The Tasmanian River Catchment Water Quality Initiative

Report on pesticide fate and behaviour in Tasmanian environments

Tasmanian Institute of Agricultural Research
University of Tasmania

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Cover: Garth Oliver with spray equipment at Huon trial site.

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Glossary of terms and acronyms

ai	Active ingredient or 'active'
ASE	Accelerated Solvent Extraction
BOM	Bureau of Meteorology
CSIRO	Commonwealth Scientific and Industrial Research Organisation
FT	Forestry Tasmania
K_d	A parameter representing binding of a pesticide to soil. In PIRI Kd is estimated as percentage organic carbon multiplied by the K_{oc}
K_{oc}	Partition coefficient between soil organic matter and water; pesticides with a low K_{oc} are more likely to move with surface water than pesticides with a high K_{oc}.
K_{ow}	Partition coefficient between *n*-octanol and water.
PIRI	CSIRO's Pesticide Impact Rating Index assessment tool
PPB, ppb	Parts per billion i.e. µg/L or µg/kg
PPM, ppm	Parts per million i.e. mg/L or mg/kg
TSS	Total suspended solids

Keywords: Pesticide, soil, half-life, sorption, leaching, PIRI

Executive summary

Six pesticides – simazine, glyphosate, alpha-cypermethrin, clopyralid, MCPA and sulfometuron methyl – have been studied to examine dissipation rates in the field, leaching in the field and sorption to various soil types in the laboratory including sorption to some fractions of the soils.

A range of different soils – Ferrosol (2), Vertosol (2), Kurosol, Dermosol – covering a broad spectrum of organic, mineral and chemical properties were selected for the study. The trial sites and soils were chosen to represent a wide range of climatic settings and geographical areas.

Standard field trials were conducted over two seasons with the pesticides applied to cultivated soils in an attempt to examine dissipation under Tasmanian conditions. The resulting data were then used by CSIRO to modify the Pesticide Impact Rating Index software for Tasmanian conditions (PIRI-Tas). Assessment of the sorption of pesticide to the soils was undertaken in the laboratory and data were also then used to modify PIRI.

Sorption coefficients and half-life values for the target Tasmanian soils varied from the previously published range used in PIRI, highlighting the value of local validation of key input data in model development. In addition, insight into the processes controlling the environmental fate of the pesticides studied was gained, and areas where further research is required to allow ‘fine tuning’ of pesticide fate predictions were identified.

The key findings include a wide range of sorption coefficients (K_d) for each pesticide, most varying over an order of magnitude depending on soil type. Organic matter was strongly correlated with sorption of all pesticides. This included glyphosate despite organic matter not being a known sorption site for this pesticide. Soil pH improved the correlations for MCPA, clopyralid, sulfometuron and simazine, but not glyphosate. We recommend that soil pH be considered in future pesticide behaviour models to improve predictive resolution. Even the normalised sorption coefficient K_{oc} was found to vary over one order of magnitude for sulfometuron methyl and by a factor of four with MCPA. Several pesticides were well outside the pre-project PIRI values (e.g. clopyralid, MCPA and simazine) and these pesticides have significantly modified risk profiles in the new PIRI-Tas version.

Fractionation of three of the field soils was undertaken to examine the role of the mineral vs. organic components on sorption for MCPA and sulfometuron methyl. In laboratory studies for MCPA, organic matter removal significantly reduced sorption of the soils tested and the reduced sorption coefficients were strongly negatively correlated to soil pH. For sulfometuron methyl, similar reductions in sorption occurred, though not to the same extent on the Vertosols, and there was no correlation with soil pH for the treated soils. More work on fractionation is required to resolve the controlling factors on sorption but soil pH and organic matter appear to be key factors for most pesticides studied.

The mean half-lives for both sulfometuron methyl and simazine tripled from spring 2006 to autumn 2007 trials, while glyphosate nearly doubled. This reflects the cooler conditions over the autumn–winter trials. Clopyralid and MCPA had mixed results and they appear to be more affected by soil moisture and leaching in combination with temperature and other factors such as organic matter and soil pH levels. Alpha-cypermethrin showed no changes with season which may relate to strong sorption to soils and perhaps the greater role of photodegradation in field dissipation.

Leaching was of a very limited nature in the spring 2006 trial with the exception of simazine at Northdown and Pyengana where approx 1% of applied pesticide leached to the 20–30 cm and 30–40 cm levels respectively. There was also minor leaching of MCPA. Leaching increased significantly in the autumn 2007 trial as might be expected due to the wetter and cooler winter conditions at most sites. Minor leaching of simazine occurred at Pyengana, the Unifarm (Kurosol only) and Northdown. In the autumn 2007 trial there was more significant leaching of clopyralid at both Pyengana and Northdown. The Unifarm Vertosol was resistant to leaching of all pesticides in both seasons.

Simazine’s (triazine) relatively high application rates (6 kg/ha), long autumn–winter half-life, low and variable sorption and demonstrated leaching potential make it the most significant environmental risk for water quality.

Variations in sorption with soil pH are significant as demonstrated by wide variations in the normalised sorption coefficient K_{oc} for certain weakly adsorbed pesticides e.g. sulfometuron and MCPA. This may partly explain regional and industry (forestry vs. agriculture) variations in environmental risk.

The Vertosols represented a special environmental case with pesticides having long half-lives in these soils, relatively weak sorption coefficients and limited leaching behaviour. This means that Vertosols retain high amounts of pesticide at the soil surface where runoff or topsoil erosion could lead to movement toward surface waters.

More research on controlled leaching of simazine, clopyralid and MCPA in a Tasmanian context is required along with data on the bioavailability (desorption) of pesticides like glyphosate, simazine and MCPA from soils and sediments.

Table of Contents

List of Figures

List of Tables

1 Introduction

This report documents field trials and laboratory experiments undertaken to determine pesticide half-lives, leaching and sorption behaviour in a range of Tasmanian soils and environments. The six pesticides were chosen as they represent a wide range of chemical families: triazines (simazine), glycines (glyphosate), pyrethroids (alpha-cypermethrin), sulfonylurea’s (sulfometuron methyl), phenoxys (MCPA) and picolinic acids (clopyralid). These pesticides are in common use in the forestry and agricultural sectors. Several are of current public concern; the list also met the criteria of the project’s consultative committee, which comprised relevant industry, community and research bodies. Five soil types were chosen representing the major cropping and forestry soils across the key drainage basins of the State (see Appendix A).

Field trials across five soil types were undertaken to measure half-lives and leaching behaviour of the six selected pesticides. Beginning in late spring 2006 and mid autumn 2007 the trials were run in order to compare seasonal, soil type and climatic effects on pesticide behaviour. Both half-life trials were sampled at 0, 1, 3, 7, 14, 28, 56, 98 and 180 days after pesticide application. Samples were ground, sieved and sub-sampled before being stored in separate freezers to ensure integrity and then extracted and analysed using state-of-the-art instrumentation.

Two half-life data sets have been established for the six pesticides at each of the five sites across the state. They indicate significant variations from the mean values used in the pre-project version of PIRI and the data generated has been incorporated in the new version of the model to reflect Tasmanian conditions (Kookana and Correll, 2008).

Drill cores were taken from both trials to measure leaching on day 56 and day 180 for the pesticides clopyralid, sulfometuron methyl, MCPA and simazine to a depth of at least 60 cm at four of the sites. The Huon site proved too rocky to extract cores. Extraction and analysis of the cores from day 56 were undertaken on both the spring 2006 and autumn 2007 trials. Very low levels of pesticide in the soils meant analysis of the 180 day samples was not required. The samples remain in freezer storage at the University of Tasmania.

Fractionation studies involved the removal of organic matter from three soils and re-measurement of sorption coefficients of two pesticides (MCPA and sulfometuron). This allowed the measurement of the sorption of the mineral component of the soil and correlation with soil pH values.

2 Literature review

2.1. Sulfometuron methyl review

Sulfometuron methyl (methyl 2-[[[[(4,6-dimethyl-2-pyrimidinyl) amino] carbonyl] amino] sulfonyl] benzoate) is in the sulfonylurea chemical family. It is used for pre- and post-emergent broadleaf and grass weed control in forestry operations and in industrial lands (Vencill 2002).

Sulfometuron methyl is degraded slowly by microbial action and in acidic soils by hydrolysis mitigated 'cleavage of the sulfonylurea bridge' (Vencill 2002). There is insignificant photodegradation under field conditions (Vencill 2002). Reports indicate that the overall rate of sulfometuron methyl degradation in soil depends on pH and soil moisture content. Increased soil moisture content results in increased degradation rates, but only by approximately 10% (Commonwealth of Massachusetts 2003). The soil half-life is reported as four weeks, with longer times in colder conditions. However, studies in Delaware and Oregon suggest a minimum of six weeks is more typical and half-lives can be up to one year in cooler locations. A more realistic estimate of half-life may be closer to two months (Commonwealth of Massachusetts 2003). Vencill (2002) also raises the issue of significantly slower degradation during the cooler periods of the year.

The pH environment also affects dissipation. The hydrolysis half-life at pH 2 and pH 5 is 100 and 475 hours respectively. At neutral or basic pHs, sulfometuron methyl is stable to hydrolysis (Vencill 2002).

Sulfometuron methyl is more strongly adsorbed to soil as the pH decreases, and as organic matter increases (Commonwealth of Massachusetts 2003). Thus it is more mobile in high pH soils with lower levels of organic matter.

Sulfometuron methyl has a pKa of 5.2 at 25 °C (Beyer *et al.* 1987). As with other acidic herbicides, sulfometuron has the ability to ionize in aqueous solutions to form anionic species. It is for this reason that the pH conditions control sulfometuron methyl's solubility in water, rate of hydrolysis, and partition coefficients, and hence its behaviour in soil and water (Michael *et al.* 2006). This is quite important, as forest environments in Tasmania range from acidic to alkaline, with pH values that range above and below sulfometuron's pKa of 5.2. The sulfometuron methyl molecule becomes hydrophobic when the pH drops below its dissociation constant (pKa) of 5.2, which obviously leads to reduced water solubility (Michael *et al.* 2006). Sulfometuron has a water solubility of 70 mg/L at pH 7 and 8 mg/L at pH 5 and is also soluble in acetone, cyclohexane and methanol (Kamrin 1997).

Published K_d values range from 0.71 to 2.85 and K_{oc} of 78 mL/g (range from 61 to 122) and is thus weakly sorbed by soil organic matter and is moderately mobile (Vencill 2002; Commonwealth of Massachusetts 2003).

Soil leaching column studies using four different soils indicate a moderate to moderately high mobility pesticide. The mobility increases as soil pH increases and soil organic matter declines (Vencill 2002).

Implications of using sulfometuron methyl in Tasmania are:

1. There is seasonal variation in degradation rates with the likelihood of significantly slower degradation in winter than occurs in other states.
2. More rapid degradation occurs in acidic soils, which dominate in many forestry areas.
3. There is increased degradation in wetter conditions; for example, wetter regions (i.e. west and north-west regions, during ‘autumn breaks’, wetter than average springs or where irrigation follows application).
4. There is greater leaching potential in slightly acidic to neutral soils with low organic carbon levels; for example, neutral soils from windblown sands.

2.2. Simazine review

Simazine (6-chloro-N,N’-diethyl-1,3,5-triazine-2,4 diamine) is a member of the triazine family. It is a residual herbicide applied at rates of 1–6 kg/ha and is used for the control of broadleaf and grass weeds in berry, nut, olive and fruit tree crops, and in hardwood and softwood forestry (Vencill 2002).

Microbial degradation is the key dissipation mechanism in soils, although hydrolysis is important in acidic and waterlogged conditions (Vencill 2002). Simazine has a mean half-life of 60 days (Vencill 2002). However, Tomlin (1994) has a reported half-life ranging from 70–110 days. Simazine is more persistent under high pH conditions. It is little affected by photodegradation or volatilisation (Tomlin 1994), though Vencill (2002) indicates moderate photodegradation if surface-applied in dry seasons. Field trials in the USA have shown half-lives ranging from 60 days in Florida to 186 days in cooler Minnesota. The Forest Herbicide Management Group (2000) has shown similar trends for atrazine in Australia where trials in subtropical Queensland provided half-lives of 12 days and those in Tasmania 140 days.

Average K_{oc} is 130 mL/g (range *ca.* 100–150) and the K_d range 0.5–4.5 depending on clay content and organic matter levels (Vencill 2002). Higher soil organic matter and clay content soils require higher application rates to maintain efficacy due to stronger sorption.

There is limited leaching potential under field conditions reported by Vencill (2002). This is supported by Tomlin (1994) who reports leaching is limited by low water solubility (400 mg/L at 20 °C)(Tomlin 1994).

Implications for simazine use in Tasmanian conditions are as follows:

1. It is used at quite high rates per hectare and has a moderately long half-life.

2. The sorption coefficient ranges over an order of magnitude, meaning soil type will significantly affect chances of leaching and desorption.
3. Degradation may vary significantly with season due to more rapid photodegradation and microbial decay in warmer months.
4. It has longer persistence on neutral soils and in colder conditions.

2.3. Glyphosate review

Glyphosate (N-[phosphonomethyl] glycine) is a non-selective systemic herbicide which is foliar adsorbed. It is used to control grasses, sedges, broad-leaved weeds and deep-rooted perennials (Tomlin 1994). It is one of the most widely used herbicides in the world.

Degradation is predominantly by microbial activity with 10–70% of applied glyphosate converted to CO_2 during one growing season (Vencill 2002). Reported half-lives vary from 1–180 days, with a half-life of 3 days for the trimesium salt and <*ca.* 60 days for the acid (Tomlin 1994). However, Vencill (2002) states that the typical half-life for glyphosate is 47 days, though laboratory half-lives are given as <25 days (Vencill 2002). The very wide range in quoted values for half-life may relate to problems associated with adequate extraction efficiency as the glyphosate is very strongly bound to iron oxides and hydroxides in soils (see below).

Soil sorption is very high, with a mean K_{oc} of 24 000 mL/g, while K_d values ranged from 324 for a loamy sand to 600 for silty clay loam (Vencill 2002). However, glyphosate has a very low K_{ow} of 26 x 10^{-5}, indicating it is very weakly bound to organic matter. Sorption correlates with the number of phosphate sorption sites (Vencill 2002). Because the pesticide is strongly adsorbed to soil, it rapidly becomes immobile following application to soils (Vencill 2002).

Implications for glyphosate use in Tasmanian conditions are:

1. Sorption will vary widely due to the range in soil mineralogy.
2. Microbial degradation is dominant and therefore seasonal variations in half-life should be expected.
3. Leaching is unlikely.

2.4. Clopyralid review

Clopyralid (3,6-dichloro-2-pyridinecarboxylic acid) is a weakly acidic herbicide commonly used to control broadleaf weeds in crop production, pastures and tree crops (Vencill 2002).

Clopyralid is degraded by microbes and non-microbial decay does not occur (Vencill 2002). Therefore, environmental factors that affect microbial activity, such as soil moisture and temperature, also affect the degradation rates. Clopyralid has an average half-life of 40 days reported across the USA but with a range of 12–70 days. Tomlin (1994) indicates laboratory-based half-lives of 10–56 days. Dow AgroSciences lists 25 days as the typical aerobic soil half-life for clopyralid (1998). The range of published half-lives is 8–250 days (from 19 soils) though it is less than 69 days in 95% of the soils studied. Shorter half-lives occur in warm, moist soils and at lower application rates (Dow AgroSciences 1998). Temperature significantly affects degradation as shown by North American and European studies indicating average half-life of 64 days under cooler temperature conditions (10 °C) decreasing to only 19 days under warmer conditions (30–35 °C) (Dow AgroSciences 1998).

Clopyralid is very water soluble at 143 000 mg/L in water buffered at pH 7 (Dow AgroSciences 1998). It is weakly adsorbed with average K_{oc} of 6 mL/g and a K_d of 0.41 (Vencill 2002). Dow AgroSciences lists K_d = 0.01–0.21 mL/g (low soil sorption) and K_{oc} of 0.4–30 mL/g (1998). The log K_{ow} = -2.63 at pH 7 meaning it favours water and is thus hydrophilic.

The pesticide has a moderate leaching potential (Vencill 2002). In Canadian studies, Elliott (2000) has shown loss of up to 1.5% of applied clopyralid leached to tile drains, largely by preferential flow, within 20 days of application. However, Tomlin (1994) indicates data on field-based leaching to groundwater shows the risk is minimal, despite published data indicating weak sorption to soils.

2.5. MCPA review

MCPA ([4-chloro-2-methylphenoxy] acetic acid) is a post-emergent selective herbicide used to control annual broadleaf weeds and is used in cereals, peas and turf (Vencill 2002). MCPA is part of the phenoxy family.

MCPA is rapidly degraded by soil micro-organisms and is of relatively low persistence, with a reported half-life in the field of 14 days to one month, depending on environmental factors such as soil moisture, temperature and organic matter content (Wauchope *et al.* 1992; Vencill 2002). Low soil moisture and microbial activity have been shown to prolong the half-life of MCPA, as has increased soil organic matter content (FDA 1996). Vencill (2002) has reported half-lives ranging from 7 to 30 days; however, a half-life of 5–6 days is typical, though it is more persistent under drier conditions. Persistence can be up to six months in dry conditions. Tomlin (1994) indicates half-lives of less than seven days but with residual activity of up to *ca.* 3–4 months. Degradation is thought to be by microbial-activated hydroxylation and cleavage of linkages (Vencill 2002). MCPA is relatively stable to light with minor volatilisation losses reported for the salt formulations (Vencill 2002).

Sorption K_{oc} is listed as 20 mL/g for the dimethylamine salt (used in this study) and is thus weakly adsorbed and mobile in the soil environment. MCPA is an acidic herbicide with a pKa of 3.7 (Benitez *et al.* 2004). As with sulfometuron methyl, MCPA has the ability to ionize in aqueous solutions to form anion species. As MCPA has such a low pKa value, the anionic form is likely to predominate in the pH conditions encountered in most Tasmanian soils.

MCPA has a very high water solubility of 866 000 mg/L at pH 7 and readily leaches in most soil types, although the mobility of the compound decreases as soil organic matter content increases (FDA 1996).

Implications for MCPA use in Tasmanian conditions are:

1. It has a significantly longer half-life in drier sites.
2. Leaching occurs in wetter and sandier soils.
3. Cooler temperatures should increase the half-life as it is microbially driven.

2.6. Alpha-cypermethrin review

Alpha-cypermethrin is a non-systemic insecticide which is used for the control of a large number of chewing and sucking insects (Tomlin 1994). It is a member of the pyrethroid group and acts on the peripheral nervous system in insects (Tomlin 1994).

The field dissipation has been sparingly studied. Bacterial degradation of individual isomers (Sakata *et al.* 1992) has been determined and photodegradation analysed on a variety of soils (Raikwar and Nag 2006). Photodegradation may well be the principal mechanism of degradation due to the high sorption, trapping alpha-cypermethrin on the soil surface (Raikwar and Nag 2006). Alpha-cypermethrin has a reported half-life of 20–90 days (FMC MSDS Sheet), with a reported half-life of 13 weeks in loamy soil (Tomlin 1994).

The solubility in water of alpha-cypermethrin is very low – *ca.* 0.01 mg/L (25 °C) – but is greatly increased in organic solvents; for example, 620 mg/L in acetone (Tomlin 1994). The pesticide has a K_{ow} partitioning coefficient at pH 7 of over eight million, indicating strong affinity for organic matter. This very strong binding to soil means leaching will be insignificant in most natural soils.

Implications for alpha-cypermethrin in Tasmanian conditions include:

1. A strong sorption to surface soils.
2. Little chance of leaching to waterways or groundwater.

3 Methods and materials

3.1. Half-life field trials and sampling

The six pesticides were applied at maximum field rates or higher to ensure detection over the trial period. They were applied to a Black Vertosol (cracking clay) and a Brown Kurosol (sandy duplex soil) on the University of Tasmania Farm (Unifarm) near Cambridge in south-east Tasmania (42° 47’ 47.2” S, 147° 25’ 14.5” E and 42° 47’ 19.7” S, 147° 26’ 22.8” E) on 17/10/2006 and 17/4/2007; on a Red Ferrosol at the Northdown site (41° 10’ 12.3” S, 146° 28’ 30.8”E) on 20/10/2006 and 20/4/2007; on a Brown Dermosol (gradational soil on granodiortie) near Pyengana in the north-east of the state (41° 19’ 15.8” S, 147° 54’ 34.2” E) on 24/10/2006 and 23/4/2007; and on a Red Ferrosol near the southern village of Glen Huon (43° 03’ 33.2” S, 146° 58’ 08.6” E) on 27/10/2006 and 19/4/2007.

The pesticides were applied at the highest label rates, in some cases exceeding label rates, using research-quality hand-held sprayers: simazine (6 and 3 kg/ha) as ‘Gesatop 600SC’®; glyphosate (3.24 kg/ha) as ‘Roundup Power Max’®, MCPA (2.0 kg/ha); clopyralid (1.2 and 2.4 kg/ha) as ‘Lontrel’®; sulfometuron methyl (0.75 kg/ha) as ‘Oust’®; and alpha-cypermethrin (0.12 kg/ha) as ‘Dominex Duo’®. The five differing soil types occur at four sites across the State. The reduced application of simazine (half) and increased application of clopyralid (double) in the autumn trial was done to enhance the extraction and analytical efficiency of the soil samples rather than for any environmental reasons. Simazine is easily detected and often ‘maxed out’ the detector in the early spring trial. Clopyralid, by comparison, is poorly detected and is better quantified at higher concentrations.

In order to check the application rate of pesticide applied to the trial plots, small aluminium foil targets were placed on the ground to collect the spray for three of the pesticides. These foils were then analysed and acted as a cross-check of the day zero application rate. They demonstrate relatively uniform application of pesticides to all sites (Appendix B).

Soil samples were collected in the field using a standardised 0–10 cm core sampler from each of triplicate plots set out in a randomised block design. A total of 10 samples were taken across each of three 2 x 5 m plots and placed in a zip-lock sample bag before being stored on ice for transport. The samples were then frozen as quickly as possible to preserve the ‘time integrity’. All frozen samples were ground, mixed, sieved and sub sampled and then stored in separate freezers. Soil moisture contents (for oven-dry correction) at sampling were measured for all the above samples.

Significant difficulties were encountered and much time consumed in the homogenising of the frozen samples. Because the samples were time dependent, it was not possible to dry the samples prior to processing, especially the T0–T28 samples. The frozen samples had to be hand ground with a mortar and pestle and then sieved through a 2 mm sieve in an effort to disaggregate and thoroughly homogenise the sample. In the very early samples, the pesticide was concentrated in the upper few millimetres of the core and had to be evenly incorporated into the overall bulk of the sample in order to reflect the pesticide to soil ratio that is quantified in the final analysis.

3.2. Extraction and analysis

3.2.1 Sulfometuron, MCPA and simazine analysis

A 4g soil sample of sulfometuron and MCPA and a 2 g sample of simazine from each of the sprayed plots was combined and ground with cellite filler before being packed into an accelerated solvent extraction (ASE) cell. The pesticide was then extracted from the soil-filled cell using a 20% methanol, 80% water mix at 100 °C and a pressure of 1500 psi. The extract from a sample of this size provides approximately 35 mL of solvent, which is then diluted to 50 mL for the purpose of accurate quantification. The extract was then filtered using a 0.45 micron syringe filter into an LC vial. Simazine, MCPA and sulfometuron are then analysed simultaneously by LCMS/MS (see Appendix D for instrument settings). ASE extraction efficiencies were tested on the highest sorbing soil (Northdown Ferrosol) at 5 μg/L and these recovery percentages ranged from 63% for sulfometuron to 87% for simazine (see Appendix F).

3.2.2 Glyphosate extraction and analysis

Method 1

Approximately 5 g of sieved and ground soil is weighed into a 50 mL centrifuge tube. Then 25 mL of 0.01 M KOH is added via a Kippax® dispenser and the sample sonnicated for 5 minutes. This is then end-over-end agitated for 30 minutes before being centrifuged at 6000 rpm for 6 minutes.

The supernate is then carefully poured into another 50 mL centrifuge tube and adjusted to pH 2.0 with concentrated orthophosphoric acid (approx 1 drop) and the pH tested using universal paper. It is then centrifuged at 6000 rpm for 4 minutes and an aliquot of 5 mL removed and filtered through a 0.45 micron syringe filter directly into an LC vial and submitted to LC analysis using the established method of post-column derivatisation and fluorescence detection (see Appendix D for instrument settings).

The rationale for using the above method, which was used for the entire spring trial, was that the dilute KOH (0.01 M) extraction solvent resulted in less matrix interference during the detection phase of the analysis. There was, however, some concern about the efficacy of the extraction solvent. During the extraction of the autumn trial it was noted that the Northdown sample set was negative for glyphosate, even at the T0 point. The sample was then re-run using a 0.1 M KOH solution and found to be positive for glyphosate. It was then decided to re-run the entire autumn glyphosate trial using the 0.1 M KOH extraction solvent. The modified extraction method is as follows.

Method 2

Approximately 5 g of sieved and ground soil is weighed into a 50 mL centrifuge tube. Then 25 mL of 0.1 M KOH is added via a Kippax® dispenser and the sample sonnicated for 5 minutes. This is then end-over-end agitated for 30 minutes before being centrifuged at 10 000 rpm for 10 minutes.

The supernate is then carefully poured into another 50 mL centrifuge tube and adjusted to pH 2.0 with concentrated orthophosphoric acid (approx 50 μL) and the pH tested using universal paper. It is then centrifuged at 10 000 rpm for 10 minutes and an aliquot removed directly into an LC vial and submitted for LC analysis using the established method of post-column derivatisation and fluorescence detection. The filtration step was omitted because of the possibility of sorption onto the filter. However, subsequent testing by AST showed no sorption of glyphosate standards on glass fibre or nylon syringe filters (David Nichols pers. comm.). Glyphosate extraction efficiencies where tested on the University Farm Vertosol and the Kurosol (refer to Appendix F).

3.2.3 Alpha-cypermethrin extraction and analysis

A 7 g sub-sample of soil is weighed into a dish and transferred to a mortar and pestle where it is further ground with Hydromatrix®. A filter is placed at the base of an ASE extraction cell and then filled with approx 10 mm of Hydromatrix®. The cell is then extracted with 35 mL of DCM: acetone 50:50 at 100 °C at 1500 psi. To this extract an internal standard is added and the extract filtered through anhydrous sodium sulphate into a turbo vac® tube. The filter paper and sodium sulphate is then washed with a further 10 mL of DCM before it is evaporated to 500 µL. A further 1500 µL of DCM is added and pipetted around the base of the tube to wash down all the extract. The extract is passed through another anhydrous sodium sulphate filter and then submitted for GCMS analysis. ASE extraction efficiencies where tested on the University Farm Vertosol and were measured at 93% (refer to Appendix F).

