Australian Government

Australian Pesticides and Veterinary Medicines Authority

DIURON

ENVIRONMENT ASSESSMENT

JULY 2011

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ENVIRONMENTAL ASSESSMENT SUMMARY

1 INTRODUCTION

The Department of Sustainability, Environment, Water, Population and Communities (DSEWPaC) evaluation of the environmental chemistry and fate is based essentially on the data package provided by Griffin Corporation Australia (DuPont) and Bayer as requested under the APVMA's Chemical Review Program. Additional information is provided by the scientific literature or other international reviews. Since release of the PRF, additional laboratory and monitoring test data have been supplied by DuPont. The assessment of these studies are included in this report.

Diuron is a selective herbicide for broadleaf weeds and some annual grasses. It belongs to the urea group of herbicides and is readily absorbed through the root system of plants and less readily through the leaves and stems. Residues in soil are toxic to plants. It is used in many agricultural situations, general weed control in irrigation ditches and drains and in non-agricultural areas (rights-of-way, commercial and industrial areas) and often used in combination with other herbicides such as bromacil and hexazinone.

Diuron is also used as an antifoulant in paints to prevent the build-up of marine growth on the hulls of boats. It is one of the several replacements for the chemical TBT (tributyl tin), which has been discontinued.

The US EPA has reviewed diuron as part of its re-registration process and the environmental assessment report for diuron was released in March 2003 (US EPA 2003). The findings of the US review are summarised in section 1.2 and, with additional detail, in the 'Environmental fate' section of this evaluation.

Environmental chemistry, fate and ecotoxicity data provided by Griffin Corporation Australia Pty Ltd (and Dupont (Australia) Ltd) and Bayer CropScience Pty Ltd form the basis of the evaluation of diuron conducted by the DSEWPaC. Additional material was obtained from other registrants, international reviews, Internet searches and other available literature sources.

This report represents the second revision of the environmental risk assessment of diuron since release of the PRF, and follows submission of significant new environmental fate and ecotoxicity data from DuPont Australia, along with a detailed modelling study performed by DuPont Australia to address potential changes to sugarcane application and management to reduce runoff of diuron in this crop. In addition, comments received by DuPont relating to the initial revision of the environmental risk assessment following release of the PRF have been provided, and considered as appropriate in this current report.

1.1 Scope of the review

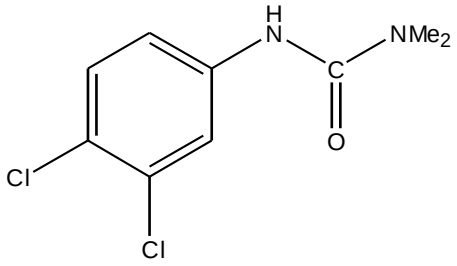
In considering registered diuron products, the scope of the review for the assessment of environmental effects includes:

- the impact of runoff water containing diuron on the Great Barrier Reef lagoon
- the impact of diuron found in sediment and water on various species of seagrass
- the potential role of diuron as a cause of die back in mangroves
- the possible contribution of diuron in runoff water to reported incidents of off target damage to farmlands.

The review is also to examine the adequacy of instructions and warnings on product labels, including the environmental warnings on the labels.

C.2 CHEMICAL IDENTITY

Table C1: Summary of chemical identity

Common name	Diuron (ISO accepted); DCMU (JMAF) or dichlorfenidim (USSR, Tomlin 1997)
Manufacturer's code	
Chemical name – IUPAC	3-(3,4-dichlorophenyl)-1,1-dimethylurea
Chemical name – CAS	N'-(3,4-dichlorophenyl)-N,N-dimethylurea
CAS Registry Number	330-54-1
Molecular formula	$C_9H_{10}Cl_2N_2O$
Molecular mass	233.1
Structural formula	

C.3 PHYSICOCHEMICAL PROPERTIES

No data were provided by applicants. The following information on physico-chemical properties is available.

Table C2: Summary of physicochemical properties

	FINDINGS
Colour/physical state	Colourless; Crystalline at room temperature
Melting point	158-159˚C
Relative density	1.48
pKa	There are no dissociable hydrogens within the normal environmental pH range (pH 4 to 9).
Vapour pressure	1.1 ´ 10-3 mPa at 25˚C.
Henry's Law Constant	7.0 x 10-6 Pa m^3/mole (calculated by DSEWPaC).
Solubility in water	36.4 mg/L at 25˚C
Octanol water partition coefficient ($LogK_{ow}$)	2.85 at 25˚C

Based on the scale of Mensink et al. (1995), diuron is moderately soluble and very slightly volatile. The Henry's Law constant is indicative of very slight volatility from water.

C.4 INTERNATIONAL REGISTRATION STATUS

Diuron is registered in many countries including the United States of America. It is proposed to be deregistered (deleted from Annex 1) in Europe following the European Union review of diuron (Official Journal of the European Union 2007).

Use of diuron has been restricted in Sweden, with use on railway embankments banned after 1994 (Torstensson et al. 2002). Following an incident in which it was claimed that irrigation water contaminated by pesticides from railway tracks had caused crop damage, the German Railways (DB) stopped using diuron for weed control on railway lines in 1996 (APVMA Scoping document). The German federal parliament subsequently imposed a legal ban on the use of diuron on railways, because of high levels of diuron in groundwater.

1.2 International reviews

1.2.1 United States of America Environmental Protection Agency

As noted above, the US EPA has conducted a review of diuron under its Reregistration Eligibility Decision [RED] program and published a draft environmental report for comment in March 2003 (US EPA 2003). The uses for diuron in the US are similar to those in Australia. Application in the US can be aerial and by ground boom spraying, applied mainly at pre-emergence. The highest application rates of 7.2–13.5 kg ac/ha (6.4–12 pounds of active ingredient per acre (lb ac/A)) are for weed control in orchards and non-agricultural sites as spot or row treatments.

The US EPA review concluded that diuron is stable to hydrolysis and photolysis, is persistent on soil and did not readily degrade. It is moderately mobile and has been found in both surface water and groundwaters. The major metabolites are sequentially demethylated compounds, which have no herbicidal effects. (NOTE: There is no apparent assessment of toxicity of these metabolites in the US EPA report, and the justification for such a statement is unclear. DSEWPaC does not share this view. Data presented in this report suggest similar toxicity of the major DCPMU metabolite to green algae and duckweed, and also very high toxicity of the m-CPDMU metabolite to green algae). The review found diuron was practically non-toxic or slightly toxic to birds and mammals; moderately toxic to most aquatic animals (fish and aquatic invertebrates); but highly toxic to one species of fish (cutthroat trout) and scud. Terrestrial and aquatic plants are very sensitive to diuron. Based on screening level risk assessments, diuron poses a potential risk to terrestrial and aquatic animals and a higher risk to terrestrial and aquatic plants. The Reregistration Eligibility Decision requested several additional environmental fate and toxicity studies, several for diuron but the majority for the metabolite DCA.

There were no recommendations at this stage due to the risk analysis having only been conducted to a screening level.

1.2.2 United Kingdom (UK)

The UK Advisory Committee on Pesticides reviewed use of diuron as an antifoulant and took the decision to revoke the use of diuron on all vessels due to environmental and human health concerns (ACP 2002 and ACP 2000). Significant levels of diuron were detected in water and sediment throughout UK estuary and coastal sites as well as freshwater sites.

1.2.3 Netherlands

A review of the fate and ecological effects of diuron was conducted by the Dutch RIVM (copy provided to the DSEWPaC). The report noted that diuron was hydrolytically stable, degraded with UV light and was moderately stable in aerobic soil with a half-life of 79–108 days. In field studies, half-lives ranged from 60 to 365 days. Leaching studies gave mixed results with some studies reviewed showing leaching (0–56 per cent recovered in leachate, 90-centimetre soil columns) while others showed no leaching below 5 centimetres of soil. Adsorption studies gave a K_{om} of between 190–340 (Koc of 330–595). Bioaccumulation was limited in laboratory studies, with bioconcentration factors of 15–85, although the only field study gave a BCF of 190–300, which indicates that the bioconcentration factor could be larger in the field compared to laboratory studies. However, the field result still indicates that bioaccumulation is limited.

The review found diuron was practically non-toxic or slightly toxic to birds, moderately toxic to most aquatic animals (fish and aquatic invertebrates) but highly toxic to one species of scud. Algae were very sensitive to diuron with an EC_{50} of 7.9 µg/L for one species.

1.2.4 European Union

Diuron is currently under review in the European Union. The results of the review were released in 2007 (Official Journal of the European Union 2007) with the result that diuron is to be removed from Annex 1 due to operator exposure and environmental exposure to birds and mammals. This will ban the use of diuron in all member Countries in the European Union. There is a grace period of one year to use all remaining stocks.

In Europe the use of diuron on vessels smaller than 25 metres in length has previously been revoked in the UK, Demark and the east coast of Sweden (Kevin et al. 2002).

C.5 ENVIRONMENTAL EXPOSURE

1.3 Mode of Action

Diuron is a strong inhibitor of the photosynthesis II system in plants via the Hill reaction. The Hill reaction involves the transfer of electrons from water to an electron acceptor, made possible by the capture of light by chlorophyll a. Diuron inhibits the transfer of electrons from water to the electron acceptor and ultimately prevents the formation of ATP and NADPH, both of which are required by plants for numerous biochemical reactions.

1.4 Environmental release

1.4.1 Amount used

The total amount of diuron used in Australia for agricultural purposes is more than 2000 tones per annum (APVMA Scoping document). Based on information presented by DuPont, Bayer, Crop Care, Nufarm and Farmoz, which together sold about 1300 tonnes of diuron per annum (about 65 per cent of the total market), the major uses are for cereals (about 500 tonnes), cotton (about 400 tonnes; mainly used in the cotton regions both as a pre-plant spray and on irrigation channels), and sugarcane (about 350 tonnes). In addition, there are uses on several other broad acre crops (lucerne, lupins, peas and summer fallow) totalling approximately 100 tonnes of diuron. It was estimated in 1996 that Queensland sugarcane used 197 tonnes per annum of diuron (Hamilton and Haydon 1996) but records of average sales figures for 2002–03 suggest this would appear to have increased considerably.

During this time, the area of replanted cane increased from the normal 15 per cent of total cane area to 30 per cent, which may have led to an increased use of diuron during this period.

