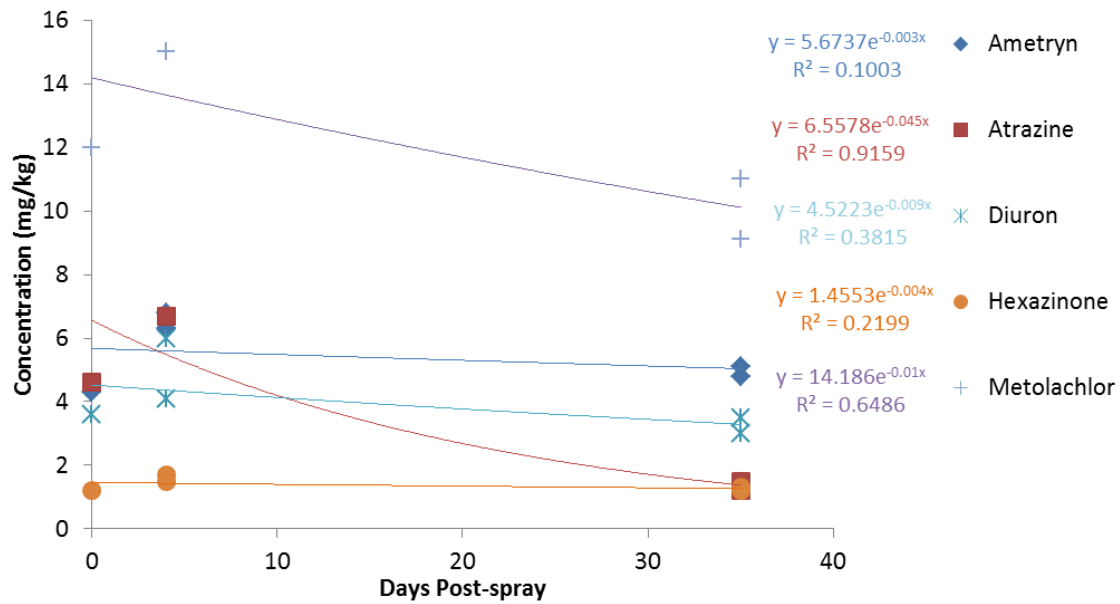


Figure 17. Concentration of herbicides in soil after time of application from bare soil from a Herbert cane farm. Values represent the analysis of a bulked, homogenised sample from multiple sample points within two replicate plots. Lines show the exponential fit for each herbicide.

Burdekin

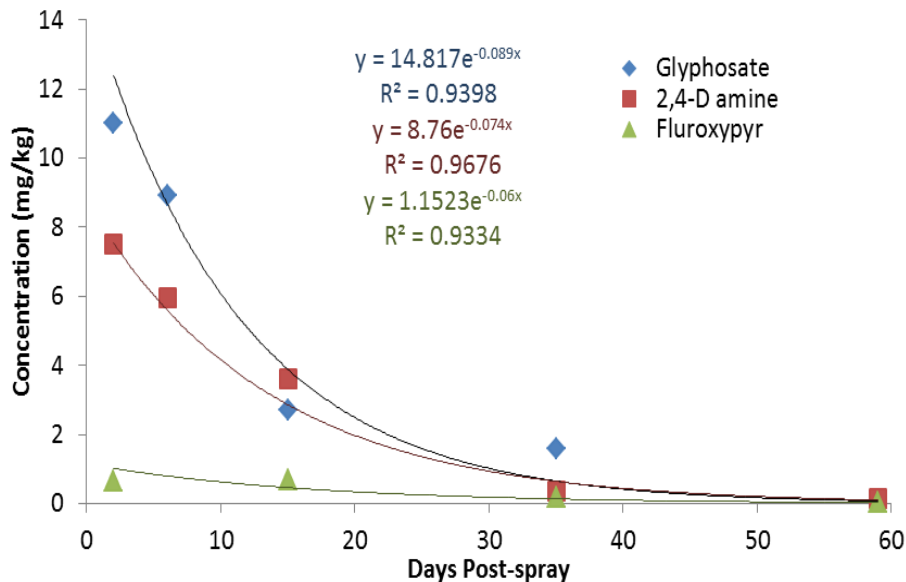


Figure 18. Concentration of herbicides applied in Mix1 in soil after time of application from the furrow of a Burdekin cane farm. Values represent the analysis of a bulked, homogenised sample from multiple sample points within the experimental plot. Lines show the exponential fit for each herbicide.