3.2.4 Clopyralid extraction and analysis

Clopyralid analysis and extraction proved to be problematic when using the technique outlined in section 3.2.1. Methanol adversely affects the chromatography and a concentration step was required to overcome poor detector sensitivity. The opportunity arose to interface the ASE system with a Gilson automatic liquid handling system in order to streamline the sample throughput.

Approximately 7 g of soil is mixed with an appropriate filler, cellite, and packed into an ASE extraction cell. This is extracted with 100% water at 100 °C at 1500 psi. An internal standard (Picloram) is added to the collection vial. A 3 g activated charcoal solid phase extraction cartridge is preconditioned with 5 mL DCM: MeOH 5:1, 5 mL MeOH, 5 mL 1% nitrate solution which is held for 5 minutes. This is then washed with 5 mL of water; 20 mL of the ASE eluent spiked with the internal standard (Picloram) is then passed through the pre-conditioned SPE cartridge. The cartridge is then dried before extraction with a solution of DCM: MeOH 5:1 containing 0.2% trifluoroacetic acid (TFA). The extract is then neutralised with 50 µL of ammonia solution and evaporated to dryness. The dried extract is then reconstituted in a 5% MeOH solution with 0.05% formic acid and analysed by LCMS/MS. ASE extraction efficiencies where tested on the highest sorbing soil (Northdown Ferrosol) and were measured at 72% (refer to Appendix F).

3.3. Sorption analysis

Triplicate 5 g samples of blank soil from each of the five sites were weighed into a 50 mL centrifuge tube and 25 mL of 0.01 M $CaCl_2$ solution added (see Table 3-1 below). Analytical-grade pesticide standard was added at five concentrations over a range of at least four orders of magnitude (Table 3-1). The selection of the concentration range depended on application rate and detection limits (based on OECD guidelines 2000). The tubes were then end-over-end shaken for 24 hours, centrifuged and the supernatant sub-sampled for analysis.

For glyphosate, a 10 ppm spike resulted in no glyphosate being detected in the supernate. The method was then modified to 1 g of soil to 10 mL of $CaCl_2$ solution. The concentration range was also significantly above the application rate. The same situation occurred with alpha-cypermethrin. The sorption to the soil was so great that no pesticide was detected in the supernate at 100 times the application rate. Thus, sorption studies on alpha-cypermethrin were abandoned on the advice of Dr Kookana of CSIRO and this was accepted by the management committee.

Table 3-1 Concentration of pesticide added to blank soil for each 1:5 and 1:10 soil: 0.01 M $CaCl_2$ extractions.

Pesticide					
sulfometuron	100 ppb	500 ppb	1 ppm	5 ppm	10 ppm
simazine	5 ppb	50 ppb	500 ppb	5 ppm	20 ppm
clopyralid	100 ppb	500 ppb	1 ppm	5 ppm	10 ppm
MCPA	10 ppb	100 ppb	500 ppb	1 ppm	10 ppm
glyphosate	1 ppm	10 ppm	50 ppm	100 ppm	200 ppm

3.4. Soil characterisation

Data on the chemical properties of the topsoils at each site are presented in Table 3-2. These data have been used to examine the properties controlling sorption behaviour. There is a wide range in organic carbon (1.5–7.6%), which is a critical soil property affecting the sorption of many pesticides.

The particle size data were generated using two techniques: the first utilises only disaggregation of the soil in a tripolyphosphate dispersant followed by 16 hours of end-over-end shaking; the second by adding pre-treatments of peroxide to oxidise the soil organic matter, and citrate-dithionate-bicarbonate treatment to reduce and dissolve the iron oxide cementing agents in each of the soils. The two pre-treatments result in significant differences for the two Red Ferrosols and minor differences in the Brown Dermosol (Table 3-3 and Figure 3-1). Only the first method was used on the Unifarm Kurosol as it is a loose sandy soil. Estimates of clay, silt and sand were made from the charts in Figure 3-1 and are presented in Table 3-3. Particle size analysis was undertaken by the Mineral Resources section of the Tasmanian Department of Infrastructure, Energy & Resources.

Soil mineralogy is critical to both sorption behaviour and soil aggregation, which may hinder sorption. Whole soil mineralogical analyses were completed by the Mineral Resources section of the Tasmanian Department of Infrastructure, Energy & Resources using X-ray diffraction (Table 3-4).

Table 3-2 Summary chemical data for the topsoils of each site, including Vertosol 2, which was selected for higher soil pH to improve analysis of the impact of pH on sorption.

	Organic carbon (%)	**Electrical conductivity (dS/m)**	**pH (1:5 $CaCl_2$)**	**pH (1:5 H_2O)**	**Exchangeable cations (meq/100 g)**				
					Ca	**Mg**	**Na**	**K**	**Al**
Vertosol (Unifarm)	2.25	0.118	5.7	6.6	15.8	12.3	0.96	0.65	0.0
Vertosol2 (Unifarm)	1.50	0.127	7.6	8.6	16.2	4.4	0.79	0.33	0.0
Kurosol (Unifarm)	1.54	0.061	4.9	6.3	1.9	0.88	0.3	0.11	0.1
Ferrosol (Huon)	4.42	0.084	5.3	6.2	11.7	3.8	0.14	1.18	0.09
Ferrosol (Northd.)	7.61	0.355	5.0	5.6	9.9	2.5	0.5	2.28	0.54
Dermosol (Pyen.)	4.57	0.155	4.4	5.5	2.6	0.85	0.09	0.31	1.09

Table 3-3 Estimated particle size classes based on data taken from charts presented in Figure 3-1 below.

Soil type	**Sand (%)**	**Silt (%)**	**Clay (%)**
Kurosol (Unifarm)	82	15	3
Vertosol (Unifarm)	30	25	45
Ferrosol (Huon)	40	25	35
Ferrosol (Northdown)	19	28	53
Dermosol (Pyengana)	71	14	15

Table 3-4 Mineralogical data on topsoils from each site.

Results (approx wt %)

Sample	**Quartz**	**Halloysite**[1]	**Hematite**	**Goethite**	**Ilmenite**	**K-Feldspar**	**Plagioclase**	**Organic**
Huon Ferrosol	45	35	5	2	2	2	*	5

Sample	**Kaolinite**	**Hematite**	**Maghemite**	**Quartz**	**Gibbsite**	**Rutile**	**Organic**
Northdown Ferrosol	40	20	15	10	5	*	10

Sample	**Quartz**	**K-Feldspar**	**Kaolinite**	**Mixed-Layer**[2]	**Chlorite**[3]	**Plagioclase**	**Amphibole**	**Gibbsite**	**Mica**[4]	**Hematite**	**Organic**
Pyengana Dermosol	50	15	5	5	5	5	2	2	2	2	5

Sample	**Quartz**	**Smectite**	**Kaolinite**	**K-Feldspar**	**Plagioclase**	**Ilmenite**	**Rutile**	**Organic**
Unifarm Vertosol	50	35	*	5	5	2		5
Unifarm Kurosol	90		*	2	2		*	5

* trace;

[1] both hydrated and dehydrated;

[2] mixed-layer mineral, probably Mica-Vermiculite or Mica-Chlorite;

[3] potential overlap with Vermiculite;

[4] includes Illite.

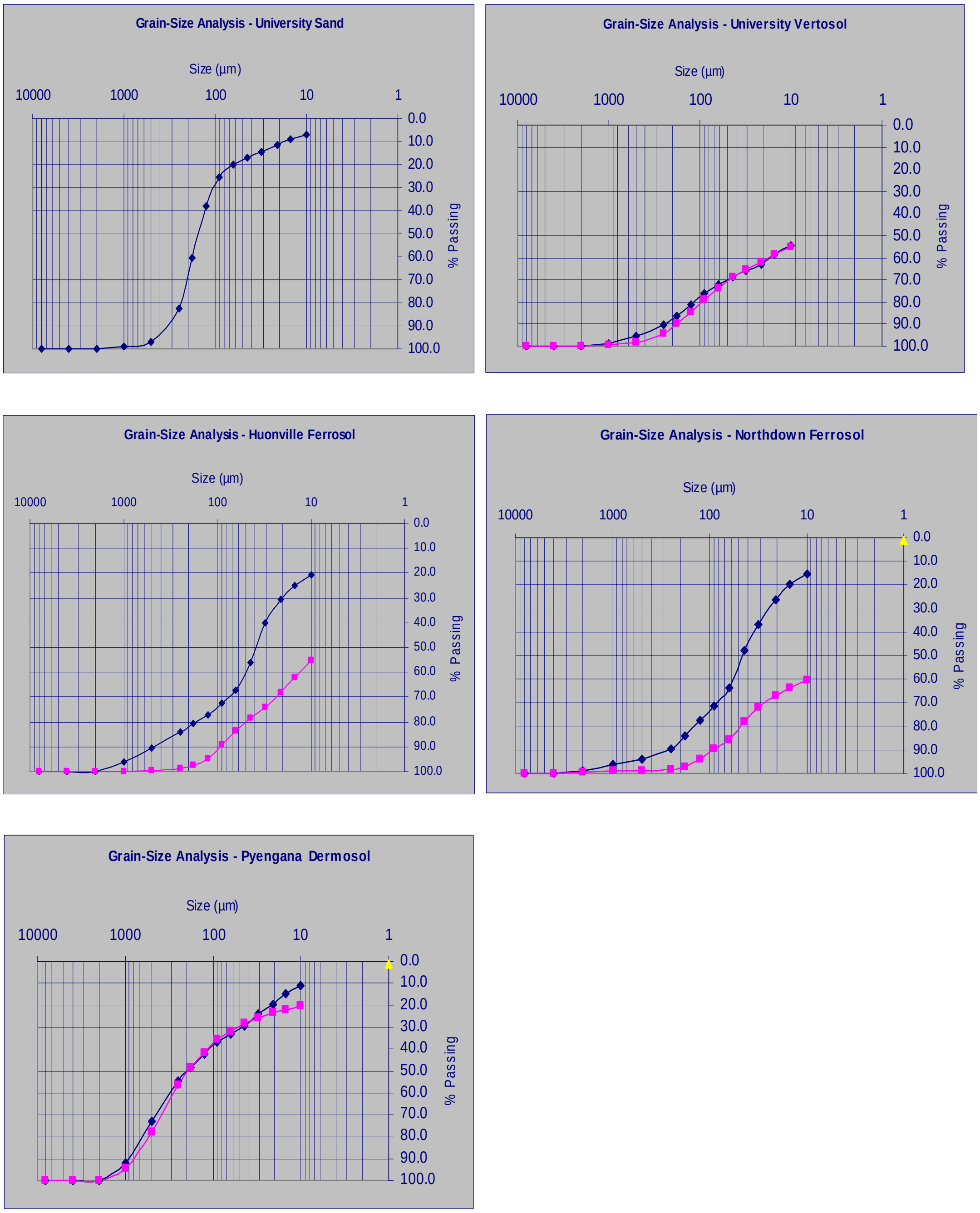


Figure 3-1	Particle size analysis graphs for the five soils types studied. Note that data have been generated with two pre-treatments. The trend lines through the diamond symbols represent pre-treatment with dispersant and 16 hour shaking only, while the lines through the square symbols represent pre-treatment to remove organic matter and iron oxides.

4 Results and discussion of half-life studies

4.1. Introduction to spring 2006 half-life

Half-lives have been calculated using the first-order equation and the results are reported in Table 4-1 below. The first-order model fitted the data rather well for Huon, Northdown and Pyengana soils (see Figures 4-3 to 4-8), and hence there was no reason for using the Hoerl equation for half-life calculation.

The two Unifarm data sets were more variable, particularly the Unifarm Kurosol (sand), and the half-life determined by the best fit model can be considered unreliable. Wind erosion late on the first day following application caused considerable variation across the Kurosol trial plots so the data have not been included here (see statistics in Appendix C).

Table 4-1 First-order half-lives (days) for spring 2006 trial.

Site	Sulfometuron	MCPA	Clopyralid	Simazine	Glyphosate	Alpha-cypermethrin
Huon Ferrosol	10	4	11	26	7	35
Northdown Ferrosol	21	21	51	11	5	14
Pyengana Dermosol	17	5	3	31	13	32
Unifarm Vertosol	25	51	93	123	65	56
Mean Spring 2006	**15**	**20**	**40**	**48**	**23**	**34**
Mean autumn 2007	56	13	39	134	54	**37**
Literature ranges	20–28	7–30	12–70	70–110	1–180	**20–90**
PIRI values	20	25	45	60	88	**45**

The mean half-life values are very close, though all are slightly lower than those values used in a pre-project version of PIRI for all pesticides except glyphosate and alpha-cypermethrin.

The total rainfall over the trial was lowest at Northdown in spring 2006 and highest at Huon and the Unifarm (see Figure 4-1). However, rainfall in the first 56 days was similar at all sites with the exception of Northdown which was considerably drier. This had a marked effect on the half-lives of several pesticides at Northdown; for example, clopyralid and MCPA.

Soil moisture levels are highest in the Pyengana and Huon sites and lowest in both soils on the Unifarm sites. While degradation is most likely related to soil moisture tension rather than simply gravimetric moisture content, the dryness of both the sandy and clayey textured soils at Unifarm indicates that soil moisture is likely to be far more limiting to degradation at Unifarm than at other sites. Pyengana, a sandy soil, clearly has the highest moisture availability throughout the season, while the two clayey Ferrosols (Huon and Northdown sites) have quite different soil moisture contents at the start of the trial.

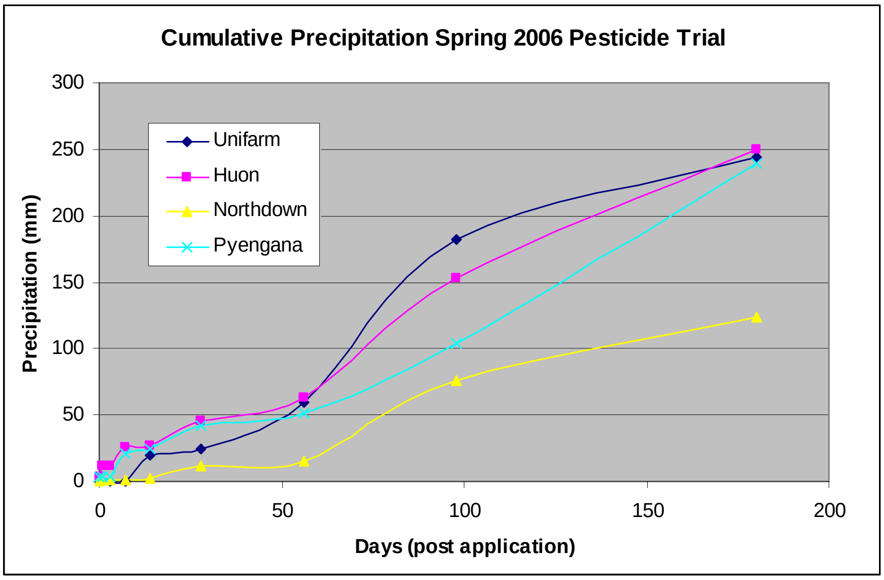


Figure 4-1 Cumulative rainfall charts from Bureau of Meteorology weather stations closest to the sites for both seasons (Huon = Grove Research Station; Unifarm = Hobart Airport, Northdown = East Devonport Airport, Pyengana = Scotsdale).

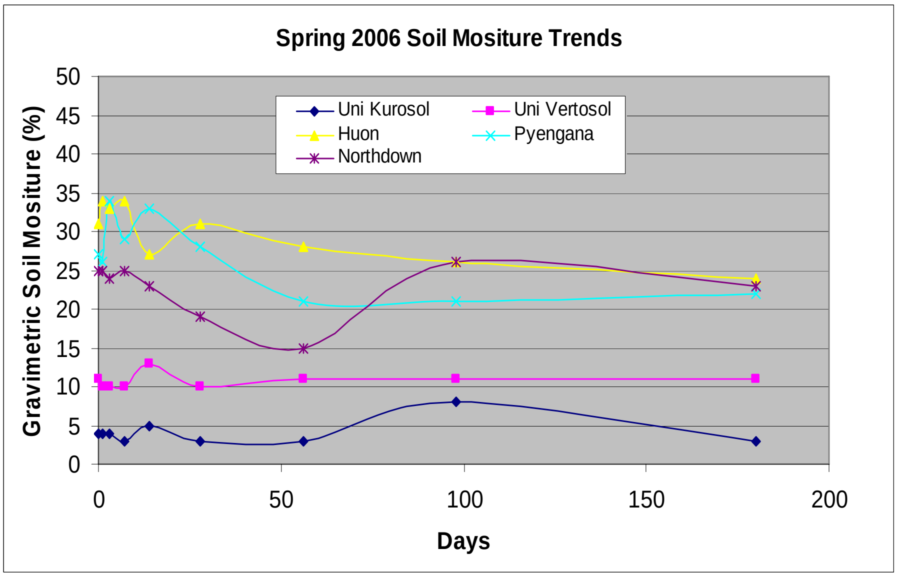


Figure 4-2 Gravimetric soil moisture levels during the spring 2006 season.

4.2. Results of spring 2006 half-life trial

4.2.1 Sulfometuron methyl

Vencill (2000) indicates half-lives of 20–28 days for sulfometuron methyl, although degradation occurs most rapidly in lower pH soils. The Tasmanian spring 2006 data indicate slightly shorter value half-lives with a mean of 15 days. Persistence is enhanced in drier conditions, higher soil pH (Vertosol) and cooler temperatures; for example, Northdown and the Unifarm. Half-lives of one week were reported under laboratory conditions (Commonwealth of Massachusetts 2003).

The Unifarm Vertosol has the longest half-life for sulfometuron methyl of 25 days. This is probably due to the dry site conditions; clayey texture and the higher soil pH (see Table 3-2). Sulfometuron methyl dissipation in Huon, Pyengana and Northdown soils ranges from 10 to 21 days. Sulfometuron methyl may be more readily leached at wetter sites; for example, Huon and to some extent Pyengana, though it was not detected in the leaching field trials at Pyengana on day 56. This is supported by similar behaviour in MCPA and clopyralid and by the fact that these three pesticides have relatively low sorption coefficients, especially clopyralid. The three pesticides persist in drier soils – Unifarm and Northdown (see Figures 4-1 and 4-2 and Table 4-1). While Northdown received less rainfall, the gravimetric soil moisture values were lowest at the Unifarm sites due to generally higher pan evaporation values in the Coal Valley than in north-west Tasmania.

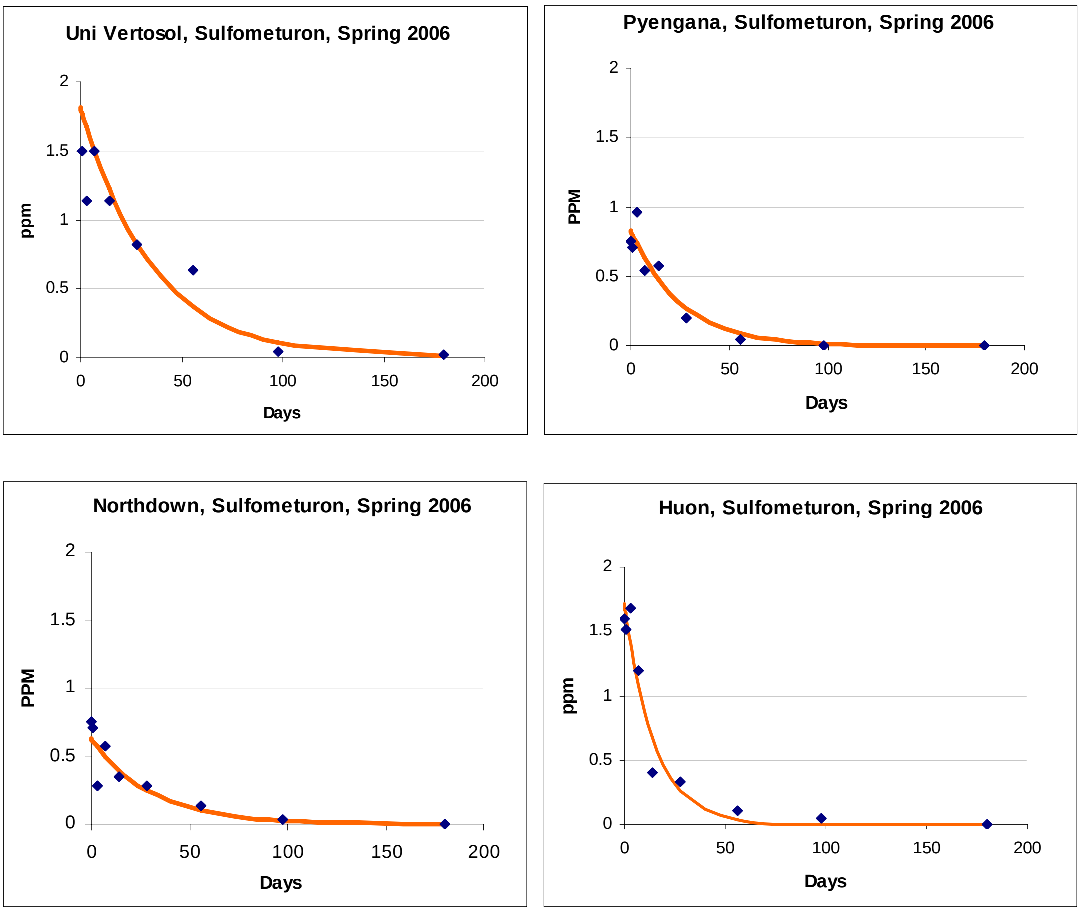


Figure 4-3 First-order equations fitted to field data for sulfometuron methyl in spring 2006 trial. Drier sites are shown on left and wetter on the right.

4.2.2 Simazine

Mean simazine half-lives are reported as 60 days (Tomlin 1994) and 70–110 days (Vencill 2002). Our data show that simazine is degraded most rapidly on the well structured, acidic and high organic carbon site of Northdown, with a half-life of only 11 days (Figure 4-4 and Table 4-1). This was somewhat surprising given the dry conditions at the site. However, photodegradation may have played a part at this site due to its north-easterly aspect, moderate slope and dry start to the season (Figure 4-1). Hydrolysis may also have played a part as the site has a 0.01 M $CaCl_2$ soil pH of 5.0. Acidic soil conditions at both Huon and Pyengana may also explain the shorter than expected half-lives of 26 and 31 days respectively. A half-life of 123 days for the Unifarm Vertosol was once again the longest half-life of any of the pesticides tested in spring. This soil has a higher $CaCl_2$ soil pH of 5.7. This site also exhibited the least leaching of simazine (Figure 5-1).

Overall, the spring 2006 half-life data for simazine are in the lower range of published data and suggest that the dry warm season has led to more rapid dissipation in most of the Tasmanian sites, a trend similar to all other pesticides. These findings are supported by Vencill (2002), who reports increased photodegradation in dry weather and hydrolysis in acidic soils; all soils had soil pH values of less than 5.7 in 0.01 M $CaCl_2$.

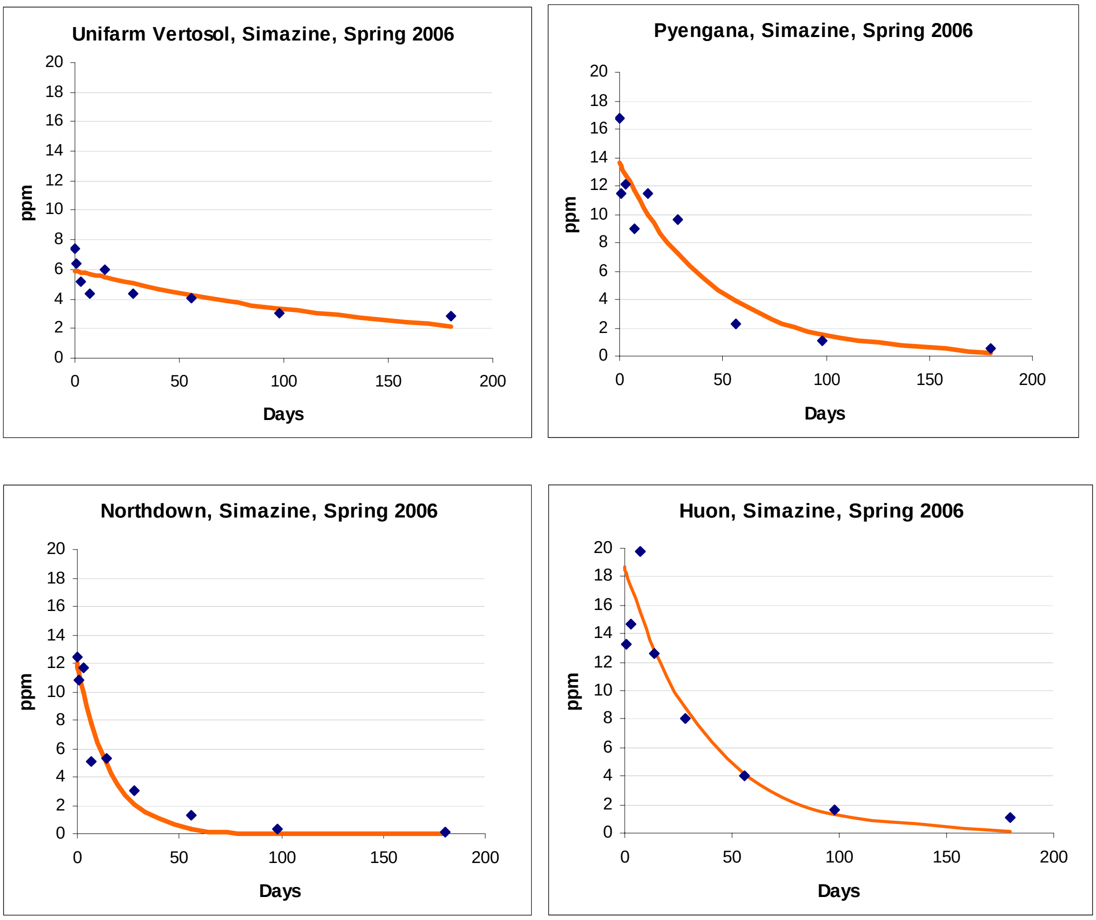


Figure 4-4 First-order equations fitted to field data for simazine in spring 2006 trial.

4.2.3 Glyphosate

The Unifarm Vertosol site is once again the stand-out with a half-life of 65 days, while all other sites were less than one-fifth of this (Table 4-1 and Figure 4-5). These values of 5–13 days are similar to some of the published values for the trimesium salt; though a potassium salt was used in these trials (Tomlin 1994). The Unifarm Vertosol appears to be protecting glyphosate, and indeed all other pesticides, from breakdown. This probably relates to the dry soil conditions and the clayey soil texture, which restrict leaching and limit soil moisture supply (higher moisture tensions).