There is no breakdown of the amount used on irrigation channels, apart from that for cotton channels, or on rights-of-way usage. However, due to restrictions on the use of atrazine in channels, usage may have increased.

By comparison, between 18–20 tonnes of diuron was used in antifouling paints in Australia during 2003.

1.4.2 Application and use pattern

1.4.2.1 Agricultural/Spray

Diuron is applied as both a pre- and post-emergent herbicide. Table C3 gives a summary of the current labels for agricultural uses.

There are a number of mixed products on the market in which diuron is used in combination with other herbicides, mainly hexazinone but also bromacil, thidiazuron and glyphosate. In these combination products diuron is used at rates lower than those given in Table C3. It should be noted that there are products with three actives but again the application rate for diuron is lower that for those in Table C3.

Diuron has been used in Australia for a considerable time and there has been considerable ‘label drift’—that is, the current labels do not reflect current usage of diuron, particularly in sugarcane. This can be seen when comparing the label rate in sugarcane (1.8–3.6 kg ac/ha) on the label compared to current usage as given by canegrowers (0.45–1.8 kg ac/ha, see Table C4).

Table C3: Summary of current labels

CROPS	WEEDS CONTROLLED	RATE	COMMENTS
Apples, pears	Barnyard grass, capeweed, crowsfoot, barley grass, fathen, guinea grass, sowthistle, amaranthus, mustard, ryegrass, wild oats, wild radish, wild turnip, cobbler's pegs, wireweed, toad rush, willow herb	Single application 3.6 kg ac/ha Split rate 1.8 kg ac/ha	Single application for winter. Split rate for post harvest then follow up in spring.
Asparagus	Annual broadleaf weeds and some annual grasses	1.35-1.8 kg ac/ha	10–14 weeks freedom from weeds
Bananas, Pawpaw		1.8-3.6 kg ac/ha	
Citrus			Applied prior to emergence of weeds in autumn and spring
Coffee		3.6 kg ac/ha then 1.8 kg ac/ha	High rate initially then subsequent applications at low rate
Cotton		0.9–1.8 kg ac/ha	One pre-emergence application. One post emergence application per season
Grapes		1.8–3.6 kg ac/ha 83 g/20 m^2, *	Applied as 'under vine' application. Under rack after harvest.
Grass seed crops		1.5-3.0 kg ac/ha	Lower rate used in second year
Lucerne		0.9–1.8 kg ac/ha	Applied after grazing
Pineapples		3.6 kg ac/ha	Applied after planting and before weed emergence
Lupins	Annual ryegrass, Capeweed, Clovers, medics, doublegee, wild radish, wild turnip,	1.0 kg ac/ha	Pre-sowing to pre-emergence
Sugarcane	Most grasses, vines and other broadleaf weeds	3.6 kg ac/ha 1.8–3.6 kg ac/ha	High rate for pre-emergence of cane. Rain or irrigate within 10 days of application
Wheat, Barley, Triticate, Oats	Capeweed, charlock, sheepweed (white ironweed), iceplant, poppies, turnips, yellow burr weed, mustard, doublegee, saffron thistle, deadnettle, wild radish	0.45 kg ac/ha or 0.25 kg ac/ha mixed with MCPA or 0.18 kg ac/ha mixed with MCPA and 2,4-D	Applied by boom or aerially. Don't spray if rain imminent.
	Soursob	0.88–1.34 kg ac/ha	Applied by boom. South Australia only.

CROPS	WEEDS CONTROLLED	RATE	COMMENTS
Rights-of-way, commercial and industrial areas	Annual grasses perennial grasses and broadleaf weeds	Initial treatment: 4–16 kg ac/ha 16–32 kg ac/ha 24–36 kg ac/ha Retreatment: 3.1–6.3 kg ac/ha 6.3–12 kg ac/ha 8.1–16 kg ac/ha	Rainfall 0–500 mm/year 500–1000 mm/year >1000 mm/year 0–500 mm/year 500–1000 mm/y1000 mm/year Applied just before rainfall
Irrigation channels and drainage ditches		35-75 kg ac/ha 10–20 kg ac/ha (NSW only)	Applied when channels not in use, during non-cropping season and before seasonal rainfall expected.
Small areas		90 g/15 L for 20 m^2	Apply in 65 L water/ha**
Bore drains (Qld only)	Prickly Acacia, Mimosa bush	32 kg ac/ha	1 m wide strip onto mud after emptying drain.
Citrus, coffee	Couch grass	0.64 kg ac/200 L	Spot spraying only

** 83 g/20 m2 corresponds to 37 kg ac/ha.*

*** 65 L/ha at 90 g/15 L corresponds to 380 g ac/ha and is in conflict with previous direction of 90 g/15 L for 20 m^2 corresponding to 40 kg ac/ha*

DuPont Australia advised the APVMA that the only use of diuron they are supporting is that in sugarcane up to an application rate of 1.8 kg ac/ha (but applied as band spray). It is unclear what other registrant views are, so the above label uses of diuron are all considered in the risk assessment.

Canegrowers, the peak industry body representing canegrowers, have presented additional information on use of diuron in sugarcane (Wrigley 2005). This is summarised in Table C4. This table is drawn up from extensive discussions with growers throughout the sugarcane industry and gives the rates used in various sugarcane regions. As can be seen in this table, there is considerable difference in the use of diuron, especially for grasses and broadleaf weeds. The range is from 0.45 to 1.8 kg ac/ha, which is considerably less than 1.8 to 3.6 kg ac/ha given on the currently registered labels.

In addition, DSEWPaC is aware that there are newer application methods being used/developed for sugarcane, such as the use of band spraying, where lower overall rates than those listed in Table C4 can be used. It should be noted that currently most canegrowers actually used diuron in combination with other herbicides and it is not often applied on its own.

Table C4: Diuron herbicide use in sugarcane as given by canegrowers

REGION	TARGET WEEDS	CROPPING SITUATION	APPLICATION RATE kg ac/ha	APPLICATION AND FREQUENCY	PORTION OF REGION TREATED
Burdekin	Itch grass, *Rottboellia, ssp* and *Panicum maximum*	Plant and ratoon cane	1.8 (as Velpar K4)	Before out of hand; one APS*	Small/localised; specialised use, spot spraying with handgun
Burdekin; Mackay	Grass and small broadleaf	Plant cane	0.9	Early post-emergence in combination with other herbicides; one APS	Large area widespread
Mackay	Grass and small broadleaf	Ratoon cane	Max 1.8 (as Velpar K4) where grasses are obvious; lower rates otherwise	Used in conjunction with trash blanket	Widespread
Herbert	Grass and broadleaf (broad spectrum)	Plant and ratoon cane	0.9–1.8 (as Velpar K4) or 1.9 (Comanche); commonly tanked mixed with Gramoxone	Before out of hand; one APS	Large area, predominately on heavier soils
Herbert	Grass and small broadleaf	Plant cane	0.45–1.35	Early post-emergence in combination with other herbicides; one APS	Large area, widespread
Mossman	Grass and broadleaf (broad spectrum)	Plant cane	1.8 as Velpar K4	Pre-emergence	50% of plant cane
		Plant and ratoon cane	Up to 0.9	Early post-emergence in combination with other herbicides	Significant areas
	Panicum ssp	Ratoon cane	1.8 with MSMA (methylarsonic acid)	Control of regrowth of Panicum sp	Significant area

**APS = application per season*

1.4.3 Frequency of application

Most of the directions on the agricultural labels imply one or two applications per year or per season, with the second application at lower rates. The directions for several of the crops on the labels do not specify the number of applications per season or per year.

1.4.4 Methods of application

The majority of agricultural applications are likely to be done with boom sprayers or other ground rigs. There will be some spot spraying and aerial application but the aerial application is likely to be limited to cotton (cotton defoliant) and cereal crops. Most post-emergence applications are to be done as a directed spray under the crop (cotton, sugarcane) and as directions are to avoid spray contact with the crop, aerial application is unlikely. Applications to irrigation ditches and drains are done using boom sprayers or other ground rigs, as is application to rights-of-way, commercial and industrial areas (railway tanker sprayer is considered a ground rig).

1.4.5 Antifoulant use

The use of diuron on vessels longer than 25 metres or all vessels has been revoked in the UK, Denmark and the east coast of Sweden (Kevin et al. 2002). The use of diuron in antifouling paints has also been revoked in Bermuda by legislation in August 2005 (MEP 2005). In Australia, there are approximately 20 marine anti-fouling paints on the market that contain diuron. Depending on the other actives in these paints, the concentration of diuron ranges from 5 g/L to 80 g/L. Cuprous oxide or cuprous thiocyanate is typically the other active used in the majority of these paints.

The labels indicate that these anti-fouling paints are to be used on all types of hulls: aluminium, steel, wooden, ferro-cement, fibreglass and epoxy sheathed and composite systems boats. These paints could also be used for trailer boats that are subject to intermittent immersion (boats immersed continuously for weeks if not months at a time). While none of the labels specify a size of hull or where it is likely to be used, the majority appear to be targeted for yachts (several for racing yachts) and other pleasure craft while others (Trawler, Cleanship and Longlife antifouling) appear to be for commercial uses and ocean-going vessels.

These paints are for use by both professional and the wider public (do-it-yourself users). The general users typically apply the paint by brush or roller to the boat hull, although pressure spray applications are also likely: generally, two coats are applied over a two-day period once a year. Professional applicators (e.g. at marina facilities) would be likely to use airless spray application. Users need to comply with relevant state environmental regulations and local government requirements. Suitable general guidance for environmental precautions in the maintenance and application of vessel antifoulant coatings is provided in the Code of Practice developed by ANZECC (Australia and New Zealand Environment and Conservation Council—ANZECC 2000). Appropriate guidance for the application and maintenance of vessel antifoulant coatings may also be available from state environmental agencies (e.g. NSW EPA 1999; Vic EPA 1998).