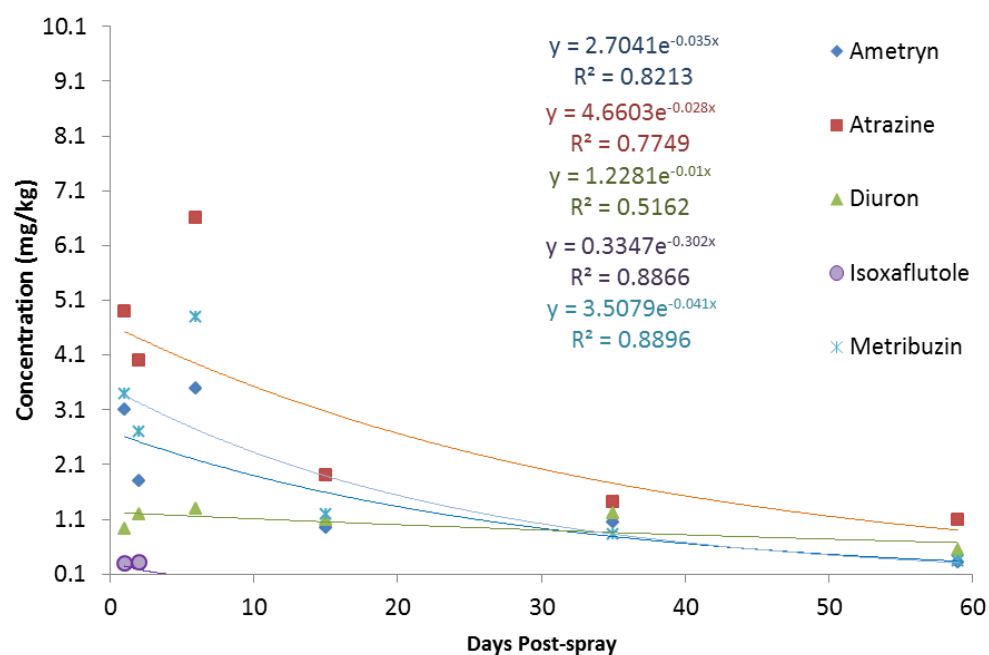


Figure 19. Concentration of herbicides applied in Mix2 in soil after time of application from the furrow of a Burdekin cane farm. Values represent the analysis of a bulked, homogenised sample from multiple sample points within the experimental plot. Lines show the exponential fit for each herbicide.

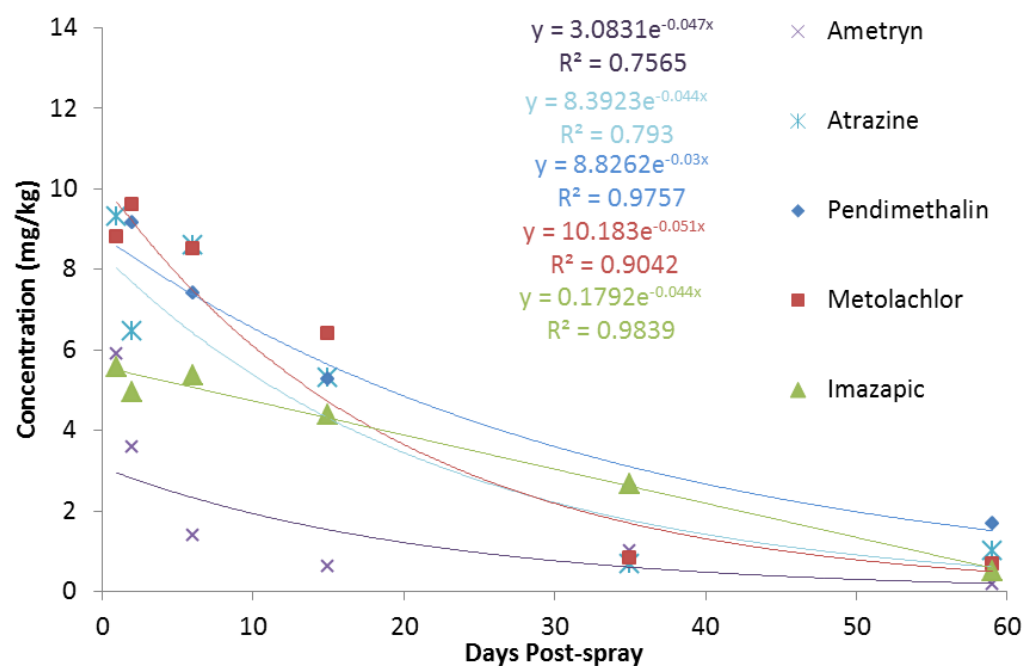


Figure 20. Concentration of herbicides applied in Mix3 in soil after time of application from the furrow of a Burdekin cane farm. Values represent the analysis of a bulked, homogenised sample from multiple sample points within the experimental plot. Lines show the exponential fit for each herbicide.

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