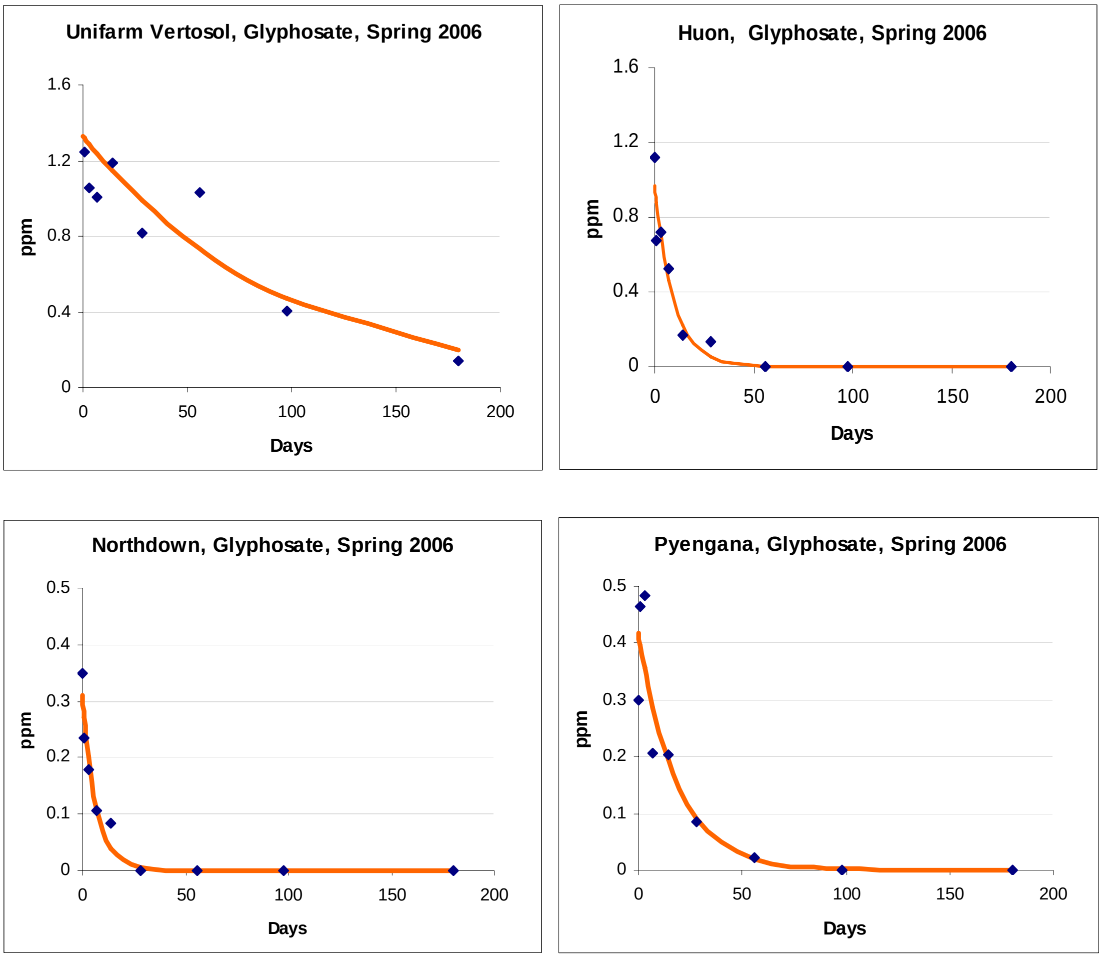


Figure 4-5 First-order equations fitted to field data for glyphosate in spring 2006 trial.

4.2.4 Clopyralid

Half-lives for the spring 2006 data were again longest for the Unifarm Vertosol (93 days) and the Northdown Ferrosol (51 days), both having drier soils (see Figures 4-2 and 4-6 and Table 4-1). These were the driest soils (gravimetric soil moisture) and this has been shown to be significant for clopyralid dissipation (Dow AgroSciences 1998; Vencill 2002). The moister soils (Figure 4-2) of Huon and Pyengana produced 11 and 3 days respectively and this may indicate greater leaching losses at these wetter sites, though this was not detected in Pyengana cores taken at day 56 (data not shown). However, leaching in autumn 2007 was considerable at Pyengana (Figure 5-4). These two sites had the highest soil moisture trends and this may be important for more rapid degradation (Dow AgroSciences 1998). The range is very wide and the higher values exceed the typical published range which shows 95% of values are less than 69 days (Dow AgroSciences 1998).

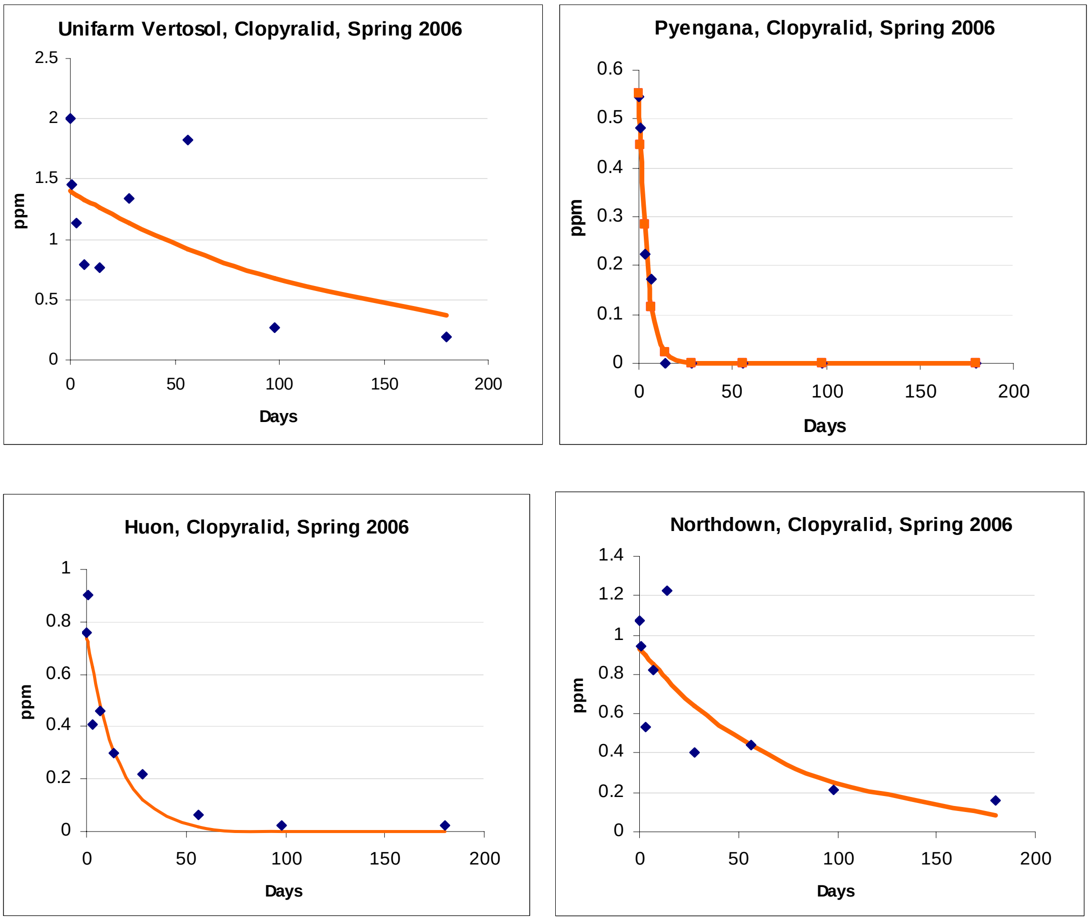


Figure 4-6 First-order equations fitted to field data for clopyralid in spring 2006 trial.

4.2.5 MCPA

The longest half-lives for MCPA were determined on the drier soils as 51 days on the Unifarm Vertosol (clay) and 21 days at Northdown (see Table 4-1, Figure 4-7). The wetter soils (see Figure 4-2) of Huon and Pyengana showed significantly shorter half-lives of four and five days respectively. MCPA dissipation is reported to be significantly affected by soil moisture and leaching, though leaching was minimal at Pyengana on day 56 (see Figures 4-2 and 5-2) (Vencill 2002). The Unifarm Vertosol soil, which was dry and clayey, appears to be protecting MCPA from dissipation with a 51-day half-life, while the Northdown site has a more typical half-life value and the two other wetter sites have similar and shorter half-lives of 4–5 days.

Thus, the spring 2006 Tasmanian data for most of the soils appear to concur with the lower published range of 5–6 days (Vencill 2002). The Vertosol at the Unifarm site is above the published ranges and would seem to indicate the importance of soil factors, particularly in the drier clayey soil. This is supported by the Northdown site which had very low rainfall at the start of the trial, thus hindering breakdown (Figure 4-1).

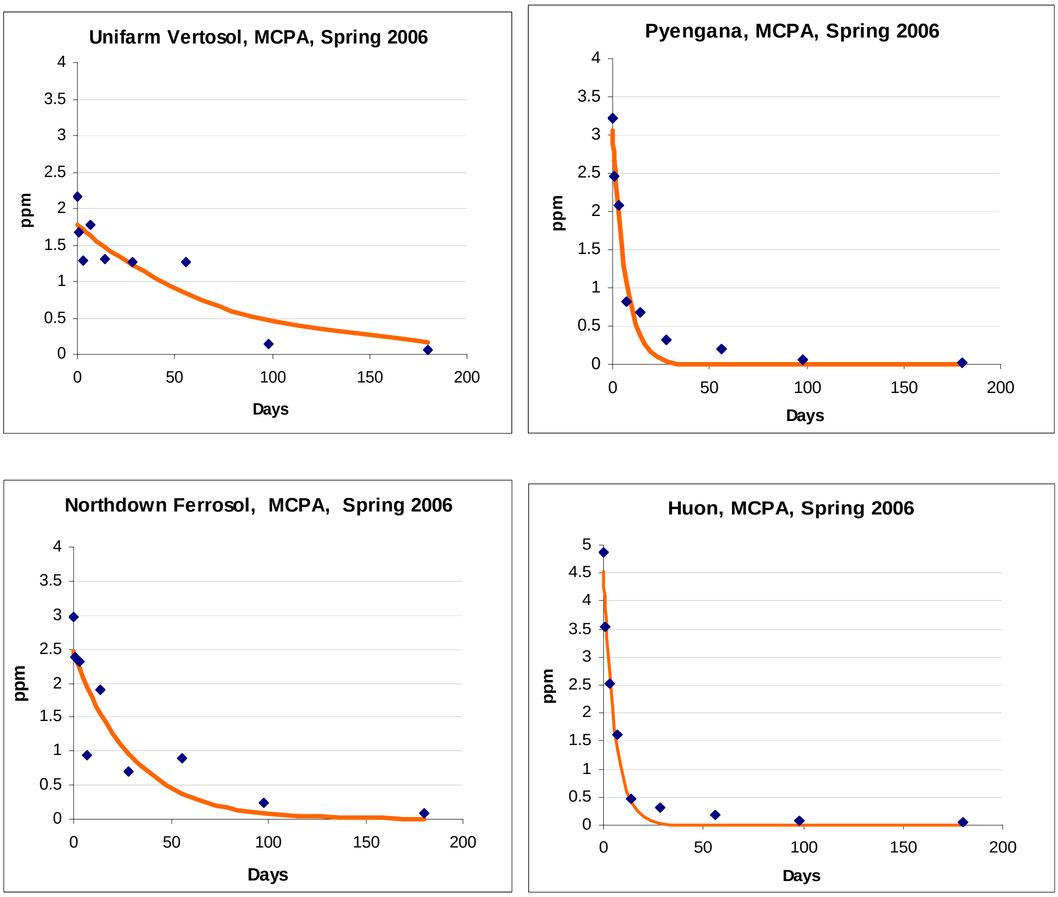


Figure 4-7 First-order equations fitted to field data for MCPA in spring 2006 trial; wetter site on left, drier site on right.

4.2.6 Alpha-cypermethrin

The mean half-life across all the sites is 34 days, slightly lower than the 45 days used in a pre-project version of PIRI. On the Unifarm Vertosol, the half-life of alpha-cypermethrin was 56 days, the longest recorded. Huon and Pyengana had similar values of 32 and 35 days while at Northdown the half-life was only 14 days.

With a mean half-life of 34 days, the Tasmanian data certainly fitted within the published range of 20–90 days but toward the lower end of that range. Photodegradation is considered a key dissipation mechanism and the northerly sloping aspect at Northdown and the dry soil conditions would facilitate the short half-lives at that site. The generally dry conditions and surface application of the pesticide may explain the shorter half-lives across the sites.

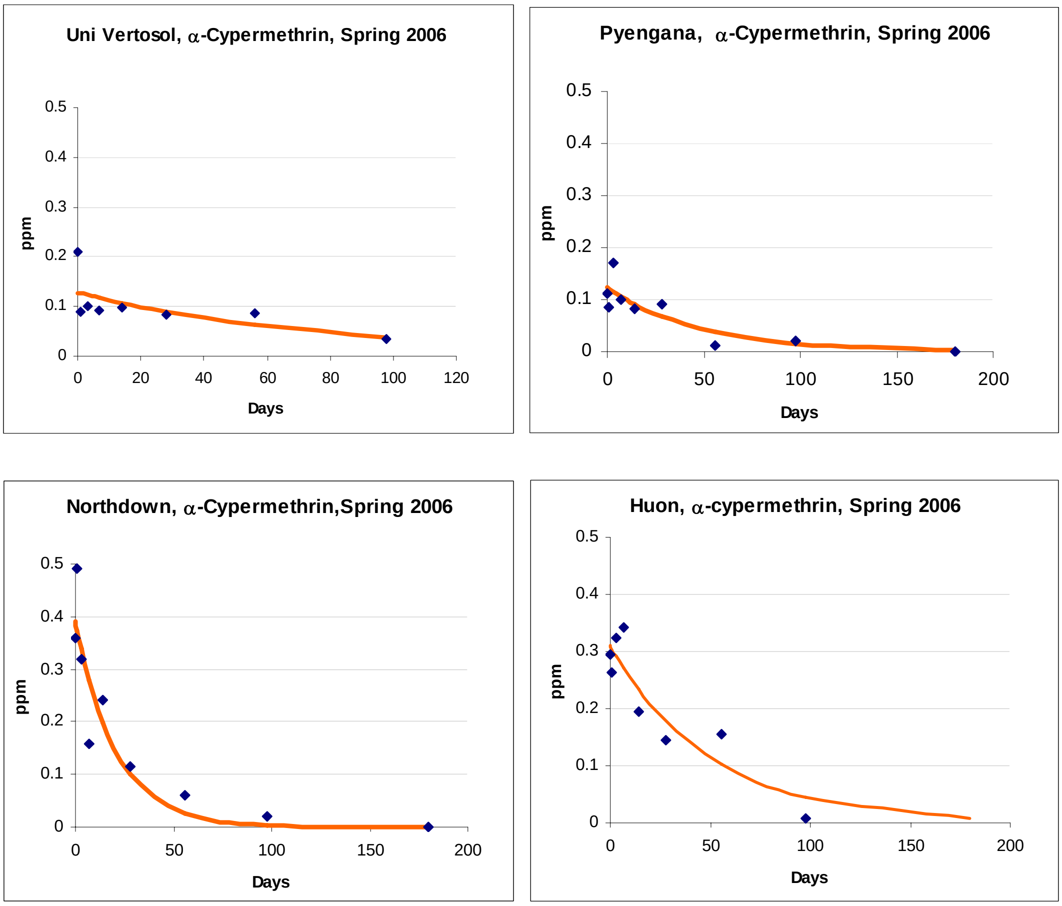


Figure 4-8 First-order equations fitted to field data for alpha-cypermethrin in spring 2006 trial.

4.3. Discussion of spring 2006 half-life trials

The longest half-lives for all pesticides are on the Unifarm Vertosol (see Table 4-1). For the weakly adsorbed pesticides (MCPA, clopyralid and simazine), these appear to be twice those values currently used in the pre-project version of PIRI. The more strongly adsorbed pesticides (glyphosate and alpha-cypermethrin) have similar half-lives to those used in the pre-project version of PIRI on the Vertosol.

Shortest half-lives for most pesticides are on Ferrosols at Northdown and Huon. The wetter Ferrosol (Huon) has the shortest half-life for leachable pesticides (MCPA, clopyralid and simazine) while the more strongly adsorbed pesticides have the shorter half-lives on the Ferrosols, especially the Northdown site. The Northdown Ferrosol as compared to the Huon Ferrosol received much less rainfall and this is supported by the soil moisture levels in the first 56 days of the trial. Dry soil conditions are known to hinder degradation of MCPA and sulfometuron.

The Pyengana site has very short half-lives for MCPA and clopyralid, but not simazine and sulfometuron, perhaps due to reasonable rains falling early in the trial and microbial degradation and leaching. Though leaching was not detected for clopyralid and only minor leaching for MCPA at 56 days, this date may have been too late to detect earlier leaching pulses which were subsequently degraded.

The data for Northdown appear to have the closest correlation with the pre-project PIRI values in the three more weakly adsorbed pesticides (sulfometuron, MPCA and clopyralid), with the wetter sites (Pyengana and Huon) having shorter half-lives than those currently used in the pre-project version of PIRI. The data for the Unifarm Vertosol may be overestimating the half-lives due to the dry soil conditions, despite receiving similar rainfalls to other sites (excluding Northdown) and the lack of leaching shown in data (see Figures 5-3 to 5-6). The Unifarm Vertosol data for the weakly adsorbed pesticides show values approximately twice those used in the pre-project version of PIRI and are perhaps a feature of Vertosols in cooler dry soils. These unique soil conditions need to be reflected in pesticide models to improve predictive power.

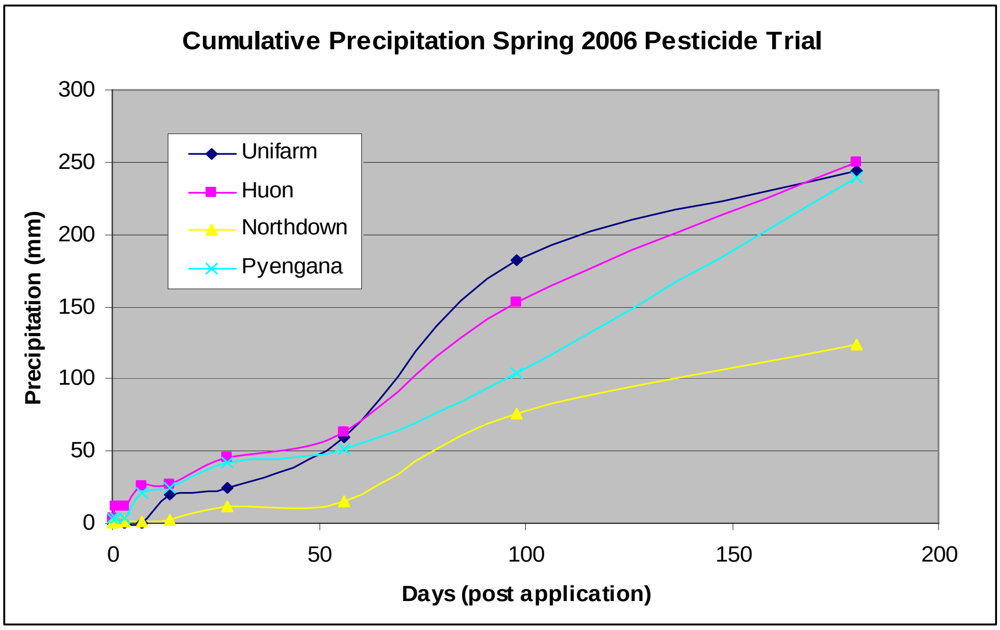
When it comes to the more highly adsorbed pesticides (glyphosate and alpha-cypermethrin) the Unifarm Vertosol carries the closest values to those used in pre-project PIRI and to other published values. In more strongly adsorbed pesticides leaching is less relevant as a dissipation mechanism. Instead, the levels of soil moisture and biological activity become important in degradation. The soils containing a high concentration of organic matter (Northdown, Pyengana and Huon) show the shortest half-lives, possibly due to greater biological decay and better soil moisture levels. The short half-lives for glyphosate on Ferrosols may also be related to very high sorption and binding by iron oxides and kaolin clays (Table 3-4).

4.4. Introduction to autumn 2007 half-life trials

The data for autumn 2007 dissipation trials on six pesticides at five sites are reported below. The pesticides were applied in mid to late April 2007 to a range of sites across Tasmania. Samples (8–10 cores) of the 0–10 cm depth range were taken from each of triplicate plots at each site at 0, 1, 3, 7, 14, 28, 56, 98 and 180 days after application and were extracted and analysed using accelerated solvent extraction (ASE) and GSMS/MS and LCMS/MS.

A table of the data is presented below along with the values currently used in PIRI and several published ranges.

Pyengana received significantly more precipitation over the autumn 2007 trial period than any of the other sites; the Unifarm received the least rainfall (see Figure 4-9). Both Northdown and Huon received similar rainfall, though Northdown was wetter, particularly after day 28, than Huon. This trend in the Ferrosols was the reverse of the spring trial where Northdown remained much drier throughout.



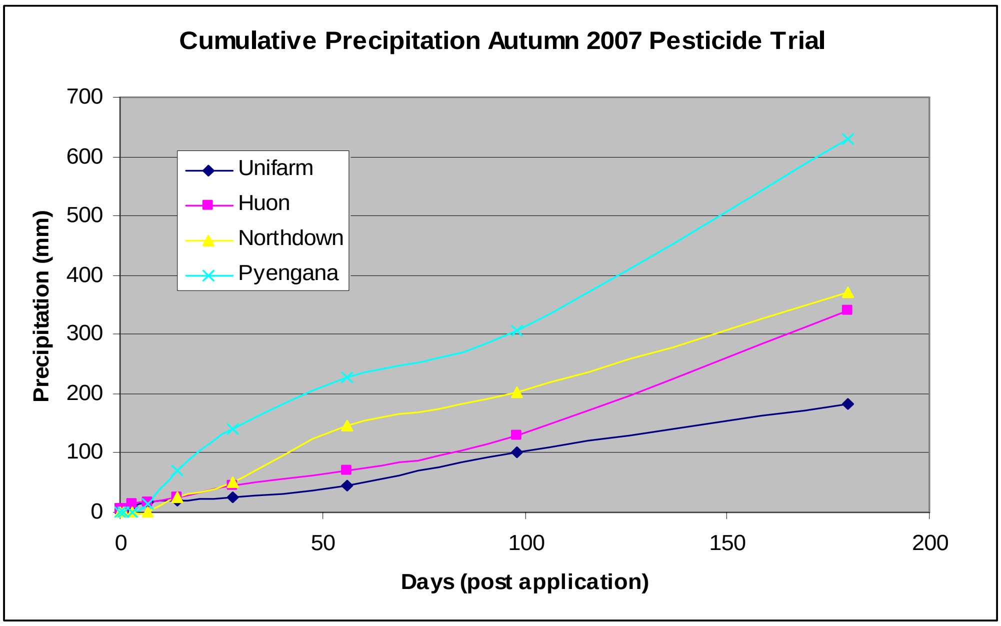


Figure 4-9 Cumulative rainfall charts for both trials from the Bureau of Meteorology stations closest to the sites for both seasons (Huon = Grove Research Station; Unifarm = Hobart Airport, Northdown = East Devonport, Pyengana = Scotsdale).

Table 4-2 shows that the average temperature across the spring trial was significantly higher than that of the autumn trial at all four locations. At all four sites the temperature difference between seasons was fairly similar and was in the range of 5.3–6.5 °C . The seasonal mean weekly air temperature trends (for the same weather stations as above) are presented in Figure 4-11 and show only minor differences between the sites but significant seasonal differences. In autumn 2007 the Pyengana site became much cooler after 28 days while the others sites didn’t cool down until approximately 40 days.

Table 4-2 Mean temperature to 180 days.

Site	Season	Mean temp (ºC)
Unifarm	Spring 2006	15.89
	Autumn 2007	10.51
Huon	Spring 2006	14.44
	Autumn 2007	8.92
Pyengana	Spring 2006	15.59
	Autumn 2007	10.07
Northdown	Spring 2006	15.78
	Autumn 2007	9.24

Table 4-3 shows that the average soil moisture content was fairly similar between seasons for all sites except for Northdown where it was significantly higher during the autumn 2007 trial. Regression analysis of the half-life data found no correlation between soil moisture content and half-life duration for any of the six pesticides tested. This lack of correlation, however, does not prove that soil moisture content is unimportant in the rate of pesticide breakdown in soil. The lack of correlation is possibly due to the fact that three out of the four sites had very similar mean moisture content levels between the two seasons, making it difficult to note any trends in half-life related to moisture content. Also, degradation is more likely related to soil moisture tension across the season rather than to the mean gravimetric soil moisture content.

Table 4-3 and Figure 4-10 show soil moisture values were lowest at the two Unifarm sites (Vertosol and Kurosol) during both trials. However soil moisture was significantly higher at Northdown Ferrosol in autumn 2007 than in spring 2006. The two Ferrosols (Northdown and Huon) show somewhat opposite soil moisture trends in the two trials which allow the impact of soil moisture on pesticide dissipation to be assessed. The Unifarm Vertosol was moister between day three and about day 40 than in the spring trial, otherwise the trends across the two trials are similar. The moisture trend for the Unifarm Kurosol is similar in both trials.

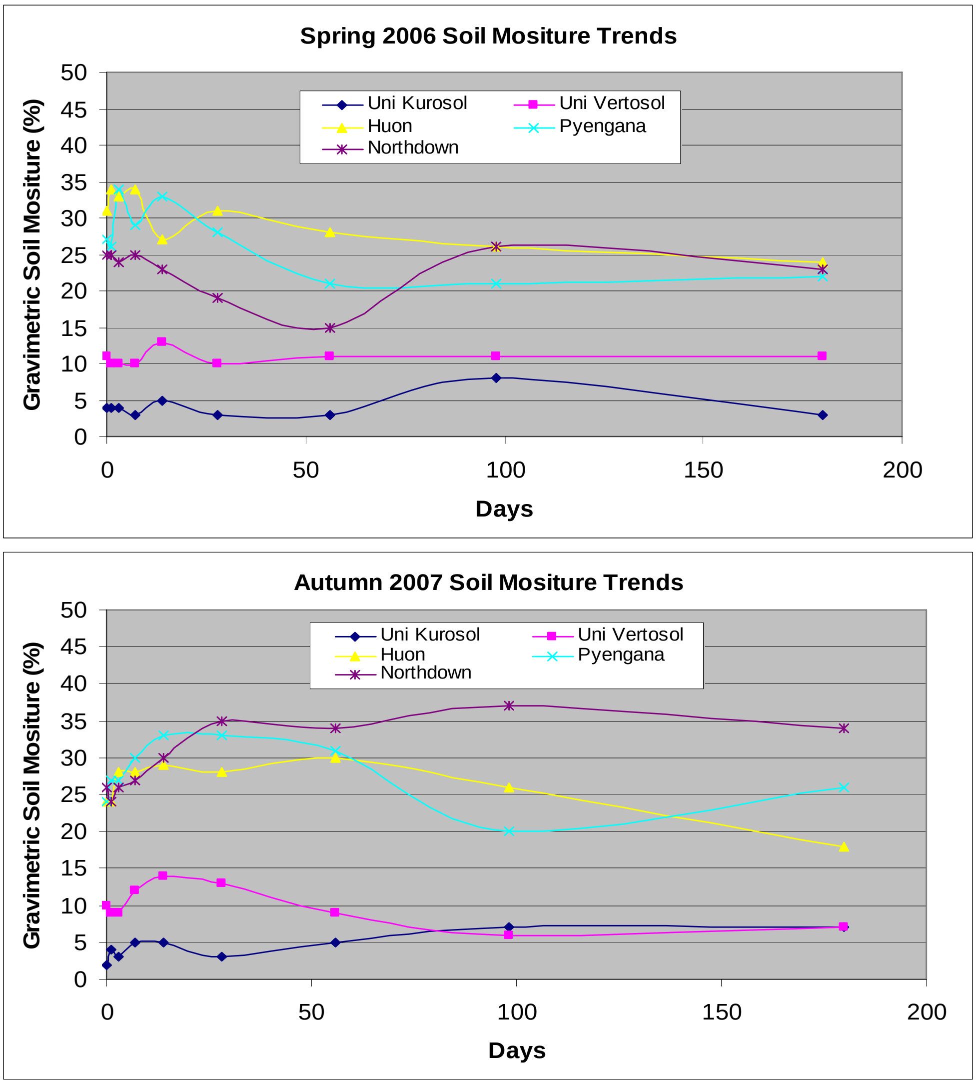


Figure 4-10 Gravimetric soil moisture trends for both spring and autumn trials.