Table C5. Summary of labels from antifouling paints that contain diuron

PRODUCT NAME	CONC. DIURON g/L	NUMBER OF COATS	L PRODUCT per m^2, FINAL	DIURON per m^2	MONTHS OF PROTECTION
VC Offshore extra	20	2 hull, 3 trailing edge	0.18 or 0.27 (spray)	3.6 or 5.5 g	12
Interspeed 2000	35–45	2 hull, 3 trailing edge	0.24 to 0.40	10.8 to 18 g	12
Coppercoat extra Trade Antifouling	40–50	2 hull, 3 trailing edge	0.33 or 0.40	16.5 or 25 g	12

PRODUCT NAME	CONC. DIURON g/L	NUMBER OF COATS	L PRODUCT per m^2, FINAL	DIURON per m^2	MONTHS OF PROTECTION
Micro extra	70	2 hull, 3 trailing edge	0.2 to 0.35	14 to 24.5 g	12
Coppercoat Ablative antifouling	35–45	2 hull, 3 trailing edge	0.23 to 0.39	10.4 to 18 g	12
Micro CSC	40–50	2 hull, 3 trailing edge	0.23 to 0.39	11.5 to 19.5 g	12
Cruiser Superior	45–50	2 hull, 3 trailing edge	0.24 to 0.40	12 to 20 g	12
Longlife	35–45	2 hull, 3 trailing edge	0.26 to 0.43	11.7 to 19.3 g	Not given
Wattyl Sigmaplane Ecol HA120	62	Minimum of 2	0.2	25.6 g	Not given
Wattyl Sigmaplane Ecol	70	Minimum of 2	Minimum of 0.19	26.6 g	Not given
Trawler Antifouling	62	Minimum of 2	0.2	24.8 g	Not given
Wattyl NewPort 77	62	Minimum of 2	Minimum 0.2	Minimum 12.4	Not given
Wattyl NewPort 88	70	Minimum of 2	Minimum 0.2	Minimum 14	Not given
Cleanship antifouling 2.95*	5	1 or 2	150 µm thick equal to 0.15 L/m^2 per coat	0.75 or 1.5 g	36 months
Longlife antifouling 2.77	80	2	75 µm dry film** equal 0.3 L/m^2 2 coats	24	Not given
40 South marine paint	50–60	2	0.2	12	12 months
Hempel's Antifouling Nautic	60–70	2	0.4 †	28	12–20
Hempel's Seatech antifouling	42–52	3–4 (roller) 2–3 (spray)	0.2 ‡	10.4	Not given
Hempel's Mille Dynamic	60–70	3–4 (roller) 4–5 (paint pad) 2–3 (spray)	0.2	14	Not given
Hempel's Mille Dynamic Alu	65–75	3–4 (roller) 4–5 (paint pad) 2–3 (spray)	0.23	15	Not given

**Also contains chlorothalonil. ** Assuming 75 µm dry equal to 150 µm wet. † Labels gives 200 mm per coat with 2 coats. ‡ Labels gives 100 µm dry as minimum total film dry, assumed to equal 200 µm wet paint.*

The coverage of the hulls is somewhat variable, with some labels (those from international companies) stating two coats for the hull and three coats for leading and trailing edges, rudders, keel waterlines and

skeg. These labels also give 'Practical coverage' as 8.7 m^2/L by brush and 7.7 m^2/L by spray, while others give 5 m^2/L. Table C4 clearly indicates that most applications are likely to occur annually, indicating an expected lifetime of one year, but the Cleanship label indicates up to 36 months protection. The concentration of diuron in the final paint on the hull various greatly, from as low as 1.5 g/m^2 to 28 g/m^2: the range is due to differences in the concentration of diuron used in the paint formulations, which in turn reflects other actives, types of hulls and there intended use, for example, racing, offshore or deep water.

The release rate of diuron from these antifoulant paints is dependent on the concentration of diuron, thickness of the paint, type of paint and its duration. The release rate of diuron will be discussed in further detail in the risk assessment section.

1.4.6 Labelling

There are label warnings to avoid spray drift onto non-target plants and to avoid using diuron on windy days on all labels. There are warnings not to drain flush or spray equipment near desirable trees, plants, or other plants or areas where there roots may extend or in sloping areas where movement of treated soil or seepage may be absorbed by plants roots. There are several warnings and a label restraint not to use on sandy or gravely soils or soils with low organic matter.

One of the label warnings under the heading 'Crop Safety' states that heavy rains after application of this product may cause severe crop damage. A similar warning may be needed for the environment to prevent contamination of nearby streams.

The labels examined generally give application details and storage and disposal details (for WG, empty bags by shaking into spray tank; for EC (and other liquid formulations) triple rinse or pressure rinse and add rinsings added to the spray tank) that conform to current requirements. Empty containers are to be broken, crushed or punctured before disposal in a local authority landfill or, if not available, buried at least 500 millimetres deep in a specific disposal pit clear of waterways, vegetation and roots. However, some labels note that disposal of the containers refer to recycling of containers at a recycler or designated collection point. Most labels carry the statement that undiluted chemicals were not to be disposed of on-site.

1.5 Environmental fate

1.5.1 Introductory comments

The evaluation of the environmental chemistry and fate is based essentially on the data package provided by DuPont Australia and Bayer as requested under the APVMA's Chemical Review Program. Additional information is provided by the scientific literature or other international reviews.

This overview report should be read in conjunction with Appendix A—Technical Report for Environmental Fate of Diuron. In the technical report, the most recent studies provided have been assessed for their reliability. The following approach for rating the reliability of studies in relation to good laboratory practice (GLP) has been used:

1 Fully reliable: GLP compliant and fully compliant with the Test Guideline specified.

2:	**Reliable with restrictions:**	GLP compliant but not fully compliant with the Test Guideline specified, but nevertheless judged to provide a reliable basis for regulatory decision-making. An asterisk is to be added to identify studies that are not standard that are judged to be reliable for the purpose conducted (e.g. mechanistic studies)
3	**Not reliable:**	Not GLP compliant or not compliant with the Test Guideline specified, and judged to not provide a reliable basis for regulatory decision-making.
4	**Not assignable:**	Insufficient information provided to allow the reliability of the test or study report to be assessed (e.g. published literature).

It should be noted that these ratings are derived from the OECD. Australia does not have mandatory GLP and consequently some allowances need to be made in addressing the validity of a study. For example, non-GLP studies cannot be considered unreliable on these grounds alone. Therefore, a degree of expert judgement has been used in applying the validity rankings associated with studies assessed.

1.5.2 Physicochemical degradation

1.5.2.1 Hydrolysis

In a study conducted according to US EPA and European Union Guidelines, there was no observable degradation at 25°C in pH 7 and 9 solutions, and only slight degradation at pH 4 and 5 with calculated half-lives of 798 and 313 days, but these are not reliable because the fit was poor and calculated half-lives were significantly longer than the duration of the experiments (30 days).

At a higher temperature of 50°C, hydrolysis was more pronounced for pH 4, 5 and 9, with half-lives of 26, 56 and 109 days respectively. These results for pH 4 and 5 are considered reliable because of the fit to first order kinetics was good and half lives reasonably close to the study duration of 30 days. However, at pH 7 there was insufficient degradation for determination of a half-life. There were two degradation products noted in the HPLC, only one of which was more than 10 per cent of AR and was identified as DCA by co-chromatography.

In a second study conducted according to US EPA Guidelines, there was only limited degradation of 1–2 per cent at all pH values (5, 7 and 9) at 25°C and it was concluded that the half-life was greater than 500 days. There were two degradates, which were identified as DCPMU and DCA.

1.5.3 Photolysis/photodegradation

1.5.3.1 Aqueous photolysis

The photolysis of diuron in buffered water was conducted according to US EPA Guidelines (US EPA 1996) and to satisfy European Union requirements. The degradation followed first order kinetics and was pH-dependent with degradation at pH 7 slower than at pH 5 or 9. The half-lives were 7.8, 16.3, 8.9, and 16.9

hours for pH 5, 7, 9 and purified water respectively. Under natural sunlight (30°N), these half-lives were calculated to correspond from 6.7 to 22.4 days. Eleven photolysis products were observed, four of which were major degradates and present in concentrations of >10 per cent each. The major degradates were not identified, a significant weakness in the study. Two minor peaks in the HPLC were identified, one as DCPMU or DCPU and another as DCA.

In a second study conducted according to US EPA guidelines, photolysis of diuron was again first order and the half-life was determined as 9.0 days, which is equivalent to about 43 days under natural (latitude 30–40°N) sunlight assuming 12 hours of sunlight. The analyses showed that major degradates were more polar than diuron, none of which were more than 10 per cent of AR and were not identified.

The photolysis of diuron under natural sunlight was calculated from the quantum yield and measured UV absorption spectrum according to ECETOC procedures. These calculated half-lives ranged from 2.2 to 5.4 days for 30°N.

1.5.3.2 Soil photolysis

The photolysis of diuron on soil was studied according to the EPA Guideline using a silt loam soil—the same as used for the aerobic and anaerobic metabolism studies. Photolysis was relatively slow with 90 per cent of the applied diuron recovered after 30 days of irradiation. The half-life of diuron was calculated as 173 days using first order kinetics. The main degradate noted was DCPMU.

1.5.4 Biodegradation

The following table summarises laboratory degradation data reviewed for this assessment and indicate that under environmental conditions, diuron has the potential to persist for long periods of time in both soil and water. Its main metabolites (particularly DCPMU and m-CPDMU) were also shown to potentially persist for long periods of time in soil or sediment.

The biodegradation data indicate two metabolic pathways for diuron degradation. The aerobic pathway involves demethylation of the urea to give the metabolites DCPMU and DCPU. The anaerobic pathway (potentially a faster route of primary degradation) involves dechlorination of the phenyl ring, a typical anaerobic degradation, to give m-CPDMU and PDMU.