Table 4-3 Mean gravimetric soil moisture content to 180 days.

Site	Season	Mean moisture content (%)
Unifarm – Kurosol	Spring 2006	4.11
	Autumn 2007	4.56
Unifarm – Vertosol	Spring 2006	10.51
	Autumn 2007	9.89
Huon – Ferrosol	Spring 2006	29.78
	Autumn 2007	26.11
Northdown – Ferrosol	Spring 2006	22.78
	Autumn 2007	30.33
Pyengana – Dermosol	Spring 2006	26.78
	Autumn 2007	27.89

Table 4-4 First-order half-lives (days) for spring 2006 trial.

Site	Sulfometuron	MCPA	Clopyralid	Simazine	Glyphosate	Alpha-Cypermethrin
Huon – Ferrosol	10	4	11	26	7	35
Northdown – Ferrosol	21	21	51	11	5	14
Pyengana – Dermosol	17	5	3	31	13	32
Unifarm – Vertosol	25	51	93	123	65	56
Mean spring 2006	**15**	**20**	**40**	**48**	**23**	**34**
Mean autumn	56	13	39	134	54	37
Literature ranges	20–28	7–30	12–70	70–110	1–180	20–90
PIRI values	20	25	45	60	88	45

Table 4-5 First-order half-lives (days) for autumn 2007 trial.

Site	Sulfometuron	MCPA	Clopyralid	Simazine	Glyphosate	Alpha-Cypermethrin
Huon – Ferrosol	53	14	20	122	10	41
Northdown – Ferrosol	42	17	12	75	-	14
Pyengana – Dermosol	34	8	11	126	33	-
Unifarm – Vertosol	64	20	87	159	99	59
Unifarm – Kurosol	86	4.4	65	186	75	34
Mean autumn 2007	**56**	**13**	**39**	**134**	**54**	**37**
Mean spring 2006	15	20	40	48	23	34
Literature values	20–28	7–30	12–70	70–110	1–180	20–90
PIRI values	20	25	45	60	88	45

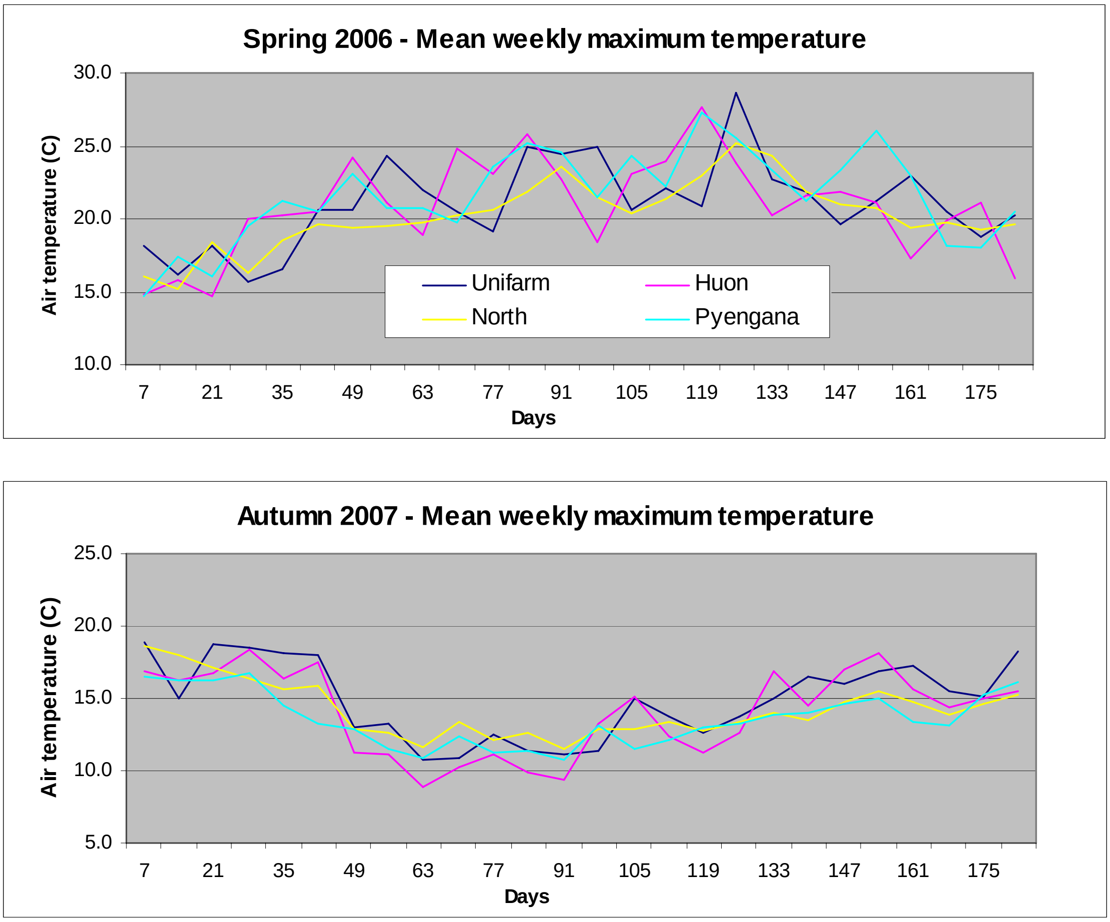
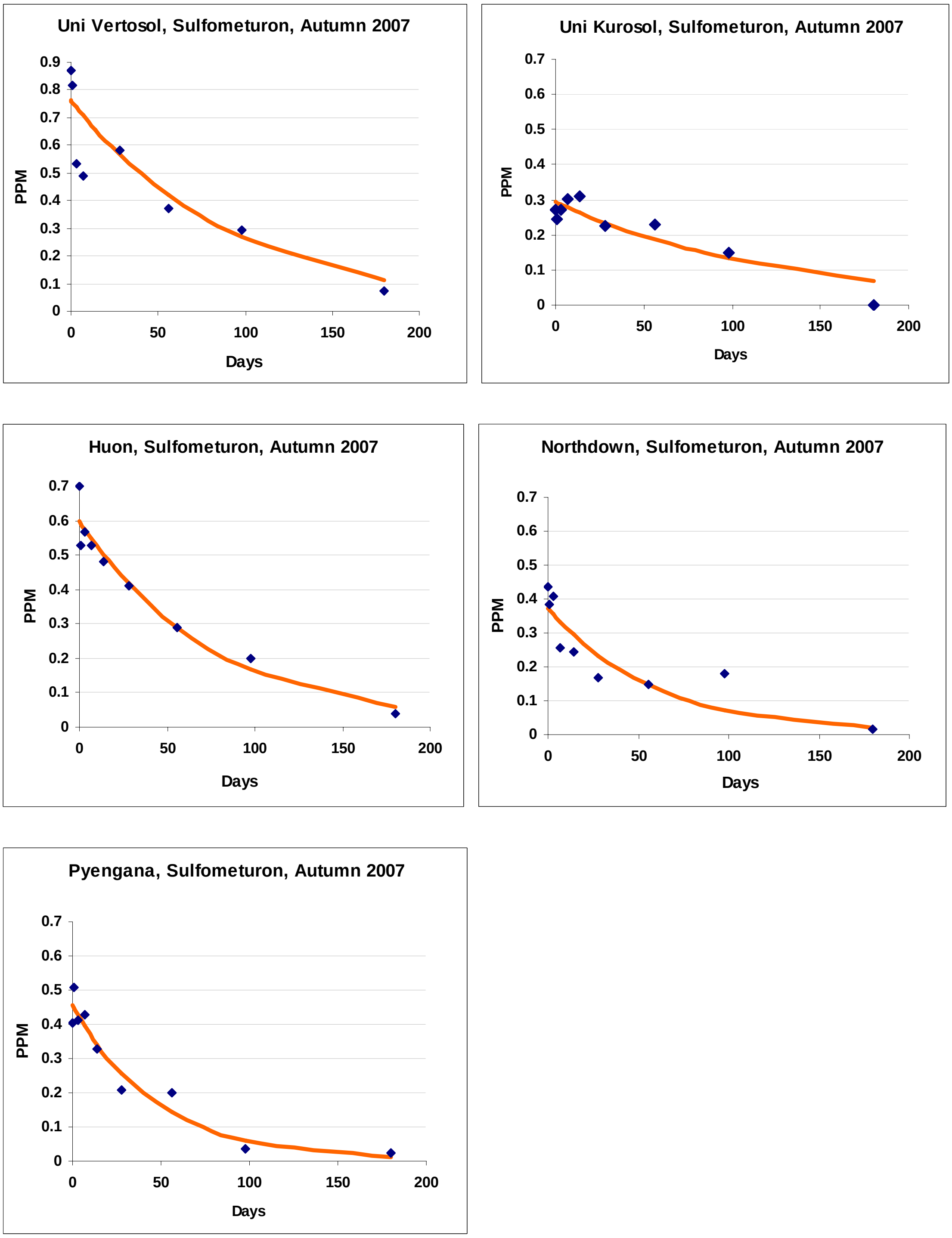


Figure 4-11 Mean maximum weekly air temperatures for the sites over both seasons.

4.5. Results of autumn 2007 half-life data

4.5.1 Sulfometuron methyl

The data for sulfometuron methyl indicate that the half-lives are generally more than double those of the spring 2006 trial at every site except Huon where they are five times longer (Tables 4-4 and 4-5 and Figure 4-12). These results appear to reflect the cooler temperatures over the winter period which would have reduced microbial activity, a key dissipation mechanism, and hence increased half-lives. Sulfometuron methyl on the Unifarm Kurosol (sand) has the longest autumn half-life. This is likely due to the dryness of the soil (see Figure 4-10) and the low levels of organic matter and thus restricted microbial activity in the soil. It should be noted that the mean autumn half-life value (56 days) is more than double that currently used in the pre-project version of PIRI. This data suggest that autumn and winter applications of sulfometuron methyl have a far longer residual activity and hence greater potential for leaching and runoff in Tasmanian autumn–winter conditions.


Uni Vertosol, Sulfometuron, Autumn 2007

Uni Kurosol, Sulfometuron, Autumn 2007

Huon, Sulfometuron, Autumn 2007

Northdown, Sulfometuron, Autumn 2007

Pyengana, Sulfometuron, Autumn 2007

Figure 4-12 First-order equations fitted to field half-life data for sulfometuron methyl.

Figure 4-13 shows that there was significant variation in the half-life of sulfometuron methyl between the spring 2006 trial and the autumn 2007 trial. Of all six pesticides tested, sulfometuron methyl showed the greatest variation between seasons. This possibly indicates that sulfometuron methyl is more sensitive to temperature than any of the other pesticides tested. Unlike any of the other pesticides tested, the longest sulfometuron half-life during the spring trial was actually significantly shorter that the shortest half-life of the autumn trial. This indicates that soil characteristics are less important that inter-seasonal factors in the breakdown rate of sulfometuron methyl.

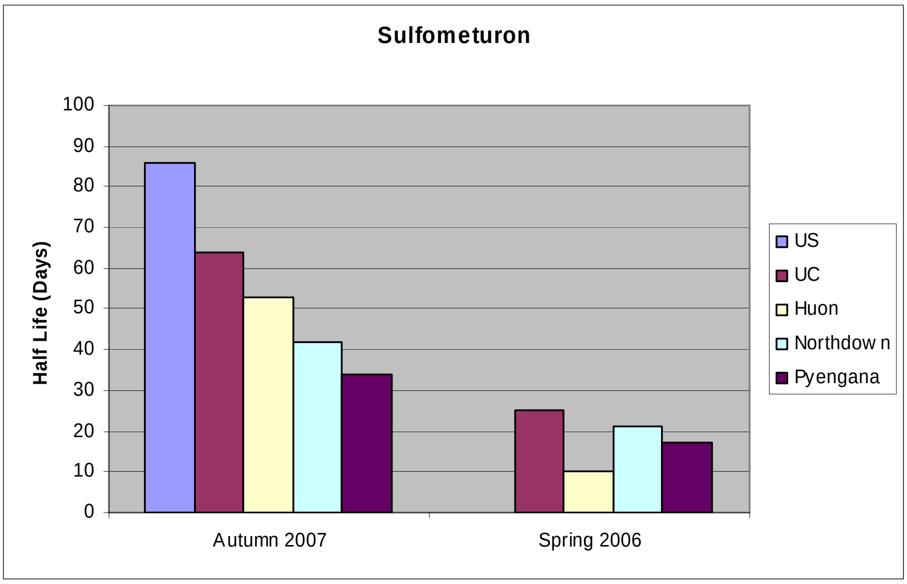
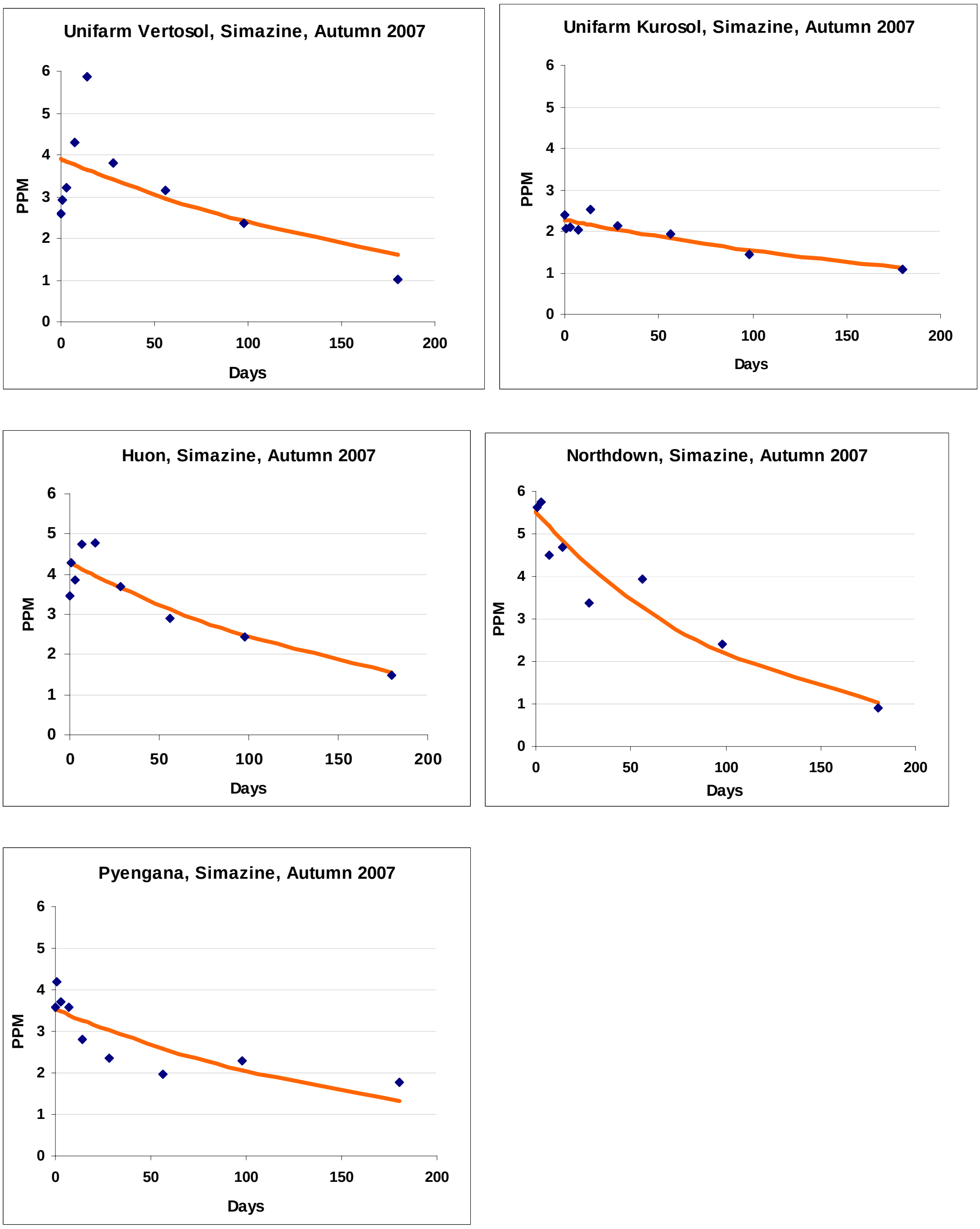


Figure 4-13 The seasonal variation in sulfometuron methyl half-lives (US = Unifarm Kurosol and UC = Unifarm Vertosol).

4.5.2 Simazine

Simazine has a half-life 3–4 times longer for the autumn 2007 trial on all soils, other than the Unifarm Vertosol (Figures 4-14 and 4-15). This seems to relate to the cooler conditions over the autumn–winter season and thus slower microbial and photodegradation activity than in the spring seasonal trial. Vencill (2002) supports this with field half-lives for similar pH soils of 60 days in Florida and 186 days in the cooler northern location of Minnesota. A draft report by the Australian-based Forest Herbicide Management Group (2000) also supports this with atrazine half-lives reported as 12 days in Queensland and 140 days in Tasmania.

It should be noted that the mean value for the autumn trial is double the value used in the pre-project version of PIRI. The data suggest that autumn and winter applications of simazine have a far longer residual activity and potential for leaching and runoff under Tasmanian conditions than suggested by pre-project PIRI input values. The long half-life for the Unifarm Kurosol is of particular concern as this soil also has very low sorption coefficients for simazine and thus runoff and leaching risks are significantly increased under Tasmanian conditions. However, only minor leaching occurred below 30 cm in our two field trials (Figures 5-1 and 5-3).



Unifarm Vertosol, Simazine, Autumn 2007

Unifarm Kurosol, Simazine, Autumn 2007

Huon, Simazine, Autumn 2007

Northdown, Simazine, Autumn 2007

Pyengana, Simazine, Autumn 2007

Figure 4-14 First-order equations fitted to field half-life data for simazine.

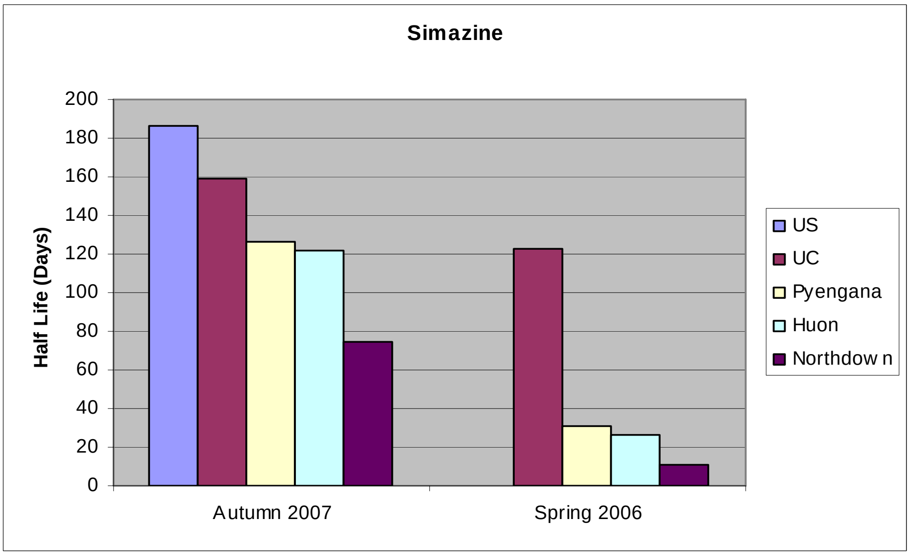


Figure 4-15 Seasonal variation in simazine half-lives (US = Unifarm Kurosol and UC = Unifarm Vertosol).

Figure 4-15 shows that as was the case with sulfometuron methyl, the breakdown of simazine occurred significantly more rapidly during the spring 2006 trial than during the autumn 2007 trial. Again, this difference is most likely due to the higher average temperatures experienced during the spring trial.

4.5.3 Glyphosate

The mean half-life for the autumn 2007 glyphosate trial is double that of the spring trial. This is a trend across many of the pesticides studied, with the exceptions of alpha-cypermethrin, and on some sites MCPA (see Tables 4-4 and 4-5). Also, the Unifarm Vertosol once again is the soil where the pesticide has the longest half-life, followed by the Unifarm Kurosol, a fact no doubt related to the drier soil conditions at the Unifarm (see Figure 4-10 and Table 4-3). The data indicate that PIRI's capacity to double half-life with every 10 °C drop in soil temperature will work well with predications in behaviour of this pesticide.

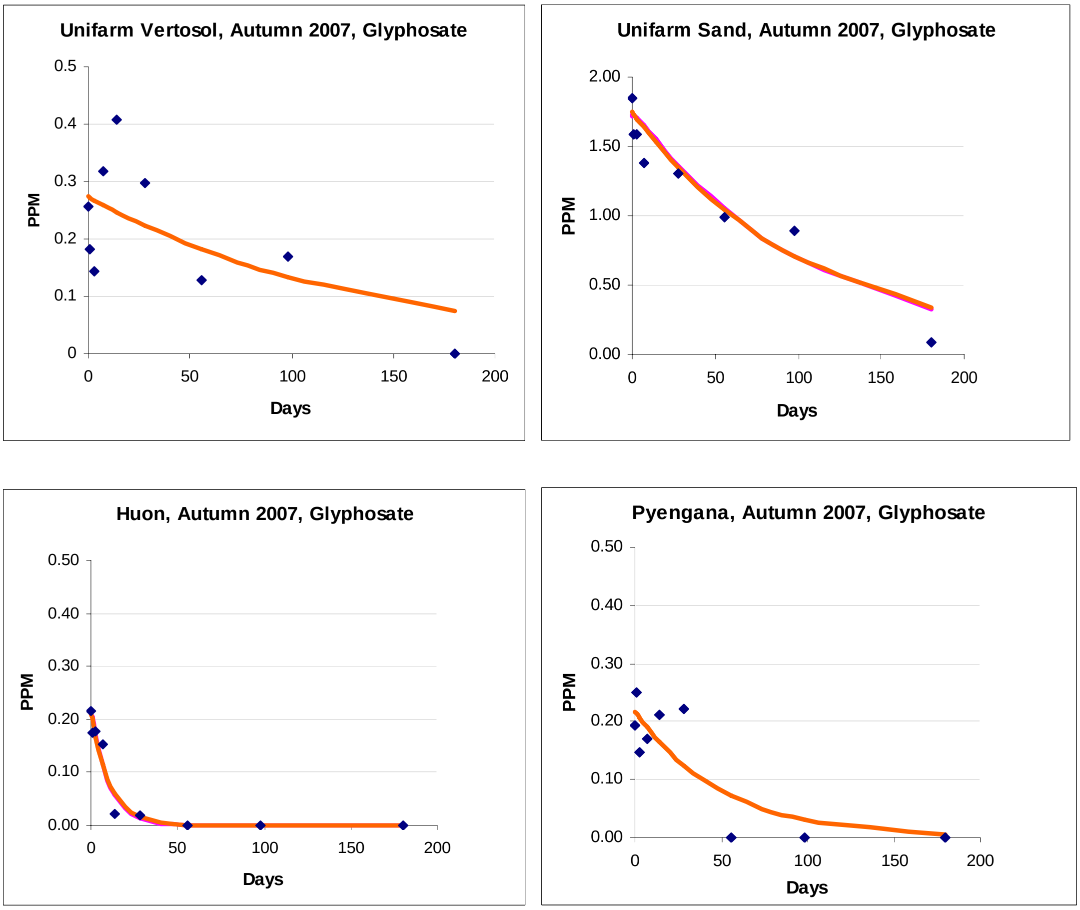


Figure 4-16 First-order equations fitted to field half-life data for glyphosate.

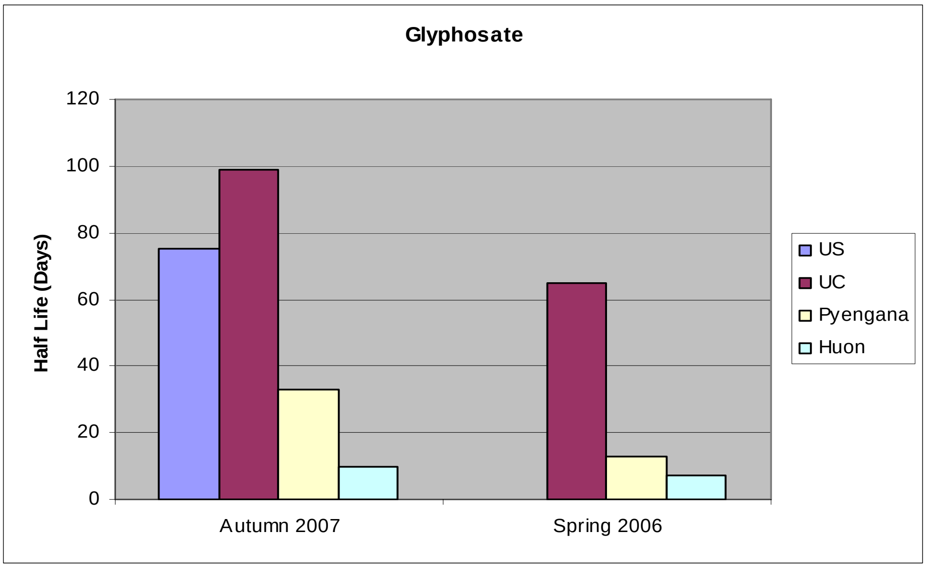


Figure 4-17 Seasonal variation in glyphosate half-lives (US = Unifarm Kurosol and UC = Unifarm Vertosol).

As was the case with simazine and sulfometuron, at all sites tested during both seasons the half-life of glyphosate was lower during the spring trial. Unfortunately though, there were only three sites where the glyphosate half-life data were reliable during both seasons. For this reason it is difficult to draw significant conclusions on the causes, though temperature seems to be important.

4.5.4 Clopyralid

Clopyralid has shown the same mean half-life (*ca*. 40 days) as was determined in the spring 2006 trial; however, there is a clear separation of the Unifarm soils and the other sites. Those at the Unifarm have a mean of 76 days while the other sites have a mean of only 14 days. This appears to reflect the nature of the Unifarm site with drier soils (Figure 4-10) and thus slower breakdown rates impacting on clopyralid in both seasons. This is also supported by the more rapid dissipation in the moister Northdown Ferrosol in the autumn 2007 trial as compared to Huon Ferrosol, the reverse pattern occurring in the spring 2006 trial. The data suggest that when moisture is limiting, temperature becomes less important to degradation.

While no leaching of clopyralid was detected in the spring 2006 trial, the pesticide did leach significantly in the autumn 2007 trial (Figure 5-4). In particular, at day 56 the Northdown trial shows 50% of the pesticide has leached below the 0–10 cm layer (Figure 5-4). This is supported by the fact that approximately 150 mm rain was received at the site prior to day 56 in autumn and only 15 mm rain was received in spring. At Pyengana, leaching also accounts for significant (approx 30%) dissipation loss of clopyralid from the topsoil.

Figure 4-18 shows that there are no consistent trends between seasons for clopyralid. This tends to indicate that temperature variation is less influential, perhaps more confounded by drier soil conditions, than for simazine, sulfometuron and glyphosate. This is supported by the behaviour at Northdown with a longer spring half-life at the dry site. Leaching of clopyralid in the autumn trial would have significantly lowered the half-life at Northdown and also at Pyengana (see Figure 5-4).

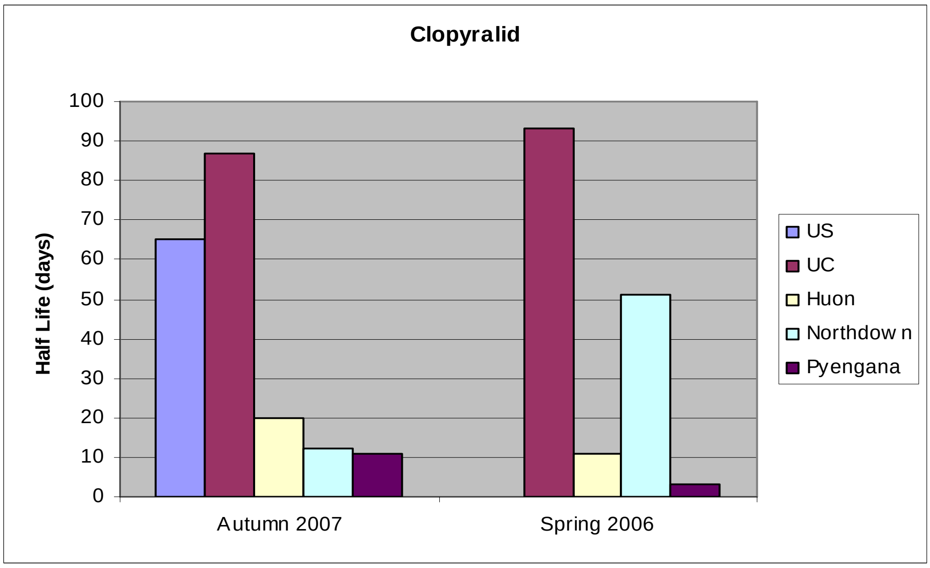
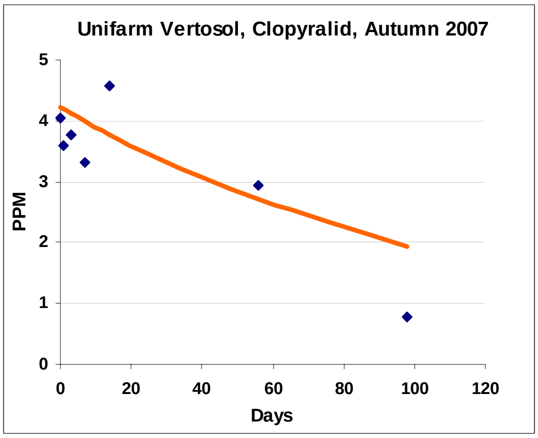
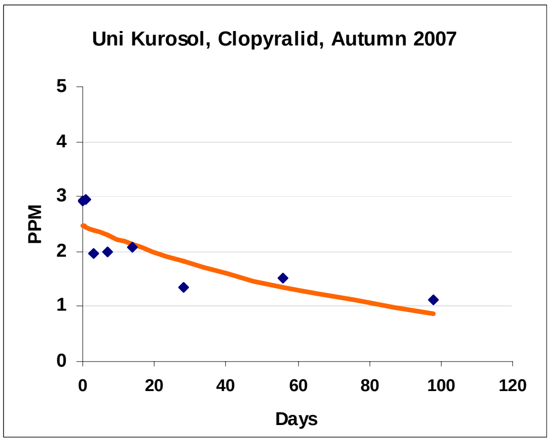
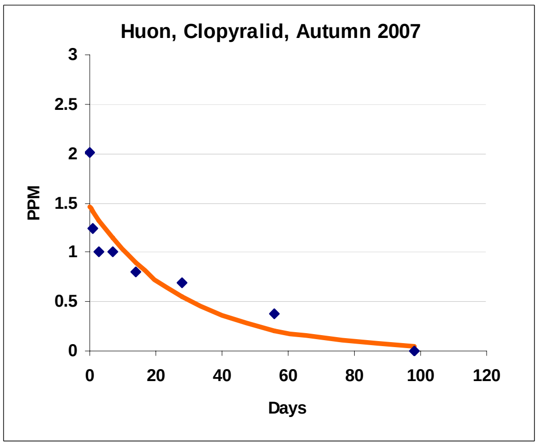
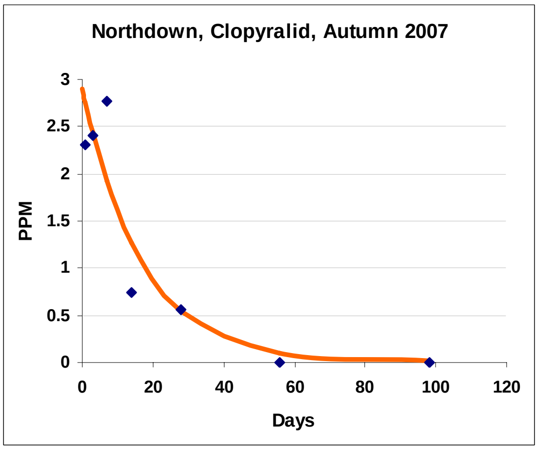


Figure 4-18 The seasonal variation in Clopyralid half-lives (US = Unifarm Kurosol and UC = Unifarm Vertosol).









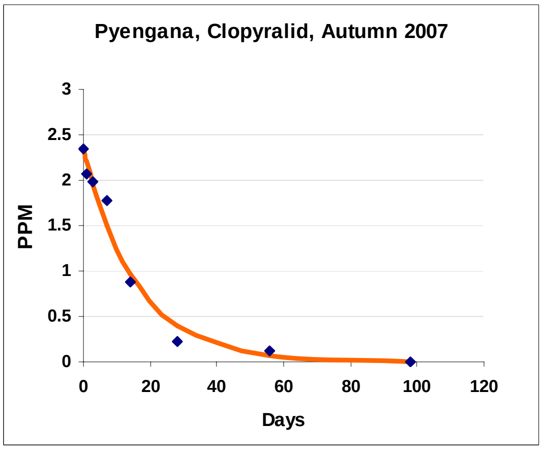


Figure 4-19 First-order equations fitted to field half-life data for clopyralid.

4.5.5 MCPA

Data for MCPA indicate the two Ferrosols, which received similar rainfalls and had similar soil moisture levels, also have similar half-lives (Tables 4-4 and 4-5 and Figures 4-20 and 4-21). The Huon half-life tripled (spring vs. autumn) while little change occurred at Northdown, as might be expected; the spring degradation was hindered by dryness and the autumn degradation was slower due to cooler temperatures. The Pyengana half-life also increased in the cooler autumn trial.

The MCPA half-life on the Unifarm Vertosol (clay) decreased by over 50% when compared to spring 2006; however, it still retains the longest half-life (Figure 4-20). This is the only instance where the half-life of a pesticide on the Vertosol was significantly reduced in the cooler autumn season (Figure 4-20). This may relate to slightly lower soil moisture values in the spring season limiting degradation (Figure 4-10). MCPA is known to have prolonged half-lives in dry soil and the autumn 2007 rainfall was less at the Unifarm than in the spring trial.

Over both trials, MCPA has consistently shown shorter half-lives (means of 20 and 13 days) than those used in pre-project PIRI (25 days).

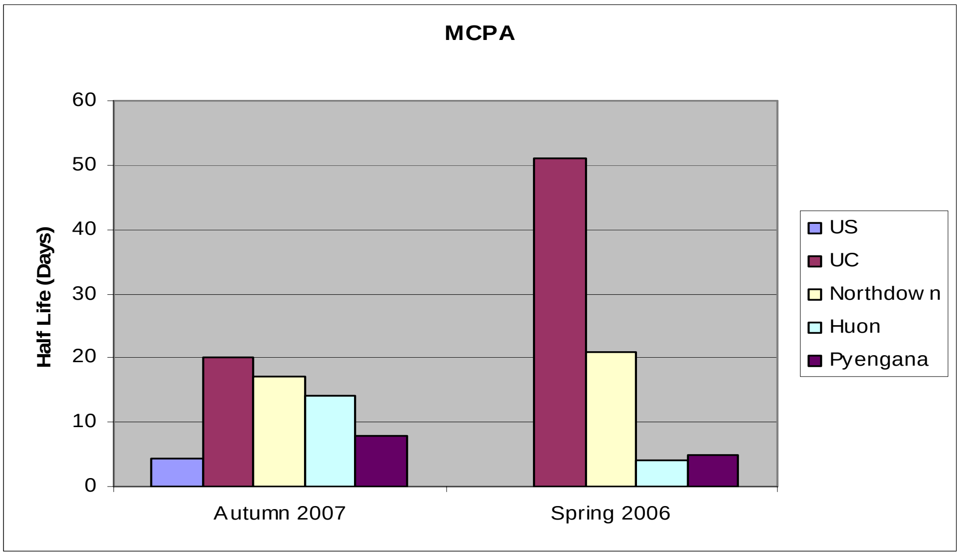
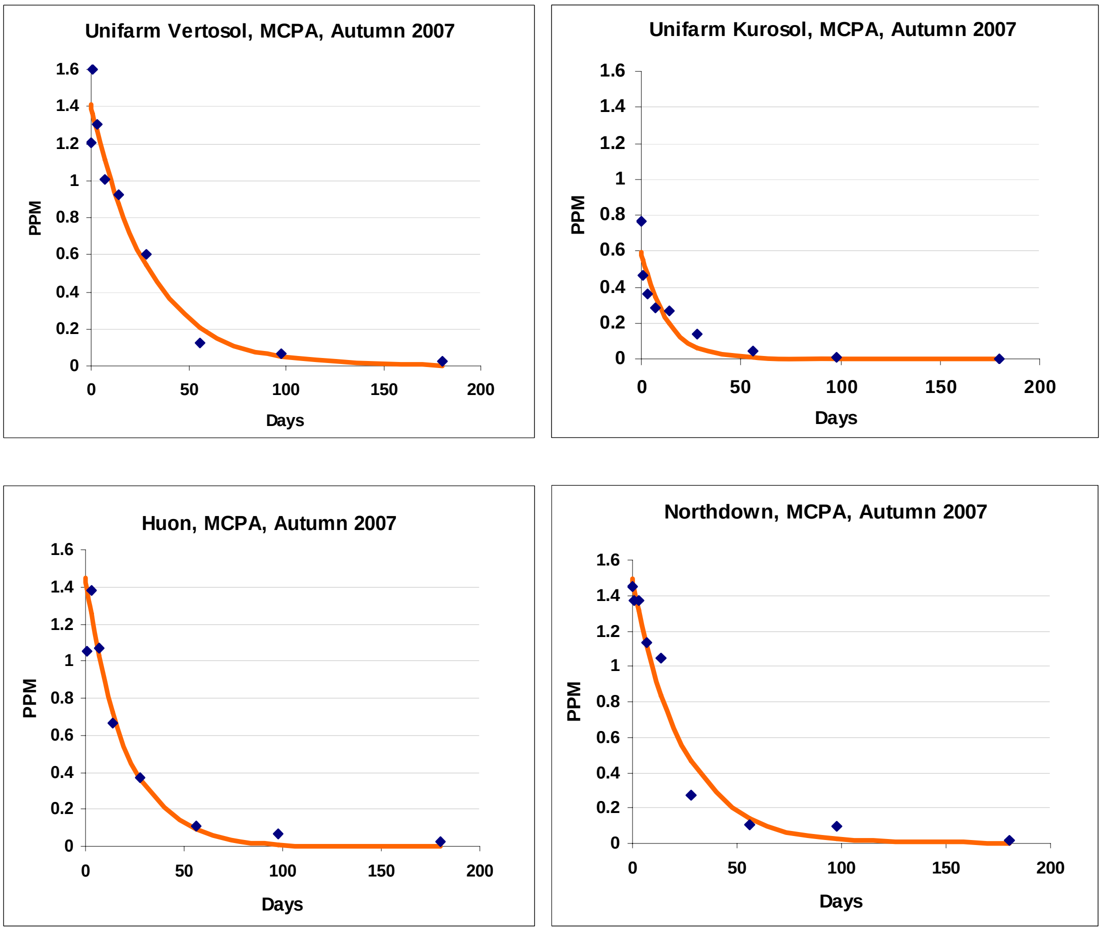


Figure 4-20 Seasonal variation in MCPA half-lives (US = Unifarm Kurosol and UC = Unifarm Vertosol).



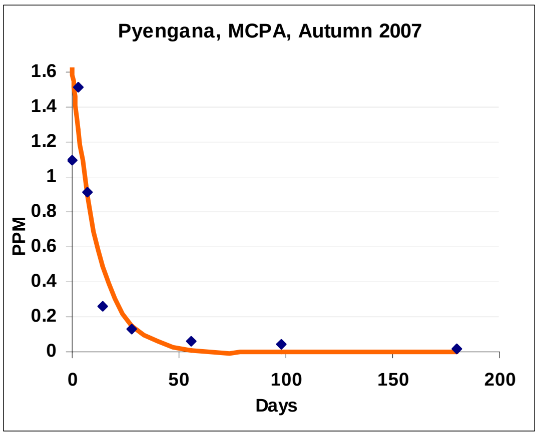


Figure 4-21 First-order equations fitted to field half-life data for MCPA.

4.5.6 Alpha-cypermethrin

Alpha-cypermethrin data are striking in that they indicate little or no differences in half-lives between the autumn and spring seasonal trials (Tables 4.4 and 4.5 and Figures 4-22 and 4-23). The data at each site are very consistent and show the least seasonal variation of the six pesticides tested. This may be due to the strong binding of this pesticide to the soil; in other words, the pesticide is unavailable for microbial decay once adsorbed and is thus less affected by soil temperature and moisture variations. An alternative explanation is that the pesticide is little affected by microbial decay and thus dissipation is not affected by season.

Photodegradation has been identified as a key dissipation mechanism and it may be that the similar photoperiods over the equinox periods following application have led to similar half-lives in each season across all pesticides. Certainly the data suggest that soil moisture and temperature have little impact on dissipation and hence climatic scaling provided in PIRI does not appear to be relevant for alpha-cypermethrin.

The Unifarm Vertosol shows the longest alpha-cypermethrin half-life, which is consistent with almost all pesticides.

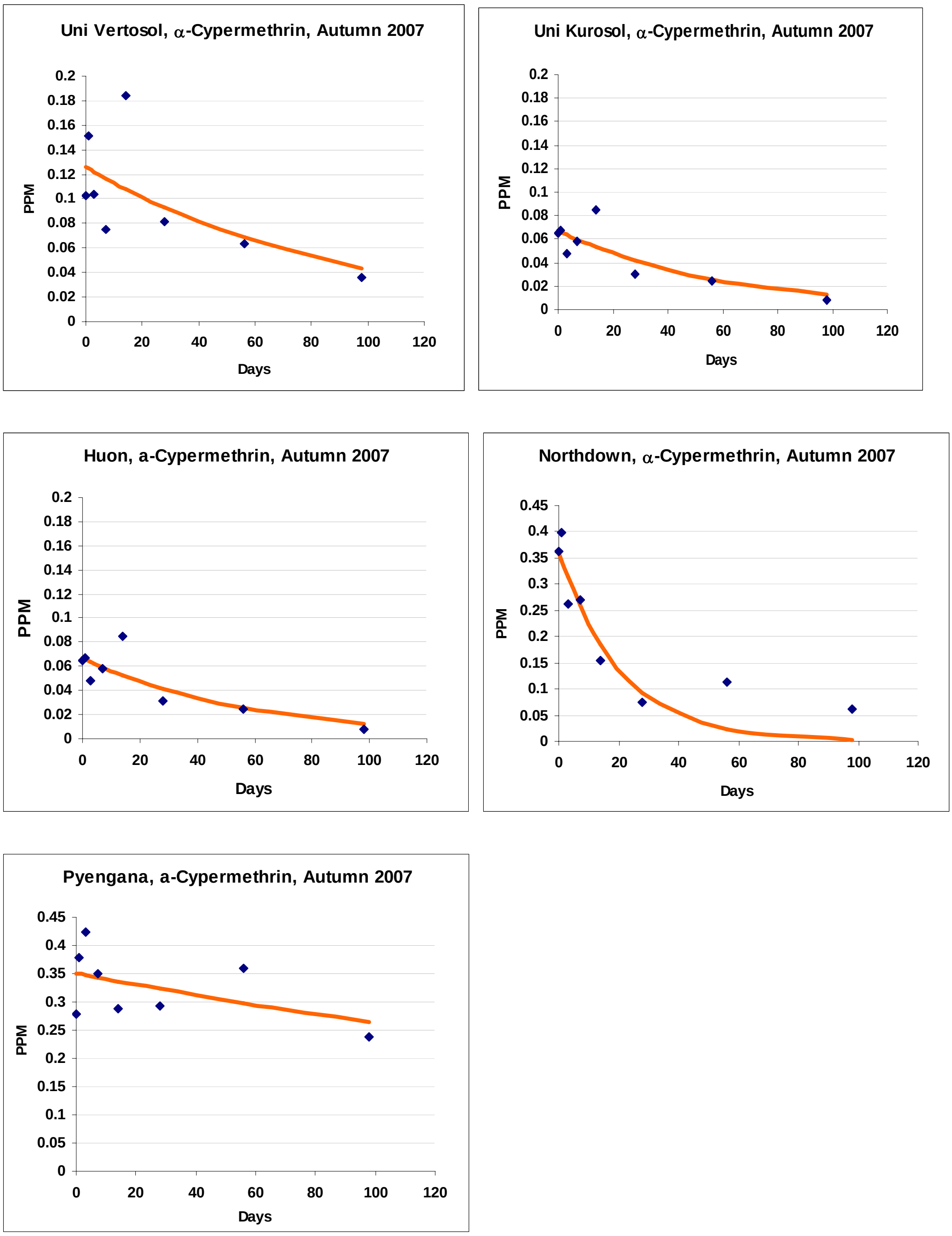


Figure 4-22 First-order equations fitted to field half-life data for alpha-cypermethrin.

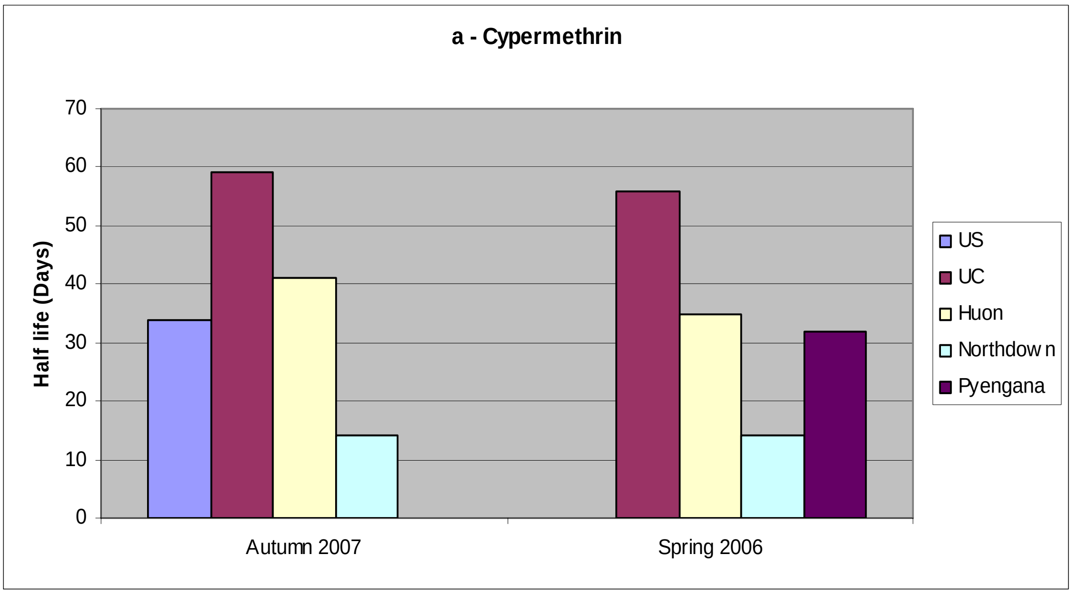


Figure 4-23 Seasonal variation in alpha-cypermethrin half-lives (US = Unifarm Kurosol and UC = Unifarm Vertosol).

4.6. The effect of soil characteristics on autumn 2007 half-lives

4.6.1 Organic carbon

Somewhat surprisingly, when the half-life data were analysed against soil organic carbon content, the only pesticides that showed a significant correlation were simazine and glyphosate (Figures 4-24 and 4-25), with R^2 values of 0.98, and 0.75 respectively. In both cases, increased organic matter content was correlated with reduced half-life.

Interestingly, half-lives for glyphosate on the two Ferrosols were significantly shorter than on any of the other soils tested. Glyphosate sorption is strongly correlated with iron oxide content and the two Ferrosols are relatively rich in iron oxides as well as organic carbon (see Tables 3.2 and 3.4). It is quite plausible that the shorter half-lives observed on these soils are not necessarily caused by faster pesticide breakdown but are actually due to irreversible binding of glyphosate to the iron oxide in the soil.

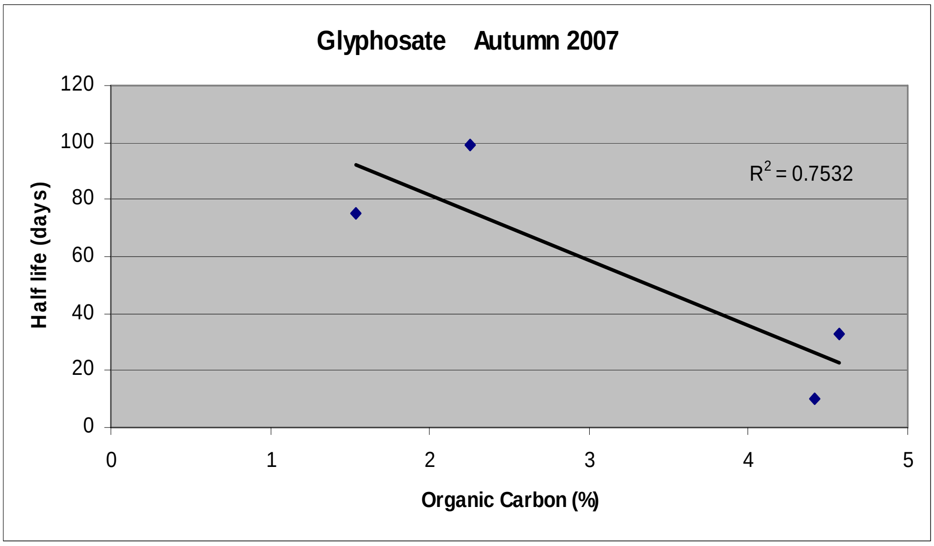


Figure 4-24 The relationship between soil organic matter content and the half-life of Glyphosate.

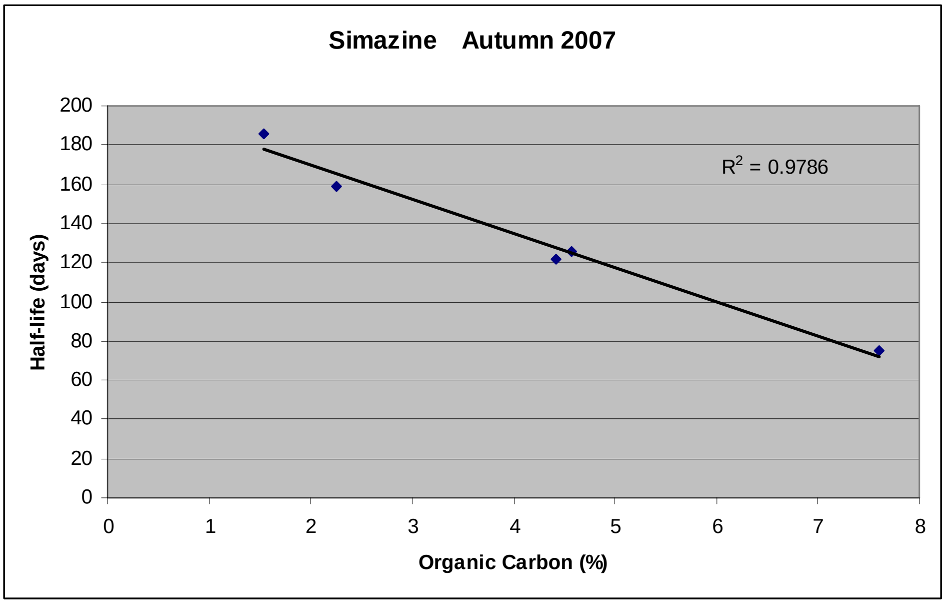


Figure 4-25 The relationship between soil organic matter content and the half-life of simazine (Autumn 2007).

4.6.2 Soil pH

Analysis of the data indicated that the only pesticide where a significant trend can be observed between half-life and soil pH was MCPA (see Figure 4-26). The general trend was that half-life decreased with increasing soil acidity. This is possibly due to increased rate of breakdown due to hydrolysis under more acidic conditions; however, the relationship is relatively weak, with an R^2 value of 0.55 (see Figure 4-26).

Interestingly, there was no relationship whatsoever between soil pH and the half-life of sulfometuron methyl (see Figure 4-27). This is quite surprising as previous research has shown that hydrolysis of sulfometuron methyl tends to occur relatively rapidly under acidic conditions (Harvey *et al.* 1985).