Table C6. Summary of all half-lives and main metabolites

METABOLISM	SOIL USED	CONDITIONS	HALF-LIFE, DAYS	MAJOR METABOLITE(S) IDENTIFIED
PARENT DIURON				
Aerobic soil	Silt loam	25°C, 75% 0.3 bar	372	DCPMU, DCPU
	Loamy sand	70% MWHC, 20°C	20	DCPMU, DCPU
	Sand,	70% MWHC, 20°C	119	DCPMU
	Sandy loam	70% MWHC, 20°C	51	DCPMU
	Sandy loam	70% MWHC, 10°C	143	DCPMU

METABOLISM	SOIL USED	CONDITIONS	HALF-LIFE, DAYS	MAJOR METABOLITE(S) IDENTIFIED
	Sandy loam	35% MWHC, 20°C	27	DCPMU, DCPU
	Sand	20°C, pF 2.5	112	DCPMU, DCPU
Anaerobic soil	Silt loam	25°C, 75% field moisture. 30 days aerobic then anaerobic	No degradation during anaerobic phase	-
Aerobic Aquatic	Silty loam (Erft River)	20°C	10.8 (water) 35 (whole system)	DCPMU
	Sandy loamy silt (Hönniger)	20°C	5.5; 67 (water) 277 (whole system)	DCPMU, m-CPDMU
	Clay loam	25°C	33	DCPMU, m-CPDMU
Anaerobic aquatic	Clay loam	25°C, anaerobic	1.2 days	m-CPDMU. PDMU, m-CPMU
M-CPDMU METABOLITE				
Aerobic soil	Sandy loam	20°C	205	Not determined
	Clay loam	20°C	546	Not determined
Aerobic aquatic	Sandy clay loam	20°C	44 (water) 415 (whole system)	Not determined
	Sandy loam	20°C	69 (water) 183 (whole system)	Not determined
Anaerobic aquatic	Sandy clay loam	20°C	57 (water) 436 (whole system)	Not determined
DCPMU METABOLITE				
Aerobic soil	Loam*	20°C	73	Not determined
	Silt loam*	20°C	89	Not determined
	Sandy loam*	20°C	40	Not determined

** Nominal classification by DSEWPaC based on USDA Soil Classification*

1.5.5 Aerobic soil metabolism

The metabolism of diuron was studied in a silt loam (Keyport soil) according to US EPA Guidelines. After incubation of 12 months at 25°C in the dark, extracted radioactivity accounted for 81 per cent of AR with 14.9 per cent remaining in the soils and 3.36 per cent as carbon dioxide (determined by precipitation with barium chloride). The half-life for the non-sterile soils was determined by first order kinetics as 372 days and for sterile control was 1920 days. Only two metabolites were identified: DCPMU and DCPU.

In another study, the degradation behaviour of diuron in three soils from Europe was conducted to Danish data requirements. The results of the study showed diuron to be fairly to slightly degradable with half-lives under ‘standard conditions’ (20°C, 70 per cent MWHC) of between 20–119 days. Reducing the temperature

to 10°C increased the half-life to 143 days from 51 days, but drier soil (35 per cent of soil's maximum water holding capacity) reduced the half-life to just 27 days. The TLC analysis identified three metabolites by comparison with authentic samples: DCPMU, DCPU and DCA, formed from progressive demethylation.

The degradation behaviour of diuron was studied in a standard German soil (Speyer 2.1, a sand soil) in accordance with EEC Guidelines. The soil was incubated in the dark with positive flow of carbon dioxide–free air for 101 days at 20°C and at field capacity. The results of the study showed diuron to be slightly degradable with half-life of 186 days (square root time, 1.5 order kinetic best fit). In a supplementary study, this half-life was recalculated using a two-compartment model to give a half-life of 112 days and a DT50 for DCPMU of 35 days. The analysis identified two metabolites by comparison with authentic samples: DCPMU and DCPU.

Aerobic soil metabolism studies were provided for the m-CPDMU metabolite (two soils) and DCPMU metabolite (three soils). Tests were performed under standard conditions at 20°C in the dark. Using first order kinetics, m-CPDMU was persistent in both soils with half-lives ranging from 205–546 days, both well in excess of the study's duration. The half-lives of DCPMU were calculated using a first order multi-compartment model, and were estimated to range from 40 days to 89 days. Further degradation products were not considered in these studies.

1.5.6 Anaerobic soil metabolism

An anaerobic soil degradation study of diuron was performed according to US EPA Guideline N-162-1 using a silt loam soil (same soil used for aerobic study). The dosed soil was incubated under aerobic conditions (stream of air) in the dark at 25˚C for 30 days; the soil was then purged with nitrogen; and incubation was continued for 60 days under a stream of nitrogen. The report notes the some of the diuron becomes tightly bound very rapidly and could be recovered only by forcing conditions. After the system was purged with nitrogen and presumably anaerobic conditions were established (no evidence was presented), the metabolism of diuron appeared to stop, with the amount of diuron recovered remaining constant (within experimental error). The half-life for the anaerobic phase was calculated as 1000 days but is not reliable. It was concluded that the study shows that under anaerobic conditions the metabolism of diuron is very slow.

1.5.7 Aerobic aquatic metabolism

The aerobic aquatic metabolism of diuron was studies according to EC Directive 95/36 and SETAC-Europe Procedures using two sediment-water systems collected from two locations in the Germany, the River Erft, a stream flowing into the Rhine where the micro-organisms have been shown able to metabolise diuron, and Hönniger Weiher, an artificial pond. The systems were incubated aerobically at 20°C in the dark for 120 days. During the incubation, both waters remained aerobic, and the Erft sediment was also mainly aerobic. The Hönniger sediment was essentially anaerobic at first (28 days) then became aerobic. Diuron moved to the sediments (half-life in the water column of 5.5 to 67 days) where it was degraded quicker in the Erft system (half-life = 35 days; whole system) than in the Hönniger system (277 days; whole system). It should also be noted that the microbes in the Erft River were probably conditioned for the degradation of diuron. There were relatively few metabolites formed that were detected. DCPMU was identified in the sediments of both systems, with the dechlorinated metabolite m-CPDMU found in the Hönniger system, both in the aquatic phase and in sediment but was not detected in the Erft system.

In another study, the aerobic aquatic metabolism of diuron was studied using a clay loam sediment in accordance with US EPA Guidelines. The radiolabelled diuron was applied to the water surface and then incubated in a dark at 25°C for 30 days. Diuron degraded under the study conditions with a degradation half-life of 33 days using first order kinetics. There were two main metabolites, m-CPDMU and DCPMU. The degradation pathway proposed is the same as for the previous aerobic aquatic metabolism study and involves two pathways, one by demethylation and the other by dechlorination of the phenyl ring. In a supplemental report, it was noted that the reductive dechlorination, which leads to the formation of m-CPDMU, is fast and explains the relatively short half-lives of diuron in the aquatic metabolism studies compared to the aerobic and anaerobic soil studies.

One literature report describing effects on phytoplankton using outdoor mesocosms characterised the dissipation of diuron in the water column. Based on triplicate results, the dissipation of diuron following cessation of exposure (day 34 of the experiment) until 173 days followed first order kinetics. The half-life as calculated to be 43 days (r^2 = 0.97) with diuron concentrations after 5 months still being 10 per cent of the applied levels.

One study considered the rate of degradation of the radiolabelled metabolite m-CPDMU in two aerobic aquatic sediment systems (20^{o}C in the dark). Based on measurements of water redox potential and dissolved oxygen concentrations, it appears conditions were more reducing than aerobic through much of the study. Using first order kinetics, the half-lives in water of this metabolite ranged from 44–69 days, and half-lives in the whole systems ranged from 183–415 days.

DSEWPaC had requested water and sediment metabolism data for the DCPMU metabolite. This metabolite is the primary soil metabolite. It is also found in diuron water and sediment metabolism studies, albeit at levels of less than 10 per cent of parent concentrations. However, the data were requested as the DCPMU metabolite appears mobile and available for runoff from agricultural soils, based on Australian data finding it at greater levels than diuron in water runoff and sediments. DuPont did not provide any additional data for this metabolite, so no further assessment of its persistence in aquatic systems could be undertaken.

1.5.8 Anaerobic aquatic metabolism

The anaerobic aquatic metabolism of 14C-diuron was studied according to US EPA Guidelines using a clay loam sediment (used for the aerobic aquatic metabolism study). The diuron was applied and then incubated in the dark under nitrogen at 25°C to give a degradation half-life of 1.2 days using first order kinetics. The main metabolite was m-CPDMU that reached 81 per cent of AR after 7 days, remained at that level till day 98, then declined to 15 per cent of AR at the end of the study. Other metabolites detected were PDMU (maximum 13 per cent of applied), and m-CPMU (maximum 18 per cent of applied). The degradation pathway proposed is rapid dechlorination of the phenyl ring to give m-CPDMU then slowly followed by further dechlorination to give PDMU, or demethylation to give m-CPMU. In a supplemental report it was noted by the author that the reductive dechlorination is fast and explains the relatively short half-lives of diuron in this study.

One study considered the rate of degradation of the radiolabelled metabolite m-CPDMU in one anaerobic aquatic sediment system (20^{o}C in the dark). Water redox potentials indicated varying degrees of anaerobicity during the study, but dissolved oxygen was always less than 1 mg O_2/L. First order kinetics suggested a water half-life of 57 days. However, the water half-life appeared biphasic, with the first half-life (calculated on

the 0–15 days of data) of 17.2 days, and a much longer second half-life calculated to be 100 days. The half-life in the whole system was 436 days.

1.5.9 Mobility

1.5.9.1 Volatility

Diuron has a vapour pressure of 1.1 x 10^{-3} mPa at 25°C and a calculated Henry's Law Constant of 7.0 x 10^{-6} Pa m^3/mole, which are both indicative of only very slight volatility. This is confirmed by a field lysimeter experiment described in the literature, in which volatilisation of diuron from the soil surface was also investigated. In this experiment, air samples were collected for the first 13 days after herbicide application (2.3 kg diuron/ha). Neither diuron nor its metabolites were detected.

1.5.9.2 Soil adsorption and desorption

The adsorption and desorption of diuron was performed by batch equilibrium studies to meet US EPA Guidelines using four agricultural soils. The Koc values ranged from 418 to 574 and indicate that diuron is moderately adsorbed to the soils tested and is rated as being of low to medium mobility. The narrow range indicates the organic matter is the major determinate of adsorption, in contrast to that from the study below. The desorption data shows that there was considerable loss of diuron from one soil, 40 per cent of the initially adsorbed diuron was lost after five cycles of desorption, compared to 7–17 per cent for the other three soils. It is noted that the soil with the highest desorption had the lowest amount of clay of the four soils studied.

The adsorption and desorption of diuron, m-CPDMU and PDMU in five soils was performed to meet US EPA Guidelines. PDMU and m-CPDMU are both anaerobic metabolites of diuron. In the preliminary studies, two soils showed less than 10 per cent adsorption, and as this was not sufficient for isotherm testing, the rest of the study was conducted using the three remaining soils. From the preliminary study the Koc values for diuron were calculated as 366 to 1750 for all five soils and show that diuron is moderately adsorbed and is rated as being low to medium mobility. Results from the isotherm tests were similar. The large range for the Koc values indicates that other factors such as physical chemical properties of the soils and content and composition of clay minerals could also be factors in the adsorption of diuron. For the metabolite m-CPDMU, the Koc values ranged from 40 to 323 and this metabolite is rated as having low to very high mobility (McCall classification). However, the isotherm results for the three soils tested indicate that it is rated as low to high mobility (Koc from 139 to 418). For PDMU, the screening results show Koc values from 33 to 138 (high to very high mobility) with similar results for the isotherm data. In all cases the metabolites were more mobile than the parent compound diuron.

The adsorption and desorption of DCPMU, a major aerobic metabolite of diuron, was examined in four soils according to US EPA Guidelines. The Koc values ranged from 651 to 4989 and indicate that DCPMU is moderately adsorbed to the soils tested. It is rated as being low to medium mobility (McCall classification). Again there was a large range for the Koc values. The adsorption and desorption of DCPU, a major aerobic metabolite of diuron, was investigated in five soils according to US EPA Guidelines. The Koc values ranged from 572 to 1178 and indicate that DCPMU is moderately adsorbed to the soils tested. It is rated as being low to medium mobility (McCall classification).

1.5.9.3 Field lysimeter studies

To evaluate the leachability of diuron under field conditions, two field lysimeters were set up in Sweden using two sandy soils (Nantuna and Langaveka). Each lysimeter was planted with a single black currant bush in order to mimic normal agricultural practices. The lysimeters received a total of 1737 mm of precipitation (including irrigation).

At a diuron application rate of 2 kg ac/ha, there were six leachate positive samples from 30 samples analysed (limit of detection 0.05 µg/L) from the Langaveka soil lysimeter; the maximum concentration of diuron was 0.73 µg/L. For the Nantuna lysimeter there was one sample above the detection limit at 0.06 µg/L from the 29 samples taken. At the higher rate of 4 kg ac/ha there were 17 positive samples from 34 samples taken from the Langaveka lysimeter with a maximum concentration of 12.55 µg/L diuron. For the Nantuna lysimeter there were 16 positive samples from 41 leachate samples, with a maximum of 1.25 µg/L. The highest concentration of diuron was associated with flow events of short duration (and low volumes) during winter. The total leaching of diuron was highest from Langaveka and represented a maximum of just 0.027 per cent of that applied.

The metabolites DCPMU and DCPU were the only two metabolites detected, with the concentrations of DCPMU comparable with diuron in the majority of leachate samples, but DCPU was lower. The major radioactivity component recovered in the leachate was carbonate ion (CO_3^{2-}), which was taken as an indication that extensive metabolisation of diuron had occurred.

The soil analysis showed that the majority of AR remained in the topsoil (0-20 centimetres) with less than 1% of AR in the remaining soil (20–105 centimetres). For Nantuna, the diuron was in the 0–5 centimetre layer and for Langaveka more had moved into the 5–10 centimetre layer. The laboratory half-lives were 20 and 119 days for Nantuna and Langaveka soils respectively at 20°C, 70 per cent of maximum water holding capacity.

These results are supported by a more recent study described in the literature in which diuron was applied at 2.3 kg/ha. Ten lysimeters were installed in a circle in the test plot. Five were 40-centimetres deep and five were 20 centimetres deep. The experiment ran for 245 days. Twelve soil pore water samples (about one for each week or after rain events) were collected from each lysimeter during the whole experiment and soil was sampled periodically. The first ‘rain’ event (artificial) was 100 millimetres on day 16. In several of the lysimeters, the peak of herbicide concentrations was evident on this day, and in these lysimeters, no herbicide was detected after 97 days in leachate. In the remainder of the lysimeters (there was no distinction between those draining at 20 or 40 centimetres, both depths appeared to behave the same), the maximum concentration peaks were detected at day 20 with a rapid decrease, although some secondary peaks appeared at 40–90 days in concordance with other precipitation events. Reading the values from a graph, initial peak concentrations of diuron in leachate were 14 and 10 µg/L at days 16 and 20 respectively, with around 4.5 µg/L at day 38, 2 µg/L at day 41, and falling thereafter. The main metabolites were DCPMU and DCA, and their concentrations were always lower than 3 µg/L. The total leached amount of diuron residues accounted for around 0.36 per cent of the initially applied chemical.

No diuron was detected below the 10-centimetre soil layer in soil, despite unchanged diuron being found in leachate water at 20 and 40 cm depth (possibly due to differences in detection levels in soil and water). The

main metabolite was DCPMU: it was generally only in the top 10 centimetres, but it was also found distributed through the soil profile to 40 centimetres at the day 8 sampling event.

It is concluded by DSEWPaC that the study shows limited leaching at the lower application rate but also indicates that at higher rates the leaching is proportionately higher.

1.5.10 Field dissipation

1.5.10.1 Field dissipation studies

Australian Field Study 1

Studies funded by the Cooperative Research Centre (CRC) for Sugar have included field and laboratory studies at four field sites in the Bundaberg region to enhance understanding of on-site and off-site movement and persistence of pesticides commonly used in cane production systems. The study was over a three-year period and the weather was considered to be dry overall for this region. All sites were under commercial cultivation and were subject to normal farming practices of cultivation and irrigation; but they were left with bare soil and were not trash covered, contrary to normal practice. The effect of trash cover was examined separately.

The results of this study show that the Koc values ranged from 1326 to 5240 and are in the range for the European and North American soils but as these were determined in a non-standard method they may not be comparable. Dissipation half-lives were calculated as between 6.5 to more than 250 days using a second order equation, but these can be misleading as values for DT_{90} (time for 90 per cent of the substance to dissipate) were not reported.

The runoff of diuron and its leaching was also examined at these test sites. Runoff of diuron was monitored: less than 0.2% of the annual application rate was detected in the runoff water. The maximum average concentration in runoff water was 113 µg/L. The average levels of diuron were 0.37–2.9 µg/L. Diuron was detected in groundwater at a maximum concentration of about 6.5 µg/L.

In the trials where the cane fields were covered in trash, diuron remained in the trash and was persistent, with 50 per cent loss occurring in approximately 21 days (estimated graphically). The level of diuron in the covered soil was not measured. However, for other pesticides where the concentration in the soil below the trash were measured, levels in the soil were less than 15% of application rate (estimated graphically by DSEWPaC).

The report concluded that this study highlighted the need for careful management of application timing and chemical selection, particularly in areas close to waterways and sensitive habitats.

Australian Field Study 2

Field studies of diuron and its metabolites DCPMU, DCPU and DCA were conducted in a farm soil and in stream sediments in coastal Queensland (Burnett catchment), Australia. The farm operated under a conventional regime of sugarcane production. A spray application of diuron at 1.6 kg/ha was made to a 6.3-hectare block nearing canopy closure in December 2005 with about 25 millimetres of irrigation applied immediately after spraying. Surface runoff was quantified with sampling activated at preset time intervals

when the flow rate exceeded 0.9 mm/hour. Soil dissipation was carried out in three contiguous interrows adjacent to the runoff catchment area with soil sampling (0–45 cm depth) conducted up to 267 days after application. Stream sediment sampling was also carried out over an approximate 5-kilometre length of stream below a catchment that contained around 3500 hectares of sugarcane farmland.

Runoff: During peak runoff, concentrations of diuron ranged between 64 and 73 µg/L and rose steeply to 280 µg/L in the last sampling. Concentrations of DCPU and DCPMU were 23–39 µg/L and 70–94 µg/L respectively in the same period. Average concentrations during the peak sampling period were 93 µg/L diuron, 30 µg/L DCPU and 83 µg/L DCPMU. The loading of all compounds during this time was equivalent to around 0.12 per cent applied diuron. This amount was detected during the first 13 minutes of a 55 minute surface flow event (about 25% of the period), suggesting the actual load of diuron lost could be in excess of 0.5 per cent of the level applied during the one runoff event.

Soil dissipation: Diuron was restricted primarily to the top 15 centimetres, with levels generally 35 µg/kg or less (read from graph) in the 15–30 centimetre layer, and 10 µg/kg or less (read from graph) in the 30–45 centimetre layer. Diuron dissipated steadily from the soil and the first order half-life was calculated to be 49 days (r^2 = 0.99). DCPMU was found mainly in the top 0–15 centimetres with low detections in the 15–30 centimetre layer. At the end of the sampling period (267 DAA), this metabolite was found in the 0–15 centimetre soil layer at a concentration of 6 µg/kg, equating to around 14 g/ha.

Sediment analysis: Diuron was detected in all sediment samples at concentrations between 3 and 19 µg/kg while DCPMU was found (again in all samples) at concentrations of 4 to 31 µg/kg. Based on values read from a graph, the mean concentration of diuron (10 samples) was about 15.1 µg/kg, and that for DCPMU was about 18.2 µg/kg.

International Field Study 1

A terrestrial field dissipation study was conducted according to US EPA Guidelines. Diuron was applied to bare soil at three sites at a target rate of 13.44 kg ac/ha with soil textures of sand, silt loam and silty clay loam. The applications averaged between 86 to 101 per cent of the target rate. All sites received natural rainfall plus additional irrigation to ensure monthly totals were above the historical (years 1961–1990) monthly averages. The samples were analysed for diuron and other metabolites but only DCPMU was detected.

The initial degradation of diuron was fast in these soils but slowed down and the diuron remaining in the upper soil segment (0–15 centimetres) after 238–301 days was 3–19 per cent of that initially applied. The half-lives (first order analysis) were calculated as 73, 141 and 135 days. The half–life of the metabolite DCPMU at the three sites was also calculated as 182, 231, 112 days.

There were occasional detections of diuron in the 15–30 centimetre soil section at low levels and several detections at lower levels on the day of application that were considered to be due to contamination. There was only one other detection below 30 centimetres above the limit of quantification (LOQ = 0.020 mg/kg) at 0.023 mg/kg. DCPMU was mainly detected in the first 0–15 centimetres of the soil, with only occasional detections lower down (15–30 centimetres, in which the highest concentration was 0.028 mg/kg).