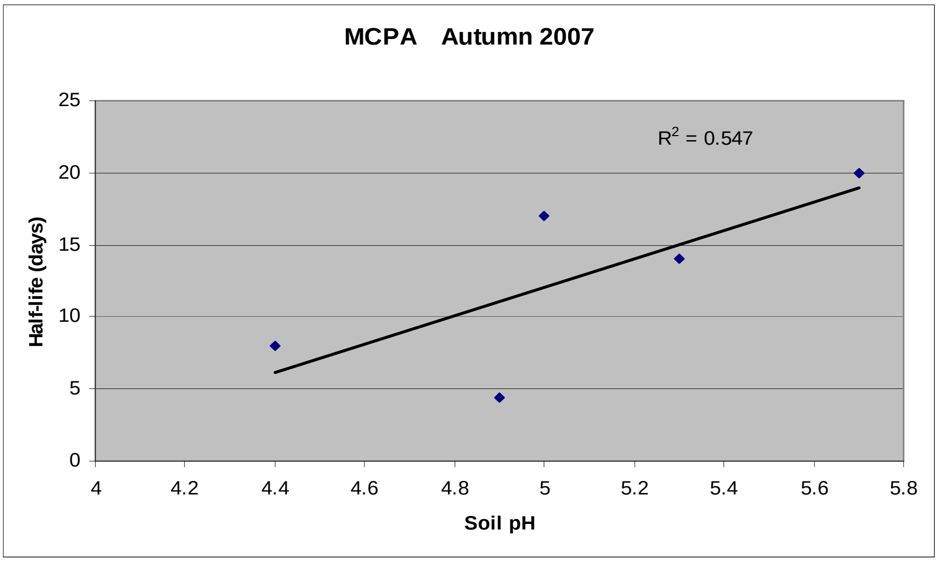


Figure 4-26 The relationship between soil pH and the half-life of MCPA.

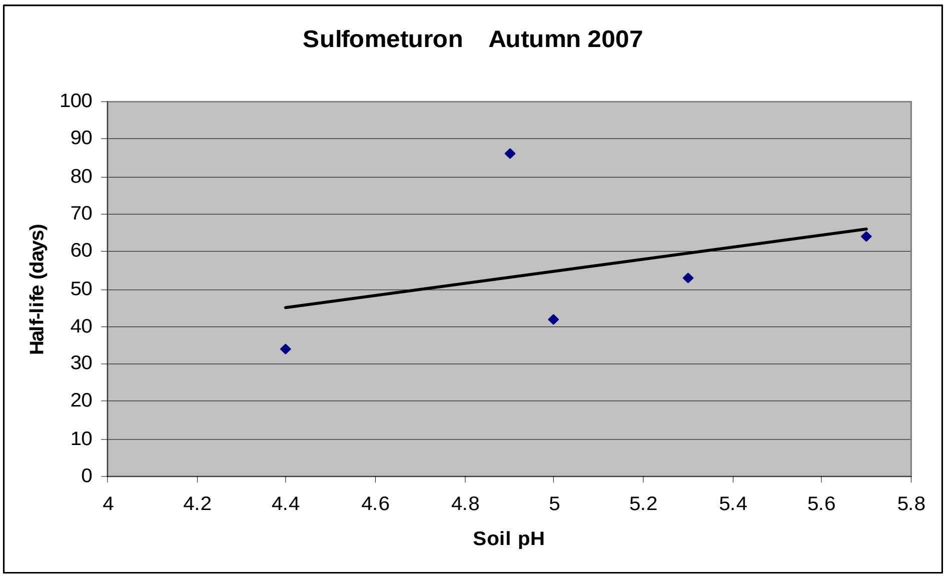


Figure 4-27 The relationship between soil pH and the half-life of Sulfometuron methyl.

4.7. General discussion of half-life trials

The field dissipation studies run over two seasons have produced some interesting results. The majority of pesticides have longer half-lives in the autumn compared to the spring trials as might be expected; alpha-cypermethrin is a notable exception as no difference occurs between seasons. MCPA shows variable behaviour. Sulfometuron appears to be more temperature-driven while MCPA and clopyralid are more sensitive to soil moisture conditions. This fact is supported by the longer than expected Northdown spring half-lives for both MCPA and clopyralid (dry conditions).

Simazine and sulfometuron appear to be the most seasonally affected pesticides with their mean half-lives effectively tripling. The glyphosate mean half-life also doubles as does the mean of clopyralid for the Pyengana and Huon trials. The simazine and sulfometuron data suggest PIRI's doubling of half-life for every 10 °C drop in mean monthly temperature may be an underestimation for these pesticides.

Pesticides on the Unifarm Vertosol have consistently higher half-lives than at the other sites, the only exception being simazine and sulfometuron on the Unifarm Kurosol in autumn 2007. This suggests that Vertosols, clayey soils with shrinking and swelling clays, should be treated as a special case in predicative pesticide models, especially in dry seasons.

5 Leaching studies

5.1. Introduction

Drill core samples for leaching analysis were undertaken at four of the field half-life sites on day 56 and day 180 for the pesticides clopyralid, sulfometuron methyl, MCPA and simazine.

Core samples were taken at day 56 after approximately 100 mm of cumulative precipitation, to allow leaching, at both the Pyengana and Huon sites. A further set of cores were collected at day 180. A hydraulic rig was used to push a 50 mm diameter tube into the soil to a depth of 60–80 cm. Two cores were extracted from each replicate (3) plot at both the University Farm sites and at Pyengana and Northdown (see Appendix A). However, Huon proved too problematic for both the pushrods and the drill rig due to large dolerite stones and boulders in the soil profile. The cores were then brushed off to remove any loose soil that might contaminate the samples. They were sub-sampled at 10 cm lengths, bagged and frozen.

The frozen cores were laboriously peeled and abraded to remove the outer soil to prevent any chance of contamination. They were then ground and sub-sampled ready for extraction as per the half-life sample cores.

Due to the high sorption rate of glyphosate and alpha-cypermethrin, cores were not taken for these pesticides. The day 180 cores were not analysed due to the low levels detected in the day 56 results; they remain in frozen storage.

5.2. Results of leaching studies

The spring trial resulted in detectable leaching to a depth of 40 cm for both simazine and MCPA at all four sites. No leaching was detected below 10 cm for both sulfometuron and clopyralid. The Unifarm sites had a much lower percentage movement of both simazine and MCPA than the Pyengana and Northdown sites. This was initially believed to be a function of rainfall; however, rainfall at the two northern sites was in fact significantly lower. It appears that lower soil moisture levels, due to higher evapo-transpiration, have restricted leaching and soil moisture levels at the Unifarm (Figures 4-10 and 4-11 and Table 4-3).

The lack of detectable sulfometuron and clopyralid in the lower levels could well be a function of dissipation at 56 days rather than absence of leaching. The initial plan for the leaching trial was to sample after 100 mm of rain had fallen. Regrettably, the dry season meant a delay to day 56 that resulted in the low detectability of these two pesticides in the cores.

5.3. Discussion of leaching studies

The dry season in both leaching trials demonstrated a weakness in the field-based dissipation method. Leaching studies need to be done before the majority of the pesticide breaks down and so must be performed as soon after application as possible. If a significant rainfall event does not occur within the first few weeks of a trial, dissipation may be too extensive to achieve useful results. The data for simazine demonstrated that a high application rate of a pesticide with a long half-life produces more robust data. The delayed drilling of cores meant that most of the pesticides had broken down in the upper 10 cm before there had been enough rainfall to facilitate movement of the pesticide down through the soil profile. The longer half-lives observed during the autumn trial (with the exception of MCPA) resulted in a slightly better indication of leaching potential.

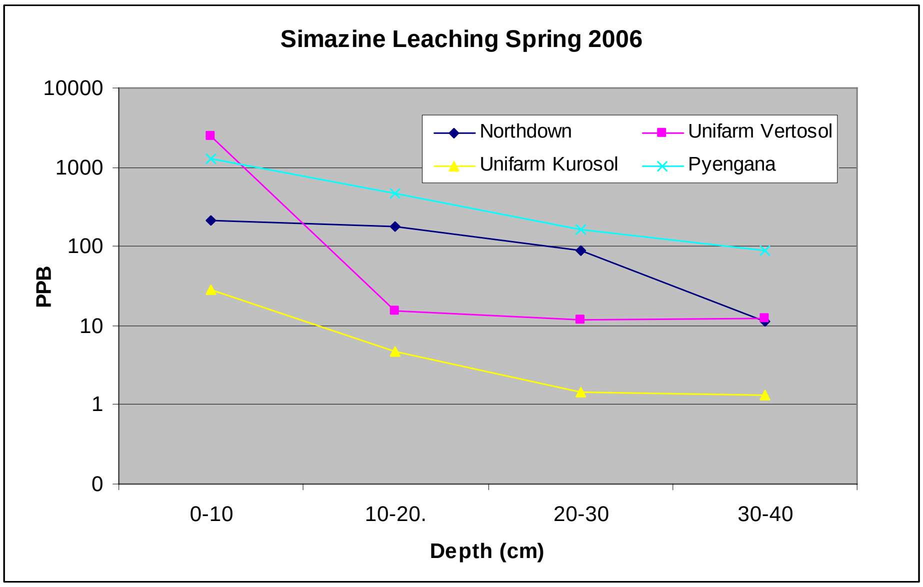


Figure 5-1 Leaching of simazine in the spring 2006 trial.

The spring 2006 trial showed leaching of simazine at all sites, though it was most significant at Pyengana where 1.5% of the pesticide has leached to 30–40 cm and Northdown where 1% has moved to 20–30 cm (Figure 5-1). Simazine was applied at 1200–1400 ppb at all sites except on the Unifarm Vertosol, which was measured at 700 ppb (see Figure 4-4). This represents a 5% leaching loss from the topsoil at Pyengana and approximately 2% at Northdown. However, these leaching loss values should be taken as minimum values in terms of dissipation as degradation may also occur at depths below 10 cm in the soil following leaching, though at a slower rate.

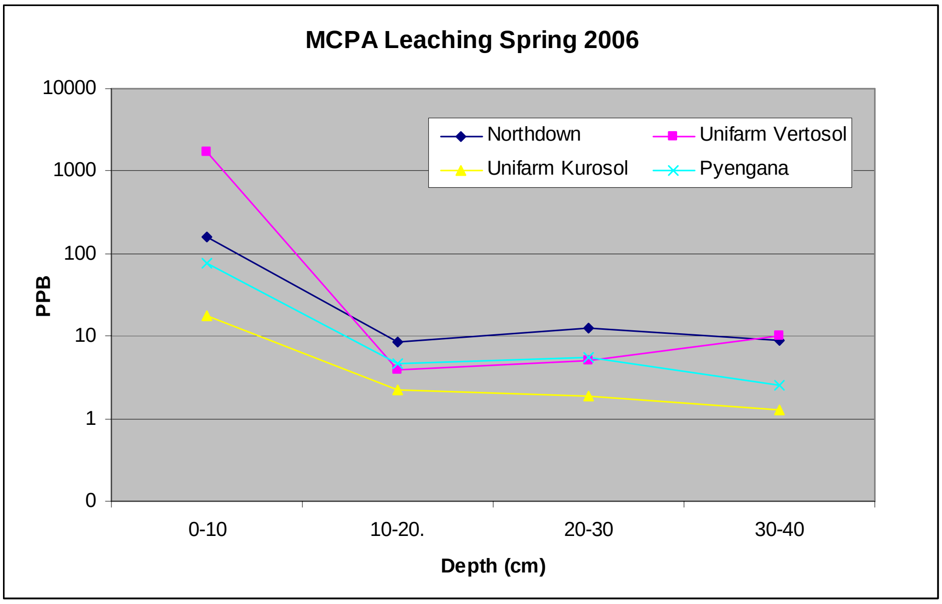


Figure 5-2 Leaching of MCPA in the spring 2006 trial.

While leaching of MCPA has occurred, it is at 10 ppb level or lower and this represents approximately 0.25% of the applied pesticide at Northdown (*ca*. 2500 ppb) and significantly less at the other sites (Figure 5-2).

No leaching was measured for clopyralid or sulfometuron in the 2006 spring trial. The clopyralid application rate was doubled in the autumn 2007 trial to ensure adequate detection limits for any leached pesticide.

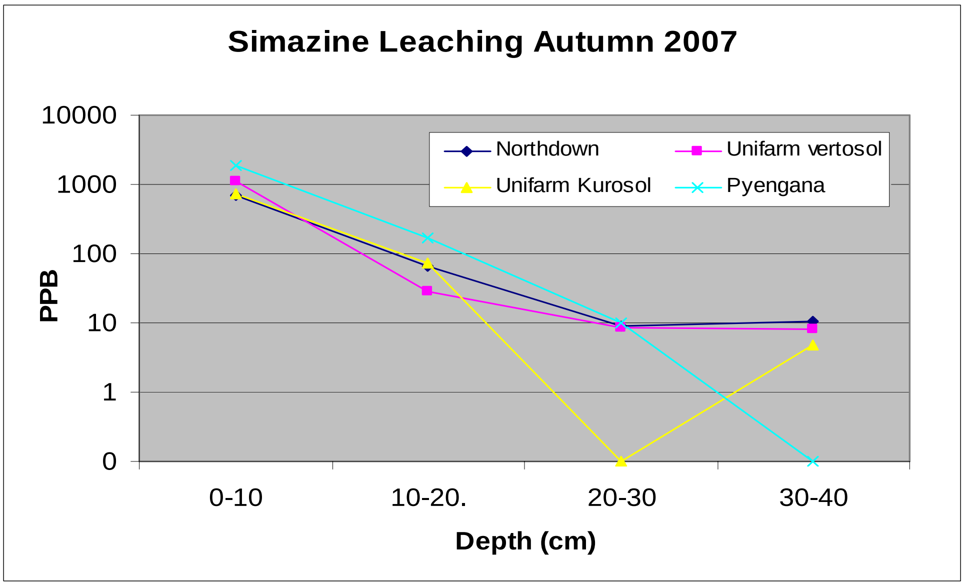


Figure 5-3 Leaching of simazine in the autumn 2007 trial.

Figure 5-3 shows that the leaching of simazine occurred to 30–40 cm at the 10 ppb level but this represents less than 0.3% of the applied pesticide, which was approximately 4000 ppb at most sites (see Figure 4-14). However, approximately 2.5% of the pesticide leached out of the topsoil to the 10–20 cm level as of day 56. This represents only a minimum value as microbial degradation will also have occurred at this depth in the soil.

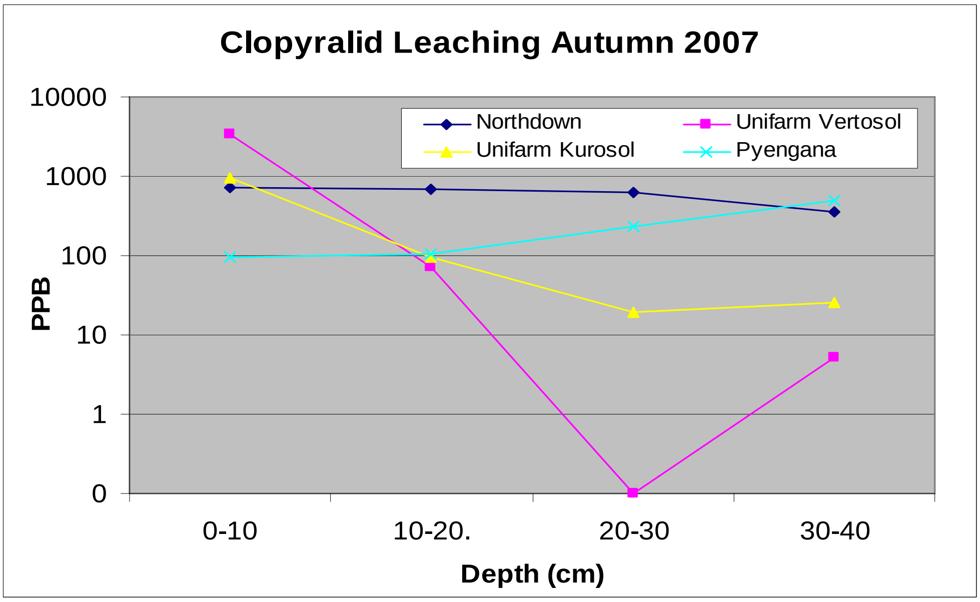


Figure 5-4 Leaching of clopyralid in the autumn 2007 trial.

The leaching of clopyralid in the autumn 2007 trial is significant, especially at Northdown and Pyengana (Figure 5-4). Leaching from the topsoil at these sites represents approximately 50% of the dissipation as measured at day 56 for Northdown and 30% for Pyengana. On the Unifarm soils, the figures are approximately 5% leaching from the Kurosol topsoil and 2% from the Vertosol topsoil.

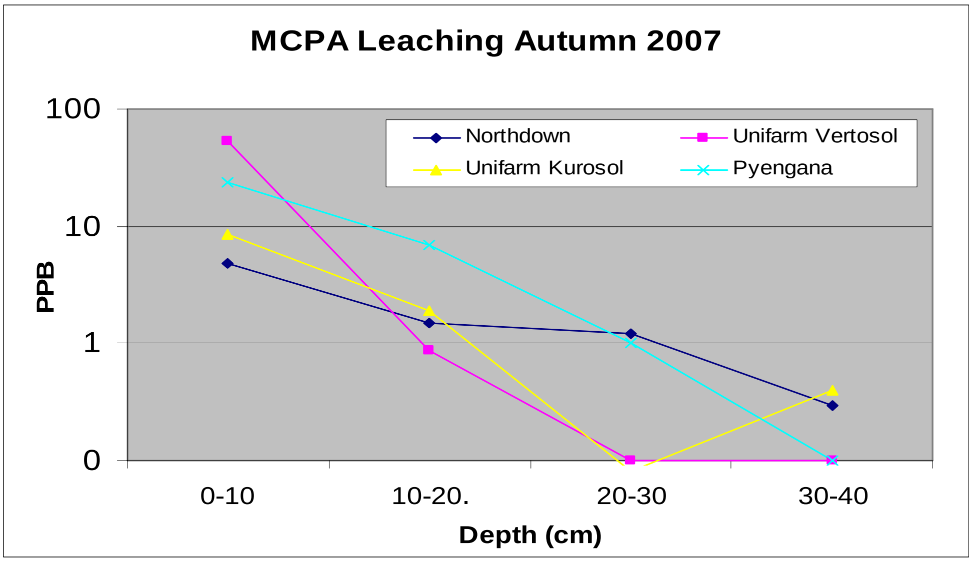


Figure 5-5 Leaching of MCPA in the autumn 2007 trial.

MCPA had dissipated significantly by day 56 in the autumn trial. Figure 5-5 shows MCPA less than 1 ppb was detected at the 30–40 cm level at day 56 and this represents less the 0.1% of the pesticide which was applied on day 0 at 1400 ppb at all sites except on the Unifarm Kurosol, which was 800 ppb (see Figure 4-21). Leaching was most marked in the Pyengana and Northdown soils down to the 20–30 cm level but this represents less than 1% of the applied amount, indicating that leaching of MCPA is not a significant dissipation mechanism.

Figure 5-6 indicates minor leaching of sulfometuron with no movement below the 30–40 cm levels. The pesticide is most mobile in the upper 10–30 cm in the Northdown and Pyengana soils. Day 0 field data indicate approximately 600–800 ppb was applied to the Unifarm and Huon Vertosols and 300–500 ppb to the Northdown and Pyengana Kurosols (Figure 4-12). Thus, day 56 data indicate leaching accounts for approximately 5% of the dissipation at Northdown and Pyengana but is insignificant at the other sites. However, degradation may also have occurred at the deeper levels in the soils and thus these values should be taken as minima.

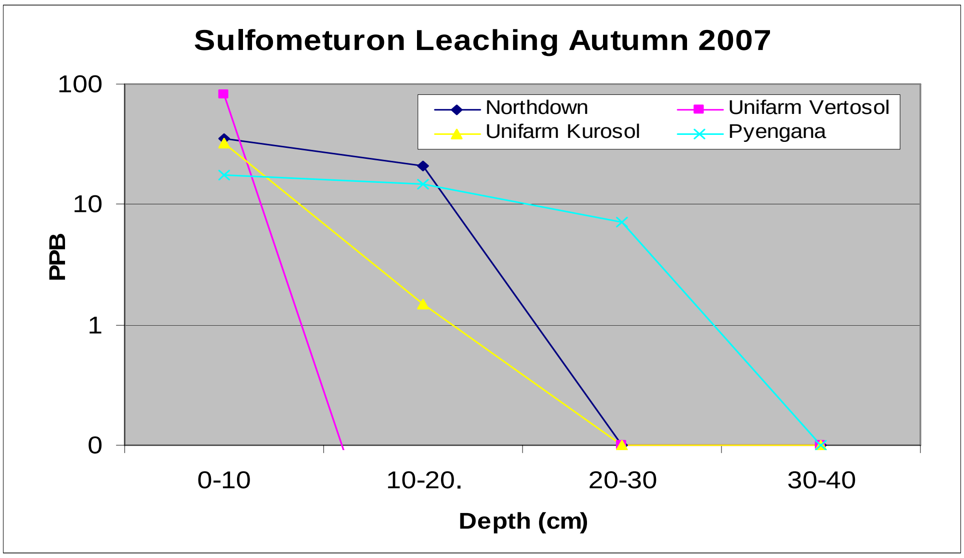


Figure 5-6 Leaching of sulfometuron methyl in the autumn 2007 trial.

5.4. Summary

The autumn 2007 trial differed from the spring 2007 trial in a number of ways. As was initially expected, there was leaching of clopyralid at all four sites tested, particularly at the wetter Northdown and Huon sites. The drier Unifarm sites resulted in most of the clopyralid remaining in the top 10 cm, with only traces of pesticide evident in the lower levels.

Some sulfometuron leaching was detected below 10 cm at the two northern sites and the Unifarm Kurosol but no leaching was detected in the Unifarm Vertosol. Simazine leached in both trials to the 30–40 cm layer, though this was less than 2% of the applied amount.

6 Sorption studies

6.1. Summary

The study has identified the following issues with respect to the use of PIRI in Tasmanian soils:

1. Simazine K_{oc} values appear to be far lower in Tasmanian soils than the value used in pre-project PIRI. Given that this pesticide is used at very high field rates by commercial forestry companies in Tasmania (*ca*. 6 kg/ha), it represents a significant environmental risk for Tasmania.
2. Clopyralid (acid) has significantly higher K_{oc} values than those used in the pre-project version of PIRI. This may explain its absence in runoff waters following spray trials in Tasmania by Forestry Tasmania (Trainer and Volker 2007).
3. Glyphosate has a more than two order of magnitude variation in sorption; soils low in iron oxides represent a greater risk than the literature and PIRI-Tas suggest. However, iron oxide rich soils (Ferrosols) show significantly higher sorption than published literature suggests and PIRI currently over-predicts their environmental leaching/runoff risk.
4. Soil pH values in combination with soil organic mater improve the correlations with sorption of simazine, clopyralid, sulfometuron and MCPA but not glyphosate. This impact of pH on sorption is most significant in MCPA.

Due to its very strong binding to soil organic matter, alpha-cypermethrin is not very mobile and so was not selected for leaching or sorption investigations in the present study.

6.2. Background

Sorption experiments on 1:5 soils:solution ratios were undertaken at five concentrations for sulfometuron, MCPA, clopyralid and simazine with 1:10 ratios for glyphosate. A summary of the sorption data is presented below with K_d, K_{fa} and K_{oc} values calculated.

The sandy surface horizon of the Kurosol at the Unifarm has the lowest Kd for all pesticides. The Northdown Ferrosol and the Pyengana Dermosol share the highest sorption values for all pesticides. The Northdown Ferrosol has the highest soil organic carbon and iron oxide values but is also the most aggregated soil, which may hinder sorption of some pesticides (Stephenson 2007 and Beinum *et al.* 2005).

In summary, clopyralid is the most weakly adsorbed pesticide and glyphosate the most strongly adsorbed. Simazine, MCPA and sulfometuron have similar sorption coefficients and they follow similar trends across each soil type. The acidic Pyengana soil has the highest co-efficient for sulfometuron and MCPA, but the Northdown Ferrosol is higher for simazine, glyphosate and clopyralid.

Organic matter levels appear to be a key driver of the sorption of all pesticides, although soil pH also seems to affect sorption of MCPA, sulfometuron methyl, clopyralid and simazine (Stephenson 2007). Glyphosate sorption varied over 2.5 orders of magnitude and reflects the significant differences in mineralogy of the soils. The Ferrosols and Dermosols are dominated by oxy-hydroxides of iron and aluminium and also kaolin clays while the Unifarm soils are both very low in these constituents. These minerals are known to provide sorption sites for glyphosate.

Stephenson (2007) has completed his honours project on the behaviour of MCPA and sulfometuron and has concluded that soil pH is an important factor affecting the sorption of both pesticides by organic matter. In the case of MCPA, pH was also shown to be a major factor in the clay sorption mechanism (organic matter removed). This was not the case, however, with regard to sulfometuron. It is likely that this difference is due to the fact that MCPA has a higher dissociation constant (pKa) than sulfometuron. The soil organic matter in the Pyengana soil seems to be particularly active in sorption of both these pesticides. The Red Ferrosol at Northdown, despite having very high organic carbon levels, seems to be an outlier with lower than expected sorption of these two pesticides than might be expected. Stephenson (2007) concluded that the very strong aggregation in the Northdown Ferrosol may hinder access to binding sites.

Table 6-1 Sorption data for simazine.

Soil type	**K_d**	**R^2**	**Organic carbon**	**K_{oc}**	**1/n**	**K_{fa}**
Kurosol – Unifarm	0.54^{a}	0.94	1.54	35^{a}	0.95^{b}	1.7^{a}
Vertosol – Unifarm	2.21^{ab}	0.99	2.25	98^{b}	0.91^{ab}	5.5^{b}
Ferrosol – Huon	3.27^{bc}	0.98	4.42	74^{ab}	0.86^{a}	12.3^{d}
Ferrosol – Northdown	5.60^{d}	0.99	7.61	74^{ab}	0.91^{ab}	12.7^{d}
Dermosol – Pyengana	4.35^{cd}	0.99	4.57	95^{b}	0.92^{ab}	9.7^{c}
Mean	3.2			75		
Published range	0.5 – 4.5			44-445		
PIRI value				130		

Means not sharing common superscripts differ ($p = <0.05$).

The K_d and K_{fa} values for simazine cover the published ranges and are highest in the organic carbon rich soils (Table 6-1). The K_{oc} values are relatively constant and indicate the importance of organic matter as a sorption mechanism. However, these values are considerably lower, the mean being only 60% of the value currently used in PIRI (Vencill 2002). This would mean that the pre-project version of PIRI is significantly underestimating the leaching risk of simazine in Tasmanian soils. Simazine is used at high field rates by commercial forestry companies in Tasmania (*ca.* 6 kg/ha); it represents a higher environmental risk than pre-project PIRI predicts. A further problem for simazine is the very low K_{oc} on the Kurosol soil (acidic sand), meaning that leaching could be a significant issue on these soils.

Table 6-2 Sorption data for clopyralid (acid).

Soil type	**K_d**	**R^2**	**Organic carbon**	**K_{oc}**	**1/n**	**K_{fa}**
Kurosol – Unifarm	0.27^a	0.94	1.54^a	18^a	0.84^a	1.02^a
Vertosol – Unifarm	0.37^a	0.96	2.25	16^a	0.92^a	0.73^a
Ferrosol – Huon	1.15^b	0.99	4.42	26^a	0.90^a	2.39^a
Ferrosol – Northdown	1.51^b	0.99	7.61	20^a	0.93^a	2.61^a
Dermosol – Pyengana	1.19^b	0.93	4.57	26^a	0.92^a	2.48^a
Mean	0.90			21		
Published values	0.41			0.4–13		
PIRI value				4		

Means not sharing common superscripts differ ($p = <0.05$).

The K_d values for clopyralid (acid) are equal to and above the published ranges (Table 6-2). The K_{oc} values are relatively constant and indicate that organic matter and acidic soil conditions are important for sorption. The mean K_{oc} value is five times higher than the value used in the pre-project version of PIRI, indicating that PIRI would over-predict leaching and runoff potential. This may help explain the low readings on clopyralid when recently tested in sprayed coupes in Tasmania by Forestry Tasmania (Trainer and Volker 2007). We undertook our sorption studies on the acid form of the pure pesticide. Sorption may also need to be completed for the triisopropanolamine salt formulations used in the product 'Lontrel'.

Table 6-3 Sorption data for MCPA (acid).

Soil type	**K_d**	**R^2**	**Organic carbon**	**K_{oc}**	**1/n**	**K_{fa}**
Kurosol – Unifarm	1.4^a	0.99	1.54	91^{ab}	0.84^b	5.2^a
Vertosol – Unifarm	1.6^a	0.99	2.25	72^a	0.75^a	10.5^b
Vertosol2 – Unifarm	0.7	0.92		44		
Ferrosol – Huon	7.3^b	0.99	4.42	165^c	0.70^a	59.8^d
Ferrosol – Northdown	9.1^c	0.99	7.61	120^b	0.74^a	60.1^d
Dermosol – Pyengana	12.4^d	0.99	4.57	270^d	0.84^b	36.8^c
Mean	5.4			127		
LSD (p=0.05)	1.6	-			0.05	3.4
Published values				110		
PIRI values				110		

Means not sharing common superscripts differ ($p = <0.05$).

MCPA (acid) K_d and K_{fa} values vary over an order of magnitude (Table 6-3). Even the K_{oc} for MCPA varies by a factor of four, which presents a problem for PIRI's reliance on K_{oc} to represent a normalised 'representative' sorption coefficient. This wide variation in Koc suggests that other factors such as soil pH and mineralogy affect sorption. It is noted that the lower pH soils have higher K_{oc} values; the reader can refer to Stephenson (2007) for a further discussion of the interaction of pH and organic carbon levels on sorption in these soils. The mean K_{oc} for MCPA is 30% higher for the Tasmanian soils studied than the published mean value (Vencill 2002).

Table 6-4 Sorption data for sulfometuron methyl.

Soil type	**K_d**	**R²**	**Organic carbon**	**K_{oc}**	**1/n**	**K_{fa}**
Kurosol – Unifarm	1.4^{a}	0.99	1.54	89^{b}	0.78^{a}	7.4^{a}
Vertosol – Unifarm	1.6^{a}	0.98	2.25	66^{a}	0.80^{ab}	6.3^{a}
Vertosol 2 - Unifarm	0.3	0.99		18		
Ferrosol – Huon	5.4^{b}	0.99	4.42	123^{c}	0.81^{ab}	20.8^{c}
Ferrosol – Northdown	5.8^{b}	0.99	7.61	76^{ab}	0.85^{b}	16.6^{b}
Dermosol – Pyengana	7.3^{c}	0.99	4.57	160^{d}	0.83^{ab}	24.6^{d}
Mean	3.6			89		
LSD (p=0.05)	0.6	-		14.5	0.05	2.3
Published ranges	0.3 – 3			61–122 (78)		
PIRI values				85		

Means not sharing common superscripts differ (p = <0.05).

The K_d values for sulfometuron methyl are equivalent to and above the published ranges (Table 6-4). Once again they are highest in the more acidic and higher organic carbon soils. The K_{oc} values used in PIRI are a little lower (15% less) than the mean for the Tasmanian soils studied, suggesting that the organic matter in these soils is more active, perhaps a feature of the lower soil pH values. Thus, leaching and runoff concentrations may be slightly over-predicted by PIRI.

Table 6-5 Sorption data for glyphosate (IPA).

Soil type	**K_d**	**R^2**	**Organic carbon**	**K_{oc}**	**1/n**	**K_{fa}**
Kurosol – Unifarm	18^{a}	0.85	1.54	1169^{a}	0.59^{a}	745^{a}
Vertosol – Unifarm	599^{a}	0.87	2.25	$26\,622^{ab}$	0.58^{a}	7050^{b}
Ferrosol – Huon	2302^{b}	0.93	4.42	$52\,081^{b}$	0.72^{b}	8556^{bc}
Ferrosol – Northdown	4318^{c}	0.92	7.61	$56\,741^{b}$	0.72^{b}	$13\,596^{c}$
Dermosol – Pyengana	1540^{ab}	0.84	4.57	$33\,698^{b}$	0.57^{a}	$13\,326^{c}$
Mean	1755			34 060		
Published range	320–600					
PIRI value				24 000		

Means not sharing common superscripts differ (p = <0.05).

The data for glyphosate (Table 6-5) show an extreme variation in K_{oc} and suggest that sorption is due to other factors such as soil mineralogy. K_{oc} may not be an appropriate predictor for glyphosate behaviour for all soils in predictive models (i.e. in peat and other high carbon soil, low iron oxides may represent a greater risk than predicted). Certainly glyphosate is the most soil-type-sensitive pesticide and is very dependent on iron oxide content of the soil. However, despite this range, the lowest K_{oc} in this study was still very high at over 1000 (Kookana and Correll 2008).

6.3. Correlations between soil characteristics and sorption

The effect of various soil characteristics on the sorption of each pesticide was tested using regression analysis. In all cases it was found that of all the soil characteristics quantified, organic matter had the largest effect upon sorption. However, a stronger relationship was obtained using a combined measure of organic matter content and soil pH for MCPA, sulfometuron methyl, clopyralid and simazine. In all four cases, sorption tended to increase with decreasing pH and increasing organic matter content. Thus, organic matter and soil pH was combined into a single value by multiplying the soil's organic matter content by the inverse of the soil's pH. For convenience, this value will be referred to as the soil's Z-value. Table 6-6 shows a summary of this data.

Figure 6-1 shows the regression relationship between sorption of simazine and organic carbon percentage, while Figure 6-2 shows the regression relationship between sorption of simazine and the soil's Z value. When using organic matter content alone, a p-value of 0.012 is obtained, indicating a statistically significant relationship. When using a combined measure of organic matter content and soil pH (Z), a lower p-value of 0.009 is obtained, indicating a stronger relationship. The same relationship is shown more clearly for clopyralid in Figures 6-3 and 6-4.

The same pattern is also true for both MCPA and sulfometuron methyl. In each case, organic matter content is clearly the most important soil characteristic affecting sorption, but by using a combined measure of organic matter content and soil pH a stronger relationship can be obtained. This was not true, however, in the case of glyphosate.

For all pesticides tested, soil cation exchange capacity was found to have no significant statistical relationship with sorption. Figure 6-5 (below) shows the relationship between soil CEC and sulfometuron methyl sorption. The data show no significant (p = >0.05) regression relationship between the organic carbon normalised sorption coefficient (K_{oc}) and soil CEC.

Table 6-6 Summary of regression analysis on the sorption coefficient (K_d) versus various soil characteristics for all soils tested.

Chemical	**Soil characteristic**	**R^2 value**
Simazine	OC (%)	0.91
	Soil pH	0.09
	CEC	0.005
	Z	0.93
Clopyralid	OC (%)	0.91
	Soil pH	0.15
	CEC	0.06
	Z	0.92
Glyphosate	OC (%)	0.96
	Soil pH	0.01
	CEC	0.09
	Z	0.89
MCPA	OC (%)	0.57
	Soil pH	0.44
	CEC	0.24
	Z	0.68
Sulfometuron	OC (%)	0.59
	Soil pH	0.36
	CEC	0.32
	Z	0.69

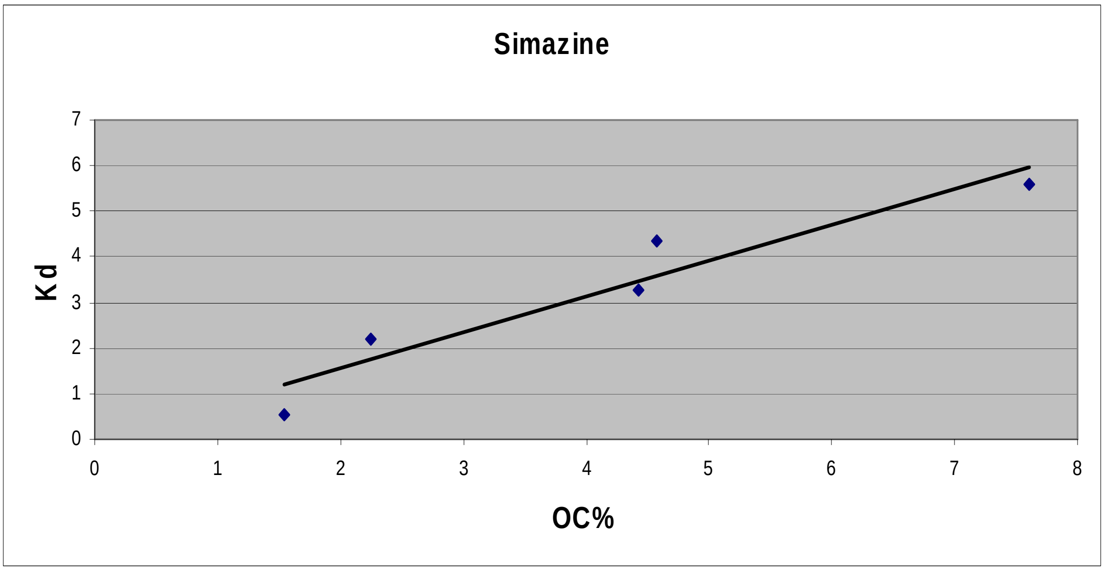


Figure 6-1 The relationship between organic matter content and simazine sorption.

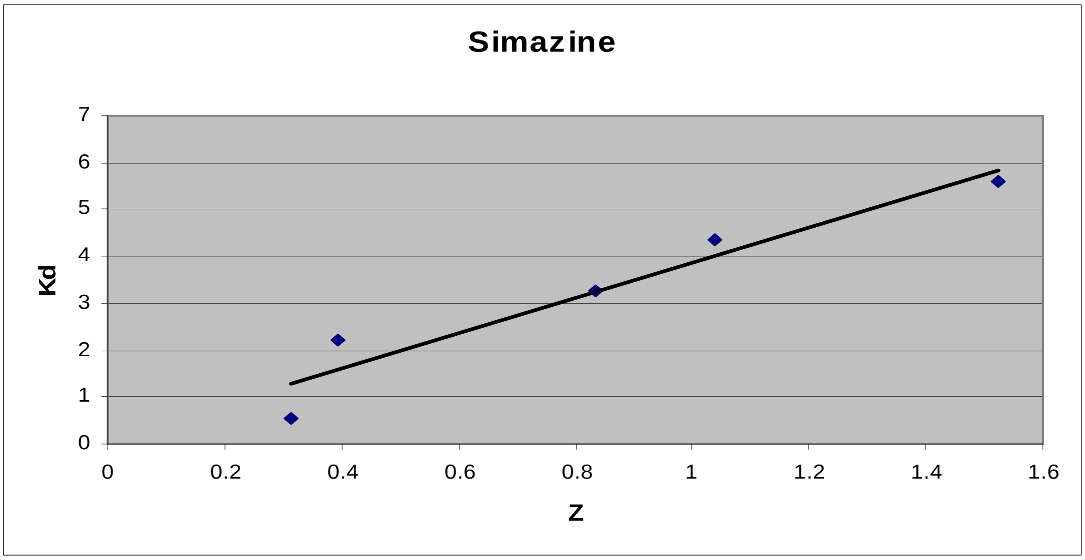


Figure 6-2 The relationship between a combined measure of organic matter and soil pH on simazine sorption.

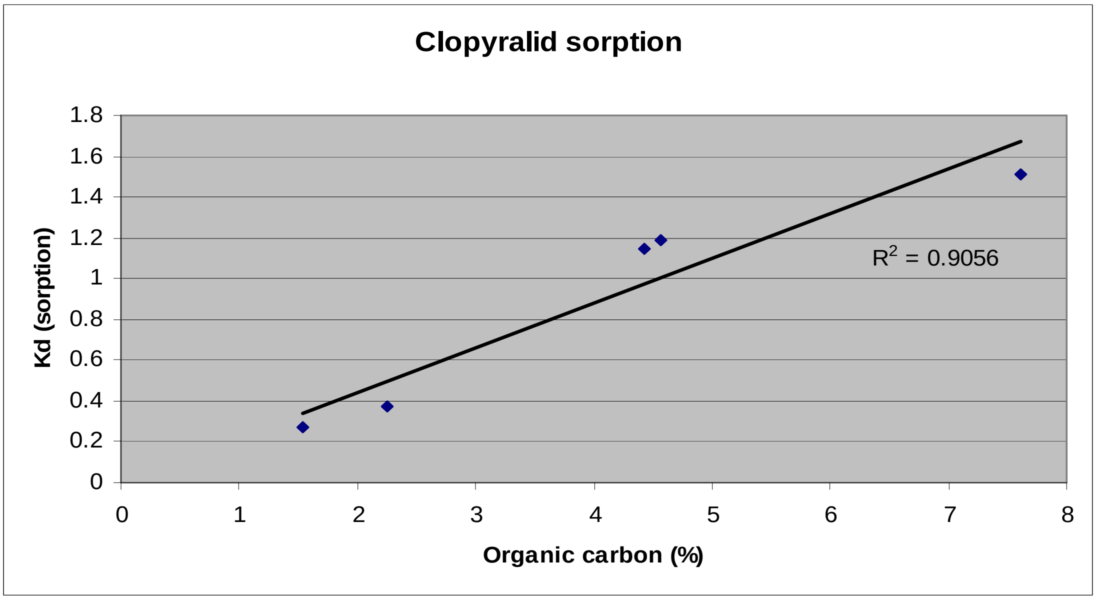


Figure 6-3 The relationship between organic matter content and clopyralid sorption.

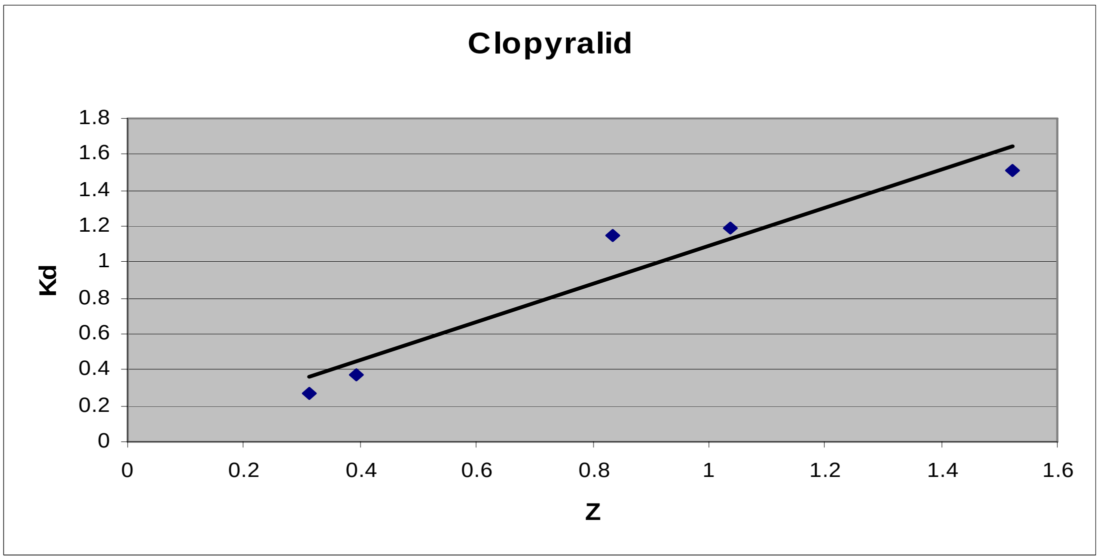


Figure 6-4 The relationship between a combined measure of organic matter and soil pH on clopyralid sorption.

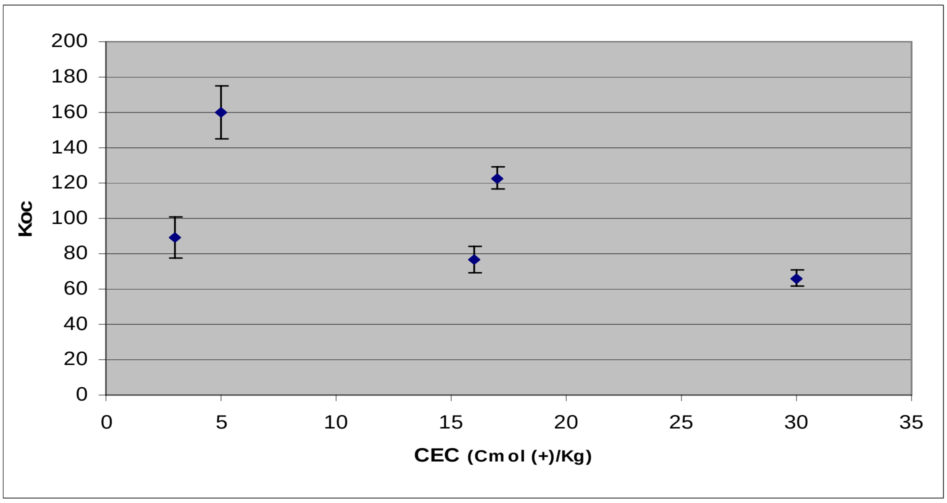


Figure 6-5 The relationship between cation exchange capacity on sulfometuron sorption.

6.4. Sorption classification

Figure 6-6 shows a diagram of the Giles classification system for sorption isotherms. The sorption patterns observed in the batch tests varied greatly between the different pesticides and soil types. These are outlined below.

1. Glyphosate loosely followed an L2 type isotherm under the Giles classification system (Giles *et al.* 1960) for all soils tested. This indicates that as the concentration of glyphosate in solution is increased, the availability of sorption sites for the pesticide is reduced (Sposito 1984). However, these sorption tests were done at very high concentrations due to analytical detection limitations.
2. Clopyralid (acid) followed an L1 type isotherm under the Giles classification system (Giles *et al.* 1960) for all soils tested. Again, this is indicative of the fact that as the concentration of the pesticide in solution is increased, the availability of soil colloids for sorption is reduced (Sposito 1984), although to a lesser extent than was the case with glyphosate.
3. Simazine followed a C1 type isotherm under the Giles classification system (1960) for all soils with the exception of the Kurosol (Unifarm sandy topsoil) which displayed an L2 type isotherm. The presence of a C1 type isotherm indicates that the availability of sorption sites remains constant as the solution concentration is increased (Giles *et al.* 1960). This difference in sorption patterns between soil types is possibly due to the fact that the sandy soil has very low organic matter content. This causes the saturation of sorption sites to occur at lower simazine concentrations than for the other soil types tested.

4. MPCA (acid) on the other hand displayed the opposite trend, with the sandy soil and clay soil on the Unifarm both following a C1 type sorption isotherm and the other soils all displaying L-type sorption isotherms.
5. In the case of sulfometuron methyl, all five soils followed a C1 type sorption isotherm under the Giles classification system (1960). Again, the presence of a C1 type isotherm indicates that the availability of sorption sites remains constant as the solution concentration is increased (Giles *et al.* 1960).

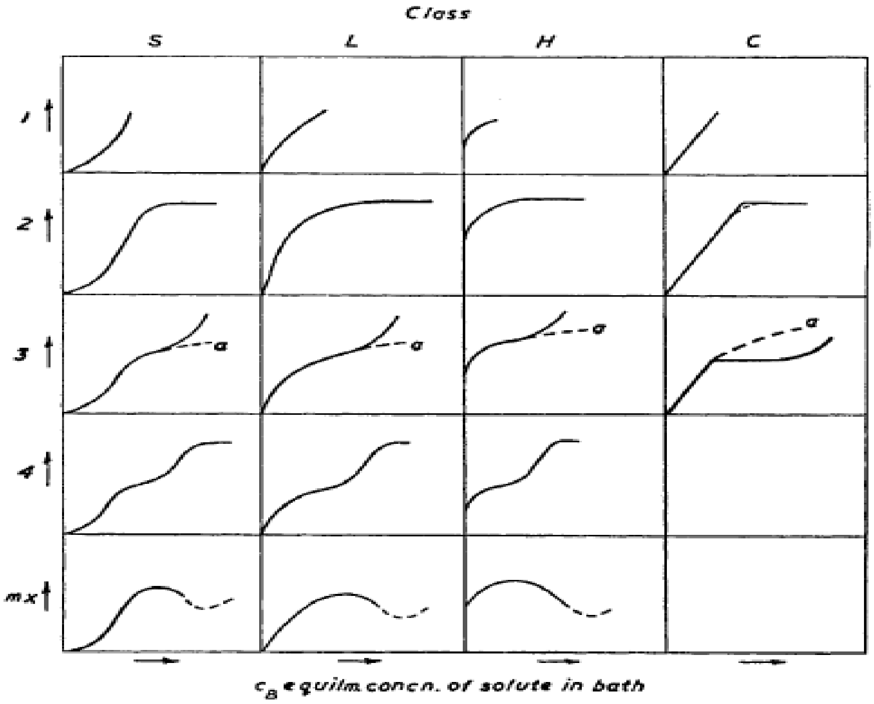


Figure 6-6 The Giles classification system (Giles *et al.* 1960).

6.5. Soil fractionation experiments

Unifarm Vertosol, Unifarm Kurosol, Pyengana Dermosol and a second more alkaline Vertosol from the Unifarm were prepared by pre-treatment with hydrogen peroxide in order to remove the soils' organic matter. This was done in order to determine the effect of organic matter on pesticide sorption. Due to practicalities, this section of the experiment was only performed for MCPA and sulfometuron methyl. The fractionation method used was that of Whitton and Churchman (1987). The samples were then used for a further soil sorption experiment for both sulfometuron methyl and MCPA. This was undertaken using the same method as for the standard sorption studies above.

The results of the experiments on the treated soils indicated that for both MCPA and sulfometuron methyl, the concentrations used above 0.1 ppm had an unacceptable level of inaccuracy and as such were not suitable for statistical analysis. In the case of MCPA this meant that there were only two reliable sets of concentrations (0.01 ppm and 0.1 ppm), while for sulfometuron methyl there was only one reliable set of concentrations (0.1 ppm). The treated soils can still be accurately compared with each other at these dilute concentrations and can also be compared to the untreated soils at the corresponding concentrations. It is important to realise, however, that the results attained are specific to the concentrations used and cannot necessarily be extrapolated to explain what would happen at higher pesticide concentrations.

Table 6-7 The effect of peroxide treatment on MCPA sorption at dilute concentrations.

Soil type	**K_d untreated soil**	**K_d – minus organic matter**
Brown Kurosol (Unifarm)	4.3^d	1.6^b
Black Vertosol (Unifarm)	9.7^e	0.47^a
Brown Dermosol (Pyengana)	40.8^f	2.4^c

Means not sharing common superscripts differ ($p = <0.05$).

Table 6-7 shows that in the case of all three soils tested, treatment with hydrogen peroxide to remove the soils' organic matter resulted in a significant reduction in the amount of MCPA adsorbed.

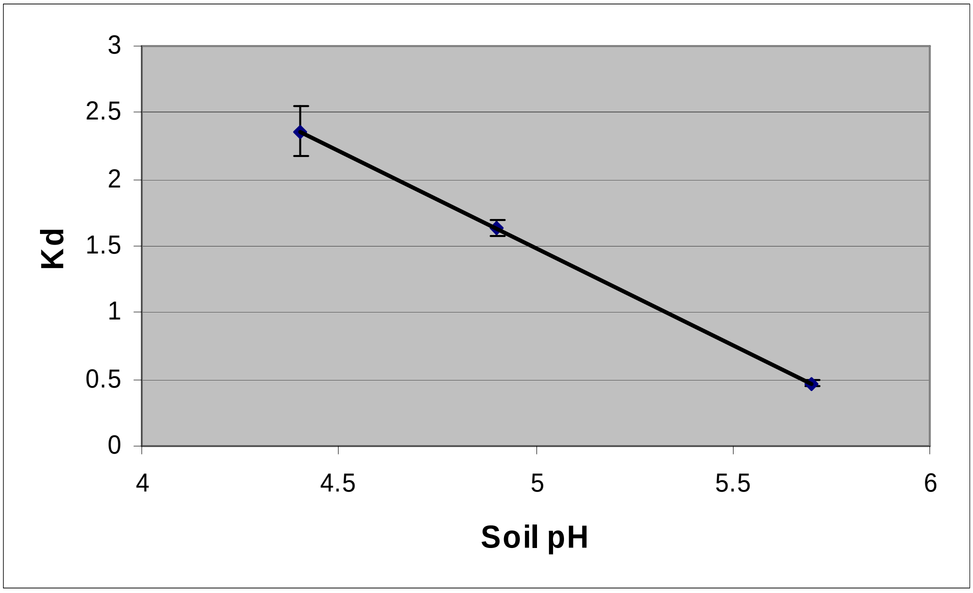


Figure 6-7 The relationship between soil pH and the sorption of MCPA by peroxide treated soil.

Figure 6-7 above shows the relationship between soil pH and the sorption of MCPA on peroxide treated soil. The data show a very strong ($p = <0.01$) regression relationship between the two variables. The data follow the linear relationship $K_d = -1.5 \times$ soil pH + 8.7 and has an R^2 value of 1.00.

Table 6-8 The effect of peroxide treatment on sulfometuron methyl sorption at dilute concentrations.

Soil type	**K_d – untreated soil**	**K_d – minus organic matter**
Brown Kurosol (Unifarm)	3.5^b	0.40^a
Black Vertosol (Unifarm)	3.3^b	2.5^b
Brown Dermosol (Pyengana)	16.8^c	1.0^a

Table 6-8 shows that in the case of the Unifarm Kurosol and Pyengana Dermosol, treatment with hydrogen peroxide to remove the soils' organic matter resulted in a reduction in the amount of sulfometuron methyl adsorbed. In the case of the Black Vertosol, however, treatment with hydrogen peroxide had no statistically significant effect on sorption. This is not to say that organic matter has no effect at all on the sorption by the Vertosol soil, but merely indicates that the difference in this instance was not statistically significant. Unlike MCPA, in the case of sulfometuron methyl, no significant relationship was noted between soil pH and the level of sorption onto the peroxide treated soil.