International Field Study 2

A terrestrial field dissipation study was conducted according to US EPA Guidelines at two sites at a target rate of 13.44 kg ac/ha. The soil was characterised as silty clay loam and sandy loam at Delaware and California respectively. During the test, the Newark site received mainly 1659 millimetres of natural rainfall. The California site was irrigated for the first three months and was irrigated for 1–4 hours per day.

The soil samples were analysed for diuron and DCPMU only. The soil samples taken immediately after application showed approximately 30 per cent of the target concentration at both sites. For Delaware, diuron was occasionally below 15 centimetres, but only at trace levels (< LOQ of 0.02 mg/kg). At the California site there were detections of up to 0.70 mg of diuron per kg soil down to 45–60 centimetres deep on days 7, 15, 29, 89 and 152. There would appear to be some indication that vertical movement of diuron occurred in the sandy soil at the California site.

The half-lives were calculated as 134 and 102 days for Delaware and California respectively using first order analysis. For Delaware, the fit was not the best, but it appears that the degradation slowed down during winter. For the California site the fit to first order kinetics was much better, presumably because the soil the temperatures were higher. The study has some problems in that the initial concentration was only 30 per cent of the target rate, for some samples only one plot was analysed and, with the normal high variability between plots, this is unsatisfactory.

International Field Study 3

A terrestrial field study was conducted at six sites in Germany under field conditions without vegetation according to BBA Guidelines. Diuron was applied to bare soil at 8 kg ac/ha during the German spring, and then the soils were sampled at approximately 30-day intervals for 300 days after the treatments. Diuron degraded with half-lives of between 67–231 days (first order analysis) for most sites, but at one site (Massen), the soil analysis showed high variability and very limited degradation. While a half-life could be calculated (533 days), the fit was poor and the result unreliable. The main metabolite found in all sites was DCPMU and reached a maximum in all soils of between 0.363 and 0.799 mg/kg before declining. There was no evidence of leaching, with diuron being found in the 10–20 centimetre soil sections on only threee occasions. There were three additional detections deeper than 20 centimetres on day 0, but these are likely to be due to contamination during sampling.

International Field Study 4

A field dissipation and transport study was conducted according to US EPA Guidelines. Diuron was applied to an irrigation ditch (slope and berms) in California at a target rate of 13.44 kg ac/ha. No application was made to the channel bed in the treatment area. There was an untreated ditch between the control, treatment and the downstream sampling areas.

The soil on the slope and berms (top of the bank forming the ditch) was a clay soil while the sediment in the irrigation channel was classified as a clay loam. The weather at the site was drier than normal, with only 221 mm of total rainfall (8.72 inches) compared to the 10-year average of approximately 500 millimetres. There was no rain for approximately two weeks before application and the first significant rainfall occurred 24 days after application when 37 millimetres fell over two days. There was no further significant rain until 159 days alter, when 19.6 millimetres (0.77 inches) fell.

The results of the soil analysis on the slope and berm showed that diuron dissipated with a DT50 (the time for 50% of the substance to dissipate) of 142 days, calculated using a non-linear regression analysis (first order analysis gives 224 days). After 178 days there was an average of 2.2 mg/kg soil (range 1.7 to 3.0 mg/kg). The sediment analysis (LOQ 0.05 mg/kg sediment) showed only positive results for 0, 2, 4 and 256 days after treatment (average concentrations of 0.76, 0.059, 0.12 and 0.065 mg/kg respectively) and only near the treatment area. The sample on 256 days could be due to runoff from the surrounding treated soil as it was the first time sampling occurred on a day when it rained (19 millimetres). There were no other detections of diuron or its metabolites in any other water sample.

DSEWPaC concludes that the dry weather limited movement of diuron and it therefore remained on the soil. The degradation of diuron on dry soil is slow but the final sediment sample may indicate that when rainfall does occur, runoff or erosion allows diuron to enter drainage channels.

International Field Study 5

A field dissipation and transport study was conducted as above (Field Study 4) according to US EPA Guidelines in Arkansas. The soil on the side of the ditch was a clay soil while the sediment in the irrigation channel was classified as a silt loam. The weather at the site over sampling period (November–May) of the study was typical, with about 860 millimetres of rainfall.

The results of the soil analysis showed that diuron dissipated from the soil with a DT50 of 105 days, calculated using a non-linear regression analysis (first order analysis gives an average of 104 days). The metabolite DCPMU was detected in these soil samples, initially from 0 days after the treatment and then slowly increased to reach maximum of 0.45 mg/kg. The sediment analysis showed positive results in the treatment area at time zero and was considered by the authors to be due to spray drift. The concentration of diuron in the sediment near the treatment area showed a reasonably consistent level of around 0.5 mg/kg except for the 179th day after treatment, with the highest value of 1.61 mg/kg. Only one metabolite was detected, that being DCPMU, with a maximum concentration of 0.13 mg/kg by 179 days after treatment. These results for sediment in the channels showed a pattern that is consistent with the hypothesis that sediment was washing off the treated area and moving downstream.

The majority of positive detections from the scheduled water samples occurred 9 to 34 days after treatment, which appears to show limited aquatic exposure. However, the raw data for 48 days after treatment show levels of diuron only slightly below the limit of quantification. If this is a general situation, then the information tends to indicate that diuron is a low level contaminant of water systems.

From the automatic water samplers (samples taken during flow-events), the peak concentration was 130 µg/L in the first two events, with high concentrations for a period of 12 hours of 120–130 µg/L (samples taken 4, 8, and 16 hours after the initial flow). Subsequent samples during events 3 to 10 (6–152 days after treatment) generally had concentrations of diuron below the limit of quantification except for 152 days after treatment (event 10, first sample) when one of two duplicate analyses gave a reading of 10 µg/L.

It was concluded that while the study shows that diuron primarily remains in the soil at the site of application, erosion causes soil-bound and dissolved diuron to enter aquatic systems, where it either is mobilised or degrades. The study gives some hints as to the likely fate of diuron, but due to the relatively insensitive limit of quantification used, further conclusions are speculative.

International Field Study 6

A study was conducted in California's northern Central Valley to examine the loss of simazine and diuron in runoff from application along highway rights-of-way. Simazine and diuron were applied at 2.02 kg simazine/ha and 3.59 kg diuron/ha next to the highway pavement. Concentrations of simazine and diuron in highway runoff were measured during both simulated and natural rainfall. Concentrations of diuron in the simulated runoff ranged from 144 to 1770 µg/L. Total mass of herbicide leaving the plots in runoff accounted for up to 5.4 per cent of the applied diuron. For natural rain runoff, concentrations of diuron ranged from 46 to 2849 µg/L. The largest amount removed in any sampled period was 8.4 per cent of the diuron in one 28-hour period.

Literature

In an existing tree orchard on a loam soil in Belgium, diuron was applied at 3 kg ac/ha to two plots, one never having received any applications of diuron while the other had been treated annually for the previous 12 years. Analysis of diuron in the 0–10 centimetre surface soil layer gave first order degradation curves with half-lives of 81 days (r = 0.9899) for the plot receiving diuron for the first time and 37 days (r = 0.9984) for the plot treated for the past 12 years. There appears to be a clear indication that soil micro-organisms can be conditioned to degrade diuron, resulting in quicker degradation rates.

1.5.11 Australian monitoring data

A more detailed description of available monitoring information is found in Volume 2. The following provides a summary of this information.

1.5.11.1 Water—Drainage channels and streams

Queensland

Extensive monitoring data are available for water in streams from various catchments in Queensland spanning several years. The range of results includes those obtained during flow events and under more ambient conditions. It is apparent from the data that sugarcane subcatchments produce the highest diuron concentrations compared to subcatchments with other land uses. The highest levels of diuron detected in streams (discounting drains where higher levels are found) occur in the 1 to 10 µg/L range, and such concentrations are generally associated with surface waters in catchments dominated by sugarcane use.

The majority of detections are below this level (less than 0.01 to 1 µg/L), and from several larger datasets around 85 per cent of samples showed levels below 1 µg/L.

New South Wales

Levels found in NSW river systems are of a similar magnitude as those found in Queensland waters. From 1991–99, diuron was detected in all river basins near irrigated cotton and not necessarily associated with runoff events. With more than 200 samples taken per year, diuron was found in a range of 5 per cent of samples (1995–96) to 27.4 per cent of samples (1991–92), with maximum concentrations again generally in the 1–10 µg/L range (highest level of 23 µg/L). Similarly, more recent data (1998–2005) from the same area (Gwydir and Namoi rivers, more than 300 samples per annum) detected diuron in around 8 per cent of

samples (2002–03) to 20 per cent of samples (1998–99). Peak levels were generally below 10 µg/L, although several were between 10 and 20 µg/L.

Monitoring in the southwestern irrigation areas of NSW over a five-year period (1990–1995) showed at times significant levels of diuron. Sampling of the main drains (1991–93) in the Murrumbidgee Irrigation Area showed that in 41 per cent of all samples taken diuron was detected in water (with the maximum of 9.5 µg/L), with a maximum 5.4 µg/L in surface water in 1994–95. Tile (subsurface) drains at 49 horticulture farms in the Murrumbidgee Irrigation Area were sampled in 1992, and around 40 per cent of farms had detectable levels (more than 0.05 µg/L) of diuron and generally the same farms were positive whenever sampled. The maximum concentration measured was 28 µg/L. During the four years from July 1997 to June 2001, water monitoring of drainage water at 15 sites in the Murrumbidgee Irrigation Area showed several detections of more than 20 µg/L of diuron. From a total of 548 samples, the 75th, 90th, 95th and 99th percentile values were reported as 0.4, 0.9, 2.26 and 12.6 µg/L respectively. More recent data (2004–06) at these sites gave similar results, although the highest level detected was 13.2 µg/L. In these data, the highest levels were found in the cooler months (April through August). Analysis of these months shows that diuron was found (0.1 µg/L or higher) in 60.6 per cent of samples (n = 137), and where detected, the 90th percentile was 2.1 µg/L. The maximum level detected was 13.2 µg/L. 11 per cent of samples were more than 1 µg/L. In the warmer months (taken as September through March), diuron was found (0.1 µg/L or higher) in 36.2 per cent of samples (n = 185), and where detected, the 90th percentile was 0.54 µg/L. The maximum level detected was 1.1 µg/L. 1.1 per cent of samples were more than 1 µg/L.

Further data for Mirrool Creek just above Barren Box Swamp in 1991 showed diuron was present most of the time but at low levels (0.06–0.17 µg/L), with similar levels found in 1994 monitoring. Daily automatic monitoring of Little Mirrool Creek in 1994 gave mean levels of 1.19 µg/L with a range 0.1 to 7.5 µg/L.

1.5.11.2 Water—coastal

A visible flood plume offshore from Mackay arising from the Pioneer River was sampled on 27 and 28 January 2005. A plume from the Proserpine–O'Connell River (Queensland) was also sampled. Diuron was found in 9 of 11 samples, with concentrations ranging from 0.05 to 0.44 µg/L. There was a clear reduction in concentrations as dilution with seawater increased.

Samples were taken from a flood plume produced from the Haughton River and Barratta Creek (Queensland) in 2007. Diuron was detected in 12 of 14 samples at concentrations of less than 0.01 µg/L to 0.08 µg/L.

From sampling during 2002–04, low concentrations of diuron, together with other herbicides, were detected in surface waters in inter-tidal seagrass meadows in Hervey Bay. The two major streams flowing into the Hervey Bay—the Mary and Burrum rivers—were also sampled. The concentration of diuron in the surface water at the seagrass meadows ranged from below detection to 25 ng/L. Sampling of the Mary River gave levels ranging from 15 to 105 ng/L and for the Burrum River, the levels in December ranged from less than 5 to 60 ng/L.

1.5.11.3 Water—offshore

Passive samplers were deployed at inshore creek and river mouth sites (the Russell–Mulgrave and Johnstone rivers) in the Wet Tropics of the Great Barrier Reef at the end of the dry season (November 2004)

and during the wet season (January 2005). Other reef sites that were sampled include Double Island, Fitzroy Island, High Island, Normanby Island, South Barnard Island and Dunk Island. These reef sites were between 8.6 to 30 kilometres from the nearest streams and the streamwater monitoring sites were 500 metres offshore. Diuron was commonly detected with levels ranging from 0.2–0.7 ng/L in November and 0.5–1.6 ng/L in January, all expressed as integrated average samples over the deployment period.

Average wet season concentrations during 2005–08 from 13 inshore reef sites from Lizard Island (northernmost sampling point) to North Keppel Island (southernmost sampling point) ranged from 0.171 to 5.41 ng/L; sampling stations were up to 35 kilometres offshore. The results of sampling throughout the wet and dry seasons of 2006–07 at these same sites indicates inshore reef concentrations are higher in the wet season. For diuron, the highest estimated concentration was approaching 20 ng/L (0.02 µg/L), but were generally less than 10 ng/L (0.01 µg/L) in the wet season. In the dry season, levels were generally less than 1 ng/L (0.001 µg/L).

1.5.11.4 Sediment

Diuron was detected in sediment at four sampled sites following dieback of mangroves in the Pioneer River estuary, principally in 1998. The concentrations were 4, 0.8 and 3 µg/kg dw in samples taken from areas affected by mangrove dieback and 0.2 µg/kg dw in one sample taken in an area of relatively normal mangroves in Bucasia–Eimeo creeks. Further sampling conducted in 2002 in the Mackay district showed diuron in all sediment samples at 0.1–8.2 µg/kg dw. Diuron was detected in core water samples taken at the same site (with a maximum level of 12.9 ng/L; range 3.3–12.9 ng/L) and in water column samples (taken at the high tide on the same day as sediment samples with a maximum of 5.2 ng/L in upstream samples and a maximum of 1.1 ng/L downstream in the Pioneer River).

The concentrations of diuron in sediment and seagrass from 16 intertidal sites (less than 1 metre deep; three samples per site pooled), located from Cape York to Moreton Bay at important dugong habitats, together with 24 subtidal sites (less than 5 metres deep, in duplicate three random grab samples, 500–1000 metres apart) located near major estuaries were been determined in 1998–99. In the intertidal samples, there were three detections in sediment (0.5, 1.7 and 0.6 µg/kg dw for Cairns, Cardwell and Moreton Bay respectively) and four in the seagrasses (0.6, 1.1, 0.8 and 1.7 µg/kg dw for Cairns, Cardwell, Pallarenda and Moreton Bay respectively). For the subtidal sites, diuron was detected at nine of the 24 sites at concentrations ranging from 0.2 to 10.1 µg/kg dw (mean where found of 3.0 µg/kg). The positive detections were mainly near streams draining the sugar growing areas.

In a study focusing on pesticide contamination of sediments in irrigation channels and drains in various areas of Queensland (published in 2000), sampling occurred along the banks or the wet/dry bed in the channel and drain. Each sample was a composite of eight subsamples taken at 10-metre intervals. Diuron was detected in 75 of 103 samples, with the most frequent detections and highest concentrations (up to 340 µg/kg) of diuron generally occurring in drains from cotton crops. The highest levels of diuron from the sugarcane areas reached 120 µg/kg sediment.

Low concentrations of diuron, together with other herbicides, were detected in sediments in intertidal seagrass meadows in Hervey Bay, Queensland. Sampling occurred in April and December 2002, both periods of low rainfall and low streamflows, and in February 2003 and 2004 during moderate flow events

(monthly rain fall 325 millimetres). The concentrations of diuron in April and December in the sediments were found from below detection levels to 0.2 ng/kg dw.

1.5.12 Overseas monitoring data

The United States Geological Survey conducted a large water quality program in 20 hydrologic basins (USGS 1998). The samples were analysed for 76 pesticides including diuron. These results clearly showed that diuron is mainly found in the surface water, with lower levels in groundwater. This appears to indicate that diuron is not a significant leacher but it does enter surface waters. The maximum concentration occurred in surface drainage from agricultural areas (14 µg/L) but surface water from urban areas also had high levels (8.04 µg/L). Sampling in larger streams gave lower levels, with a maximum of just 1.2 µg/L.

The Environment Agency (UK) conducts routine monitoring of pesticides in freshwater. The results for diuron in 1996 and 1997 were summarised for fresh and marine waters. The level of diuron reported in the freshwater varied considerably, with the upper range of values reaching 51280 ng/L. The higher values reflected large urban areas where diuron is used for weed control in right-of-way situations. Diuron is not registered for use in UK agricultural crops. The concentration of diuron in marine areas due to its use as a biocide was monitored monthly during the boating season (April–October 1998) at three sites in the UK; the level of diuron was higher in marinas than the surrounding estuaries. The highest level (6742 ng/L) was from a locked marina in April containing approximately 275 boats with limited flushing during winter. The levels of diuron fell after April to 112 ng/L in August (peak of the boating season in the UK). It was concluded that the UK results show that use of diuron in both urban areas and as a marine biocide can lead to high levels in nearby systems.

1.5.13 Bioaccumulation

No data were provided for assessment. The properties of diuron, particularly its low octanol-water partition co-efficient, suggest it will have a low potential to bioaccumulate and this appears to be confirmed by laboratory bioconcentration factors of 15–85 and a field study bioconcentration factor of 190–300 reported in the Netherlands (data not provided to the APVMA for review). These values are indicative of slight to moderate concentration potential (Mensink et al. 1995).

1.5.14 Soil accumulation

No soil accumulation studies were provided. The potential persistence of diuron in soil combined with high application rates gives it the potential to accumulate in soil. At an application rate of 1.8 kg/ha (typical broadacre rate), soil residues following application with mixing in the top 10 centimetres of soil (soil density of 1500 kg/m^3) would be 1.2 mg/kg soil.

Using the method based on Smith (1982), a soil half-life of six months would result in an annual carryover of 24.2 per cent, and maximum soil residues immediately following application (assumed one application per annum) of around 1.6 mg/kg soil would result. However, with a worst-case half-life of one year, annual carryover would be 50 per cent and a maximum soil residue immediately following application of 2.4 mg/kg is predicted to occur (after around seven years use in the same area).

1.5.15 Modelling studies

Modelling was undertaken by DuPont to consider practical best management practice for diuron use in sugarcane in Queensland. The Pioneer River watershed was selected as the subject for the modelling study and was modelled with the Riverine Water Quality model using extensive information on soils, topology, long-term hydrolygy and climatic data, land use and digital image data from publicly available sources. Runoff was estimated with the Pesticide Root Zone Model using different scenarios developed to account for soils, cropping practices and weather throughout the watershed. Runoff and drift loadings were applied to the receiving waters defined by the Riverine Water Quality model so that concentrations of diuron could be calculated at many locations in the watershed. Modelling of baseline agronomic practices showed a relatively good agreement between predicted and measured water concentrations within the Pioneer River and Dumbleton Weir.

To evaluate the impact of best management practices, a series of scenarios were developed including some of the following changes to management practices:

- application rate was reduced (band spraying reducing per hectare rate to 0.9 kg ac/ha)
- no application of diuron in the wet season
- improved cultivation using reduced tillage
- presence of a vegetative buffer strip
- presence of a sugarcane trash layer
- proximity of paddocks/farm to stream.

The first two practices would appear the easiest to implement consistently, and a combination of these two practices resulted in an overall predicted average reduction in maximum levels of almost 81 per cent based on the 12-year modelling cycle is used. When combining multiple practices (dry season application, reduced rate, presence of trash and no treatment on slopes steeper than 5 per cent) were modelled, mass loadings were predicted to be reduced by around 94 per cent.

Since the provision of this modelling, DSEWPaC has concluded that the main two assumptions are hard to sustain. The window concept (altering the timing of application) does not reflect a risk-based approach to the application of herbicides. It does not take into consideration local weather conditions or seasonal weather patterns. Secondly, the crop cycle in cane is variable and dependent on the seasonal conditions. The crush may finish anywhere between October and January, and crops either planted or ratooned after the harvest period would be disadvantaged as row closure (DuPont has proposed to limit use to this stage) doesn't occur until 120–150 days after harvest (potentially up to the end of April).

Regarding utilisation of band spraying to reduce the application rate by 50 per cent, DSEWPaC was advised that diuron products are applied as both band and full cover with the exclusion of the plant line area. In situations where cane is more advanced and there are concerns about crop safety, then directed application is used. This is effectively applying in a band, with sprays being applied on the furrow to base of the plant. DuPont Australia estimated that 70–85 per cent of the band area would be covered, not the 50 per cent assumed in the modelling.