7 Conclusions and recommendations

The research results from this TIAR project have been reviewed and many included in the new version of PIRI-Tas. Three K_{oc} coefficients and two of the half-lives have been modified in PIRI-Tas to reflect the data presented and to refine local pesticide risk outputs. Work on a review of other pesticides in the same chemical families (i.e. sulfonylurea's, glycines, triazines, pyrethroids, phenoxys, picolinic acids) is suggested to ensure the results are fully and more widely applied.

This study has shown a wide range of half-lives, most of which are affected by season, alpha-cypermethrin being a notable exception. Pre-project PIRI adopted a doubling in half-life for every 10 °C drop in temperature; this would under-predict risks of autumn and winter applications of simazine (triazines) and sulfometuron (sulfonylurea's) due to a three-fold increase in half-life in Tasmanian conditions from spring/summer to autumn/winter. Changes in PIRI-Tas to use a 2.6 multiplier for temperature will help to resolve this issue. However, PIRI-Tas may over-estimate the risk for alpha-cypermethrin and MCPA due to absent or weak seasonal effects associated with these pesticides.

Sorption coefficients (K_d) on differing soils range over 0.5 to 1 orders of magnitude for most pesticides and over to 2 orders for glyphosate (glycines). They all were positively correlated to soil organic matter levels but these correlations are improved with the use of soil pH, with the exception of glyphosate. In four of the five pesticide studies the K_{oc}, which is a normalised sorption coefficient based on soil organic matter, varied by a factor of three or more, which makes a single sorption coefficient for each pesticide in pre-project PIRI what questionable. In fact for sulfometuron there was an order of magnitude variation in K_{oc}. It may be that knowledge of the nature of the organic matter (e.g. pasture, cropped, forest, the soil pH and texture class) could be incorporated to reduce this variation. Certainly this study has shown that soil pH can improve the correlation with sorption in several pesticides (MCPA, sulfometuron, clopyralid and simazine). CSIRO have now included an algorithm in PIRI-Tas which adjusts the K_{oc} based on soil pH and the pKa of the pesticide (Kookana and Correll, 2008).

There was significant leaching of clopyralid on the well drained soils (Pyengana and Northdown) over the autumn–winter trial period. Simazine also appears to be somewhat mobile and at high rates of application this could also be an issue for autumn applications on free-draining soils.

Simazine's (triazine) high application rates (*ca.* 6 kg/ha), extended autumn–winter half-life, low and variable sorption and demonstrated leaching potential mean it represents the most significant environmental risk for Tasmanian streams if not applied using best practice and knowledge of the soil and environmental conditions.

The Vertosols (dark cracking clay soils) represented a special environmental case with pesticides in these soils having very long half-lives, relatively weak sorption coefficients and limited leaching potential. These soils are common on floodplains in Tasmania and thus surface runoff and topsoil erosion represent potential pathways for pesticides to move to waterways, especially if augmented by surface drains (e.g. raised beds or hump and hollow).

More research using controlled leaching studies on simazine, clopyralid and MCPA would be useful in a Tasmanian context. Further studies on desorption and bioavailability of pesticides like glyphosate, simazine and MCPA from soils and sediments would help elucidate issues on aquatic health.

There is a good argument for more study of leachable pesticides on sub-surface soil horizons in order to present a picture of the fate of pesticides below the topsoil.

Appendix A – Site photographs, location map and drilling core sampling

Pesticide ½ Life and leaching trial sites

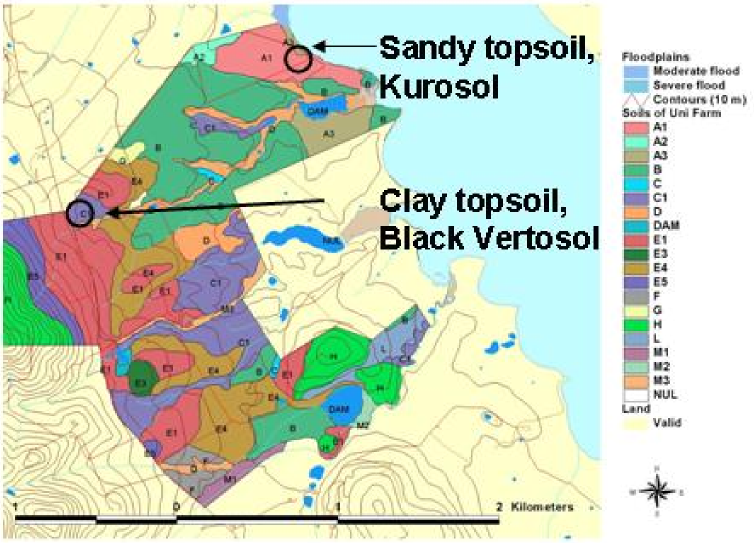
Northdown site east Devonport (overlooking Devonport Airport), soil is a "snuffy" Red Ferrosol, site is quite exposed and in intensive agricultural setting. Geology is Tertiary Basalt and the elevation is 90 m)

The Pyengana site is on a Gunns Ltd block on the confluence of the South George River and the Margaret Creek. Soil is yet to be described but is a sand loam on granodiorite (note outcrops at site)

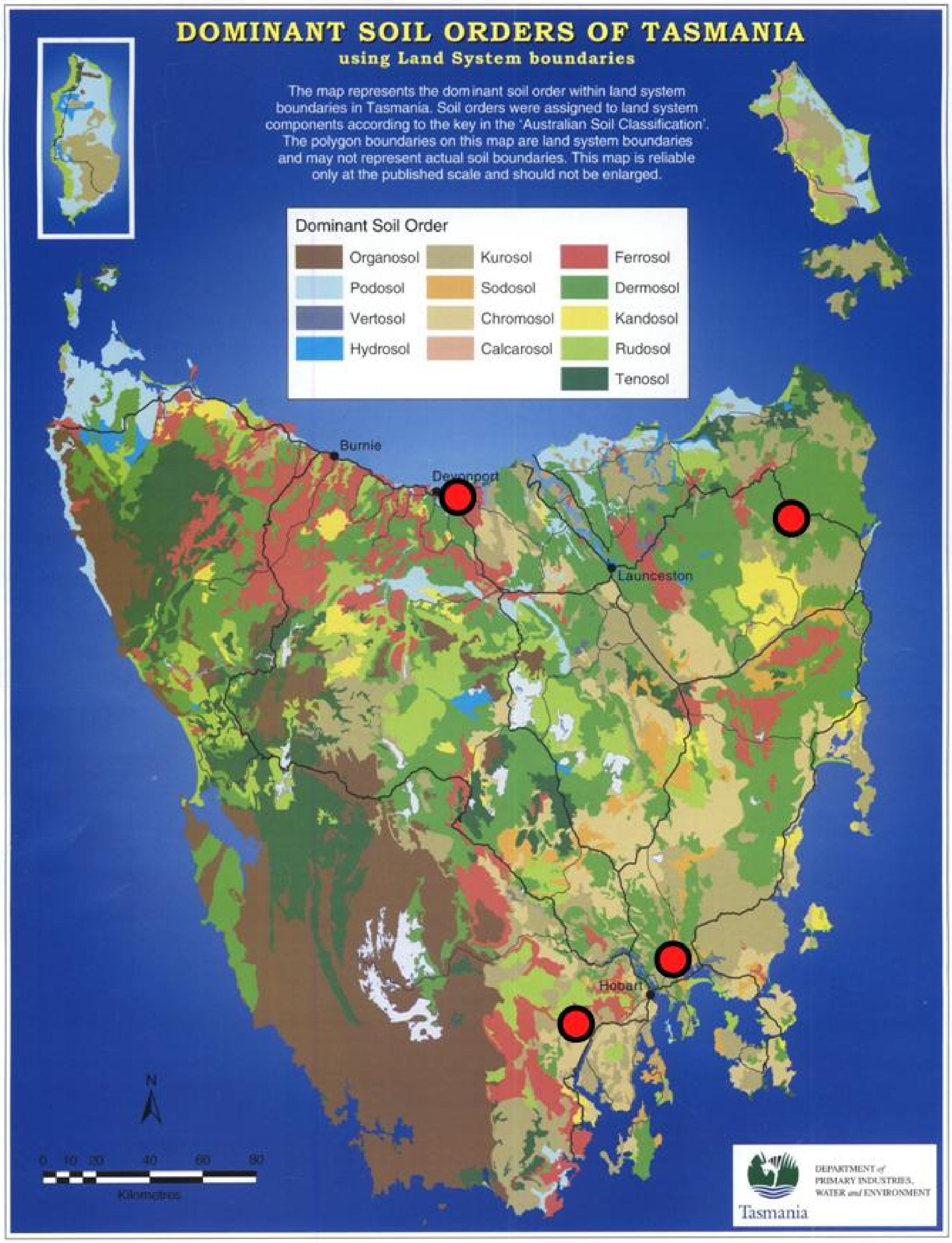
Glen Houn site is above the Huon River on Sunny Hills Road on a Gunns Ltd block called "Waston FH - GT181A" and is on a Red Deromosl on dolerite (see photo above).

University Farm, Cambridge, Coal River Valley overlooking the Pittwater Estuary and Ramsar site. Site 1 is an acidic sandy topsoil profile with acidic clayey subsoil (Kurosol, mapped a soil series A1). Geology is Tertiary sediments, elevation is 5 m asl.

Site 2 on the University Farm is a neutral, reactive black clay topsoil (Black Vertosol, mapped as soil series C1 (see soil map below). Geology is doleritic colluvium over Tertiary sediments, elevation is 40 m asl.



General Location of Sites



The map represents the dominant soil order within land system boundaries in Tasmania. Soil orders were assigned to land system components according to the key in the 'Australian Soil Classification'. The polygon boundaries on this map are land system boundaries and may not represent actual soil boundaries. This map is reliable only at the published scale and should not be enlarged.

Drilling rig and leaching sampling operation at University Farm Black Clay site 11/12/2006

Appendix B – Concentrations of pesticide applications assessed from aluminium foil traps on each plot

LCMS/MS data on application rate of pesticides.

Based on aluminium foil traps set on soil surface.

2006 Trial application measured in kg/ha on foil traps

	Glyphosate 3.2 kg/ha	**A-cypermthrin 0.12 kg/ha**	**Clopyralid 1.2 kg/ha**	**Simazine 6 kg/ha**	**MCPA 2 kg/ha**	**Sulfometuron 0.75 kg/ha**
Huon	2.89	0.08	1.18	7.59	2.69	1.61
Pyengana	1.13	0.10	0.99	8.02	2.31	1.79
Unifarm Kurosol	2.40	0.12	0.82	8.00	3.53	1.29
Unifarm Vertosol	2.65	0.09	1.04	7.32	3.18	1.64
Northdown	1.93	0.09	0.75	7.57	2.80	1.34

2007 Trials application measured in kg/ha on foil traps

	Glyphosate 3.2 kg/ha	**A-cypermthrin 0.12 kg/ha**	**Clopyralid 2.4 kg/ha**	**Simazine 3 kg/ha**	**MCPA 2 kg/ha**	**Sulfometuron 0.75 kg/ha**
Huon	3.29	0.12	2.30	3.76	1.95	1.17
Unifarm Kurosol	1.84	0.10	2.04	5.67	1.84	0.79
Unifarm Vertosol	1.23	0.11	1.83	5.60	1.87	0.94

The tables above show the measured application concentrations (kg/ha) on three aluminium foil disks or traps (8 cm dia.) placed on each plot as compared to the target rate specified. Actual application rates may vary from the target rate due to winds and variations in spray operator (walking pace) and spray equipment. This does not affect the half-life calculation so long as sufficient pesticide can be extracted throughout the trail period to provide a dissipation curve. However overall the data show the targets rates were generally achieved and that sufficient pesticide was applied to allow for adequate dissipation studies, a fact supported by statistical analysis of the data (see Appendix C).

Appendix C – Table of statistics on half-life field trials (2006 and 2007)

Site	Sulfometuron	MCPA	Clopyralid	Simazine	Glyphosate	alpha-Cypermethrin
Huon Ferrosol	C_0: .723±0.115 k: 0.0670±0.0134 RMSE: 0.168 RMSECo 9.75	C_0: 4.598±0.212 k: 0.1727±0.0214 RMSE: 0.256 RMSECo 5.57	C_0: 3.798±0.397 k: 0.0650±0.0206 RMSE: 0.585 RMSECo 15.40	C_0: 18.74±1.827 k: 0.0268±0.0088 RMSE: 3.200 RMSECo 17.08	C_0: 0.977±0.079 k: .1060±0.0242 RMSE: 0.105 RMSECo 10.75	C_0: 0.310±0.027 k: 0.0197±0.0061 RMSE: 0.050 RMSECo 16.13
Northdown Ferrosol	C_0: .630±0.079 k: 0.0330±0.0136 RMSE: 0.132 RMSECo 20.95	C_0: 2.468±0.302 k: 0.0336±0.0135 RMSE: 0.506 RMSECo 20.50	C_0: .187±0.0249 k: .0135±0.0065 RMSE: 0.049 RMSECo 26.20	C_0: 12.06±0.917 k: 0.0634±0.0146 RMSE: 1.358 RMSECo 11.26	C_0: 0.315±0.022 k: 0.151±0.0287 RMSE: 0.027 RMSECo 8.57	C_0: 0.394±0.048 k: 0.0487±0.0186 RMSE: 0.074 RMSECo 18.78
Pyengana Dermosol	C_0: .833±0.069 k: 0.0406±0.0108 RMSE: 0.111 RMSECo 13.33	C_0: 3.092±0.181 k: 0.149±0.0238 RMSE: 0.225 RMSECo 7.28	C_0: .562±0.0309 k: 0.226±0.0327 RMSE: 0.0351 RMSECo 6.24	C_0: 13.69±1.179 k: 0.0225±0.0066 RMSE: 2.133 RMSECo 15.59	C_0: 0.419±0.050 k: 0.0542±0.0202 RMSE: 0.077 RMSECo 18.38	C_0: 0.124±0.017 k: 0.0216±0.0101 RMSE: 0.030 RMSECo 24.19
Unifarm Vertosol	C_0: .820±0.222 k: 0.0283±0.0116 RMSE: 0.385 RMSECo 21.15	C_0: 1.787±0.160 k: 0.0136±0.0044 RMSE: 0.315 RMSECo 17.63	C_0: 1.400±0.251 k: .0075±0.0055 RMSE: 0.534 RMSECo 38.14	C_0: 5.907±0.428 k: 0.0057±0.0019 RMSE: 0.935 RMSECo 15.83	C_0: 1.331±0.124 k: 0.0106±0.0037 RMSE: 0.253 RMSECo 19.01	C_0: 0.127±0.021 k: 0.0123±0.0079 RMSE: 0.041 RMSECo 32.28
Unifarm Kurosol	C_0: .054±0.197 k: 0.0933±0.0501 RMSE: 0.269 RMSECo 25.52	C_0: 1.757±0.382 k: 1.292±0.701 RMSE: 0.305 RMSECo 17.36	C_0: .250±0.0675 k: 0.0063±0.0074 RMSE: 0.146 RMSECo 58.40	C_0: 5.617±1.181 k: 0.0203±0.0164 RMSE: 2.129 RMSECo 37.90	C_0: 1.503±0.324 k: 0.0133±0.0104 RMSE: 0.639 RMSECo 42.51	C_0: 0.176±0.052 k: 0.722±0.527 RMSE: 0.047 RMSECo 26.70

The table above shows statistics on spring 2006 half-lives – Parameter estimates and root mean square errors (RMSE) and also root mean square errors ($RMSEC_o$) normalised against the estimated starting concentration based on the 1st order equation (not actual field data) i.e. ($RMSE/C_o$) x 100. A value of 25 ($RMSEC_o$) or greater is taken as indicating questionable curve fitting and this is supported by the Unifarm Kurosol site, which was affected by a significant wind erosion event post application and shows poor fits for all pesticides except MCPA.

Site	Sulfometuron	MCPA	Clopyralid	Simazine	alpha-Cypermethrin
Huon Ferrosol	C_0: 0.600±0.025 k: 0.0130±0.0020 RMSE: 0.049 RMSECo 8.2	C_0: 1.456±0.102 k: 0.0496±0.0109 RMSE: 0.159 RMSECo 10.9	C_0: 7.345±0.883 k: 0.0353±0.0139 RMSE: 1.468 RMSECo 20.0	C_0: 4.294±0.240 k: 0.0057±0.0014 RMSE: 0.525 RMSECo 12.2	C_0: 0.067±0.0082 k: 0.0170±0.0076 RMSE: 0.0155 RMSECo 23.1
Northdown Ferrosol	C_0: 0.373±0.035 k: 0.0167±0.0055 RMSE: 0.066 RMSECo 17.7	C_0: 1.498±0.074 k: 0.0417±0.0066 RMSE: 0.119 RMSECo 7.9	C_0: 14.61±1.497 k: 0.0597±0.0187 RMSE: 2.243 RMSECo 15.4	C_0: 5.529±0.272 k: 0.0093±0.0018 RMSE: 0.564 RMSECo 10.2	C_0: 0.363±0.035 k: 0.0483±0.0149 RMSE: 0.055 RMSECo 15.2
Pyengana Dermosol	C_0: 0.456±0.025 k: 0.0207±0.0039 RMSE: 0.0458 RMSECo 10.0	C_0: 1.647±0.212 k: 0.0865±0.0323 RMSE: 0.295 RMSECo 17.9	C_0: 11.79±0.500 k: 0.0642±0.0082 RMSE: 0.738 RMSECo 6.3	C_0: 3.529±0.240 k: 0.0055±0.0017 RMSE: 0.525 RMSECo 14.9	
Unifarm Vertosol	C_0: 0.714±0.066 k: 0.0108±0.0036 RMSE: 0.128 RMSECo 17.9	C_0: 1.409±0.085 k: 0.0350±0.0076 RMSE: 0.142 RMSECo 10.1	C_0: 4.082±0.532 k: 0.0080±0.0047 RMSE: 1.031 RMSECo 25.3	C_0: 3.486±0.341 k: 0.0044±0.0021 RMSE: 0.711 RMSECo 20.4	C_0: 0.113±0.012 k: 0.0118±0.0048 RMSE: 0.0225 RMSECo 19.9
Unifarm Kurosol	C_0: 0.285±0.0205 k: 0.0081±0.0022 RMSE: 0.0407 RMSECo 14.3	C_0: 0.668±0.0739 k: 0.158±0.0527 RMSE: 0.0883 RMSECo 13.2	C_0: 2.489±0.242 k: 0.0106±0.0041 RMSE: 0.461 RMSECo 18.5	C_0: 2.208±0.0668 k: 0.0037±0.0006 RMSE: 0.141 RMSECo 6.4	C_0: 0.063±0.0036 k: 0.0204±0.0041 RMSE: 0.0064 RMSECo 10.2

The table above shows autumn 2007 trial data with the calculated starting concentration C_o and the RMSE (root mean square error). RMSE has been normalised using the C_o concentration to allow uniform comparison of a normalised RMSEC_o value across the data set; in other words, (RMSE/C_o) x 100. A value of 25 or greater is taken as indicating questionable curve fitting.

The RMSEC_o data indicate that clopyralid provided the most variable data and poorest first-order fit. Both clopyralid and alpha-cypermethrin had the most involved extraction procedures and analytical issues with respect to spectral analysis. (Clopyralid elutes very early and alpha-cypermethrin is affected by contaminants extracted from some of the soils.)

Appendix D – LCMS/MS settings – clopyralid, simazine, sulfometuron, MCPA

Analytical Services Tasmania LCMS/MS method: 1515 pesticides

Column	Varian Pursuit Polaris C18A 5 um 50 x 2.0 mm
Solvent A	0.1 % (v/v) Formic acid
Solvent B	Methanol
Injection	Full-loop (100 µL)
Flow	0.3 mL / min.

LCMS/MS gradient program

Time (min)	% Solvent A	% Solvent B
0.00	80	20
1.00	80	20
14.00	10	90
14.01	10	90
17.00	10	90
17.36	80	20
23.00	80	20

LCMS/MS general parameters

Needle voltage	+5000 V / -4700 V
Shield voltage	+/-600 V
Drying gas temperature	200 °C
Q1 + Q3 mass peak width	2.0 amu
Scan width	0.7 amu
Detector voltage	1800 V

Optimised MS multiple-reaction-monitoring conditions

			MRM Product Ions (m/z) / CID Voltage			
Rt (min)	**ESI**	**Precursor (m/z)**	**Qant.**	**Confirm**	**Segment Time (min)**	**Analyte**
1.87	Neg	190	146 /+8.5	128 /+7.5		Clopyralid
6.22	Pos	202	124 /-14.5	132 /-15.5		Simazine
6.85	Neg	363	182 /+15.0	122 /+20.0		Sulfometuron methyl
9.03	Neg	199	141 /+15.0			MCPA
	Neg	201		143 /+15.0		MCPA

LCMS/MS detection limits of compounds

Compound	Method detection limit (µg/L)	Upper Range Limit (µg/L)
Clopyralid*	nd	10
Simazine	0.2	10
Sulfometuron-methyl	0.7	10
MCPA	0.1	10

*Non-NATA accredited analytes, nd = not determined.

Detection limits are based on analysis of 1 litre water and are not based on soil. Soil based detection limits will be calculated in future validation studies.

LCMS/MS runs parameters for simazine, sulfometuron methyl and MCPA

Time	%A (0.1% formic acid in water)	%B (Methanol)
0:00	65	35
0:20	65	35
5:00	10	90
7:15	10	90

Collect delay / solvent divert = 2:30

Flow rate = 0.3 mL/min

LCMS/MS runs parameters for clopyralid (+ picloram internal standard)

Time	%A (0.1% formic acid in water)	%B (Methanol)
0:00	93	7
0:50	93	7
4:00	15	85
7:30	15	85

Collect delay / solvent divert = 1:12

Flow rate = 0.3 mL/min

Appendix E – HPLC and GSMC/MS specifications

HPLC Fluorescence

This method is based on USEPA Method 547 'Determination of Glyphosate in Drinking Water by Direct Aqueous Injection HPLC, Post-Column Derivatisation and Fluorescence Detection'. Chromatographic separation is achieved using a cation exchange column and potassium dihydrogen phosphate mobile phase. Post-column reaction is used to oxidise glyphosate (a secondary amine) to glycine (a primary amine) with sodium hypochlorite. Glycine then reacts with an o-phthaladehyde (OPA) and mercaptoethanol mixed reagent to form an isoindole that is measured fluorometrically. Detection limit is claimed to be 10 µg/L.

Measurement is made on a high performance liquid chromatograph (HPLC) fitted with a Varian 9100 auto sampler, Varian 9070 fluorescence detector and Star chromatography software. The analytical column used was a Hamilton PRP X400 cation exchange column (Alltech P/N 79473). The post column reactor (PCR) was a Timberline RDR-2D with a C18 Adsorbosphere 10 mm column guard and Cartridge (Alltech P/N 28015).

Alpha-cypermethrin GCMS/MS analysis

GSMS/MS analysis was undertaken using a Varian CP 3800 gas chromatograph interfaced with a Varian Saturn 2000 mass spectrometer. The column was a VF 5 MS with 30 m length, 0.25 mm internal diameter, a 0.25 micron film, 1 µl split/split less PTV injection, 0.1 mg/kg detection limit, quantification ion 163 with a retention time of 31.19 minutes.

Temperature program

Temp (°C)	Rate (°C/min)	Hold (min)	Total (min)
67	0.0	2.50	2.50
130	40.0	0.00	4.08
150	12.0	0.00	5.74
255	5.0	0.00	26.74
270	15.0	0.00	27.74
300	40.0	6.00	34.49

Appendix F – Pesticide recovery testing

Simazine, MCPA, sulfometuron and alpha-cypermethrin recovery efficacy

A series of tests were undertaken to determine the recovery efficiencies of the Accelerated Solvent Extraction (ASE) methods used in the half-life field studies. NATA certification criteria were used to direct sample numbers and concentration ranges. It should be noted that spiking soils under laboratory conditions does not fully mimic field application of pesticides via a spray unit. However, air-dried soil samples were sequentially spiked using with doses of pesticide from a precision syringe and loaded in to an extraction cell. Care is taken to distribute the pesticide over as much of the soil matrix as possible so as to enhance soil – pesticide contact and hence sorption. These sample were then extracted by ASE in the same manner as the field samples.

The strongly sorbing Northdown Ferrosol was used to determine the recovery percentages and the linearity over a concentration range of nine values for simazine, sulfometuron, clopyralid and MCPA (see Table 1). The University Farm Vertosol was used for alpha-cypermethrin due to matrix interference issues on the high organic carbon soils (see Table 1).

Table 1 Pesticide recovery percentages using ASE on spiked soils

Pesticide	% Recovery	Linearity R^2
Simazine	82.7	0.9976
Sulfometuron	62.3	0.9632
MCPA	78.1	0.9965
Clopyralid	72.1	0.9833
Alpha-cypermethrin	92.7	0.9995

As can be seen in Table 1 recoveries were all above 60% and most were near 80% or better. Linearity of extraction efficiency over nine concentration ranges was also very high. Both these findings support the suitability of the extraction and analysis methods chosen for the study and the reliability of the field half-life data.

Glyphosate recovery efficacy

Glyphosate extraction efficiency, more so than any other of the pesticides, was influenced by soil matrix effects. The concentration of the KOH extracting solution used needs to be balance with both efficacy and matrix interference (solubilised organics). This balance varies significantly with soil type.

Table 2 below shows three different soils spiked to reflect a target of 200 µg/L and extracted with the two different strength KOH solutions. No pesticide was recovered from the highly sorbing Northdown Ferrosol with either KOH extracting solution. The Vertosol showed poor recovery at 0.01M KOH but matrix interference occurred with the 0.1M extraction solvent. The Kurosol showed good recovery with 0.01M KOH but matrix interference with the 0.1M KOH occurred as level is above 100% recovery.

Table 2 Glyphosate extraction efficiency on three spiked soils (at 200 µg/L) using 0.1 and 0.01 M KOH solutions

0.01M KOH	**Sample number**	**Unifarm Vertosol**	**Northdown Ferrosol**	**Unifarm Kurosol**
	1	4.2	-	166
	2	6.7	-	151
	3	5.2	-	173
	4	6.5	-	155
	5	6.3	-	181
	Average	5.8		165
	SD	1.1		12.4
	Recovery %	2.89	0	82.7
0.1M KOH	**Sample number**	**Unifarm Vertosol**	**Northdown Ferrosol**	**Unifarm Kurosol**
	1	272	-	293
	2	259	-	321
	3	263	-	313
	4	264	-	283
	5	244	-	277
	Average	260		298
	SD	10.4		18.8
	Recovery %	130.06	0	148.73

The data in Table 2 certainly indicate there are problem with both matrix interference and extraction efficiencies for glyphosate at different KOH concentrations. In this report we presented data using the more standard 0.1 M KOH extraction. While this appears to be more “efficient” at glyphosate extraction (with recovery >100%) this must in part be due to unknown organic matrix interferences. Certainly this study indicates more work is needed on glyphosate extraction from soils and may in part explain the widely varying half-life figures in the literature.

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