1.5.16 Conclusions on environmental fate

Diuron is stable to hydrolysis within the environmental pH range. In water, some photolysis of diuron may occur and half-lives from various studies ranged from 6.7 to 43 days. On soil, photolysis is not expected to occur to any significant level: a half-life of diuron of 173 days was determined in one study.

The biodegradation data indicate two metabolic pathways for diuron degradation. The aerobic pathway involves demethylation of the urea to give the metabolites DCPMU and DCPU. The anaerobic pathway (potentially a faster route of primary degradation) involves dechlorination of the phenyl ring, a typical anaerobic degradation, to give m-CPDMU and PDMU.

In aerobic soil laboratory studies, degradation of diuron varied considerably, with half-lives ranging from 20 days to 372 days from several different soils. The major metabolite identified was DCPMU, which was also persistent in field studies. A separate aerobic soil metabolism study for this metabolite in three soils indicated aerobic soil half-lives between 40 and 89 days. Similarly, the m-CPDMU metabolite was shown to persist in an aerobic soil study (two soils tested) with half-lives of 205–546 days, both well in excess of the study duration. It is apparent from such data that diuron has the potential to be very persistent in soils. In one anaerobic soil study, no degradation of diuron was observed through the anaerobic phase.

Based on two aerobic water–sediment systems (one study), when applied to water, diuron may move to sediment, but this process is not necessarily fast or complete. In one system, diuron moved to sediment with a water-column half-life around 11 days, and a whole-system half-life of 35 days. However, in the second system, dissipation from the water column was bi-phasic, with a first phase half-life of 5.5 days and a very long second phase half-life of 67 days (more than 2 months). For the whole system, diuron was persistent, with a half-life of 277 days. These data suggest that diuron has the potential to persist in both water and sediments. One study considering the anaerobic degradation of diuron in a water–sediment system showed rapid degradation (half-life of 1.2 days) through dechlorination of diuron. This result is in contrast to field measurements showing unchanged diuron in Australian sediments at up to 1 metre depth. The fast half-life was the result of dechlorination to the monochlorinated metabolite, m-CPDMU, found in almost stoichiometric amounts, and this metabolite was persistent. A separate aerobic aquatic metabolism study for this metabolite (two water–sediment systems) found half-life dissipation from the water column of 44–69 days (persistent in water), with whole system half-lives of 183–415 days, indicating it does not readily degrade in sediments. In an anaerobic water–sediment system, m-CPDMU demonstrated biphasic dissipation from the water column with a first half-life around 17 days and the second phase half-life around 100 days. It persisted in sediment with between 48 and 54 per cent AR found in sediments from day 15 to day 100, the end of the study period.

The Koc of diuron was calculated to be 366–1750 for nine soils; diuron is rated as being of low to medium mobility. The desorption data showed that, in one soil, up to 40 per cent of the initially soil adsorbed diuron was re-mobilised back to the water column. For other soils, the level of desorption was lower (7–17 per cent), but still significant. The leachability of diuron was studied using field lysimeters and showed very limited leaching.

In Australian field studies, conducted at three sugarcane farms in the Bundaberg region, the DT50 for diuron ranged from 6.5 to 20 days at two sites but was given as more than 250 days each year over a three-year period at the third farm, again showing that diuron has a wide range of degradation rates. There was no

evidence of vertical movement, and the concentration of diuron in surface runoff water ranged from 0.37 to 120 µg/L. In groundwater the maximum concentration was 6.5 µg/L. In a more recent experiment on a sugarcane farm in south-eastern Queensland, diuron dissipated steadily from the soil, and the first order half-life was calculated to be 49 days with residues mainly confined to the top 15 centimetres soil. DCPMU was the main metabolite found, and both diuron and DCPMU residues remain in the soil 267 days after application. Average concentrations of diuron and metabolites during a runoff event were 93 µg/L diuron, 30 µg/L DCPU, and 83 µg/L DCPMU. In sediment sampling from a stream below a sugarcane catchment, both diuron and DCPMU were found at all sampling points along a 5-kilometre stretch of the stream. Average concentrations (based on a graph) appeared to be about 15.1 µg/kg for diuron while that for DCPMU was about 18.2 µg/kg.

The overseas terrestrial field studies (12 sites) gave soil DT50s ranging from 67 to 231 days, with one site having limited degradation, which indicates that diuron is slightly to very slightly degradable under field conditions. There was only limited evidence of vertical movement at one site. In a field study where diuron was used for weed control in two channels, the concentration of diuron reached 130 µg/L after rain. When diuron was used for weed control along roadsides, the concentration of diuron in runoff following rain reached 2849 µg/L, which was up to 8.4 per cent of the applied diuron.

In a series of studies conducted in the Pioneer River estuary, peak levels of diuron during flood events were 5–8.5 µg/L and mean levels were 2.6–4.95 µg/L. It was concluded that the source of diuron in these river systems was almost exclusively from sugarcane runoff. Other monitoring studies performed in Queensland catchments confirmed higher diuron levels resulting from sugarcane farming. Based on a large sample size, the majority of surface water results from streams, where detected, range from 0.01 to 1 µg/L. While ambient concentrations were generally at the lower end of the range, some ambient values (up to 8.5 µg/L) were still recorded to be higher than most water concentrations found during event flows.

Diuron has been detected in sediments and seagrasses near important dugong habitats and in surface waters in Hervey Bay and the Mary River at low concentrations. At reef sites on the Great Barrier Reef, diuron was detected at very low levels up to average levels of around 20 ng/L from passive samplers. In irrigation channels and drains in various areas of Queensland, diuron was detected in 72 per cent of all sediment samples at up to 340 µg/kg sediment dry weight. The highest frequency of detections and levels of diuron occurred in drains from cotton crops.

Diuron has been detected in all river basins near irrigated cotton in NSW with monitoring spanning from 1991 to 2005. The data show a significant decrease in number of detections and levels found since 1999. For the data spanning 1999–2005 in this region, the maximum level found was 19.5 µg/L with a 90th percentile of 1.93 µg/L (n = 2248). Non-detections accounted for 88 per cent of the dataset. Diuron monitoring data are also available for the Murrumbidgee Irrigation Area in NSW spanning from 1990 to 2005. The data tend to show several detections each year where diuron is found at significant levels (1 to more than 20 µg/L). The most recent data (2004–06) provided as part of compliance reporting show that diuron is found at higher levels in cooler months (more than 0.1 µg/L in 60.6 per cent of samples, maximum of 13.2 µg/L; 90th percentile of positive detections of 2.1 µg/L) compared to warmer months (more than 0.1 µg/L in 36.2 per cent of samples, maximum of 1.1 µg/L; 90th percentile of positive detections of 0.54 µg/L). However, it is apparent that these data from monthly samples are unlikely to represent peak concentrations, or provide detail on duration that elevated concentrations may exist in surface waters.

In the US, a large water quality monitoring program showed that diuron is mainly found in the surface water with the maximum concentration from agricultural area (14 µg/L), but urban areas also had high levels (8.04 µg/L). In the UK, routine monitoring for diuron in 1996 and 1997 showed a range of values reaching 51.3 µg/L. In marine areas, the highest levels occurred in marinas with a maximum of 6742 µg/L due to antifoulant use of diuron.

1.6 Environmental effects

1.6.1 Introductory comments

Since the release of the PRF, a significant amount of environmental toxicity data has been provided to the APVMA by DuPont. These regulatory studies reviewed by DSEWPaC are rated as reliable (high level of confidence in the study and according to the relevant Guideline although there could be minor problems that do not affect the results), acceptable (scientifically sound and meet most of the requirements of the relevant Guideline but with a significant problem or lack of critical information) or for information only (not suitable for regulatory use).

In addition, data have been obtained from the US EPA Pesticide Ecotoxicity Database, current as of March 2002 (US EPA 2004) or provided by the registrants. The same data have been used by the US EPA in their Re-registration Eligibility Document for diuron, which is publicly available (US EPA 2003). These studies have been reviewed by the US EPA and rated by them as either 'Core' (that is, fulfilling current guideline requirements, though possibly with minor inconsistencies from standard recommended procedures—acceptable for use in a risk assessment) or 'Supplemental' (scientifically sound, but performed under conditions that deviated substantially from recommended protocols—may be useful in a risk assessment).

There are numerous additional reports in the open scientific literature or in the US EPA ECOTOX database <http://www.epa.gov/ecotox/>. In general, these have not been consulted for this assessment except those specifically designed for reef organisms and plants for which there is a high level of concern and are key to the scope of this review.

This overview report should be read in conjunction with '—Technical report for environmental effects of diuron'.

1.6.2 Avian

Based on reviewed studies looking at the toxicity of diuron to birds (and other results available in summary from only), diuron is most toxic to bobwhite quail in both acute oral and short term dietary studies, and can be considered slightly toxic to this species. For other bird species where results are available, diuron is practically non-toxic under acute oral or short-term dietary exposure conditions. For reproduction results, mallard duck was the most sensitive species, with a NOEC of 10 mg/kg diet based on effects on egg-laying (see tables C7, C8 and C9).

Table C7. Summary of acute oral toxicity of diuron to birds

SPECIES	LD50 (mg ac/kg bw)	NOEC (mg ac/kg bw)	REFERENCE
Technical			

Mallard duck	>2000	Not recorded	US EPA 2004
Bobwhite quail	940 (712-1183) 1104	<292 260	US EPA 2004 Leuschner 2001

Table C8: Summary of dietary toxicity of diuron to birds

SPECIES	LD50 (mg/kg DIET)	NOEC (mg /kg DIET)	REFERENCE
Technical			
Mallard duck	>5000	Not recorded	Heath et al. 1972
Bobwhite quail	1730 (1482-2035)	Not recorded	Heath et al. 1972
Ring neck pheasant	>5000	Not recorded	Heath et al. 1972
Japanese quail	>5000	Not recorded	Heath et al. 1972

Table C9: Summary of chronic toxicity of diuron to birds

SPECIES	LOEC (mg ac/kg DIET)	NOEC (mg ac/kg DIET)	REFERENCE
Technical			
Mallard duck	33	10	Temple et al. 2007
Bobwhite quail	300	100	Leuschner 2002

1.6.3 Fish

1.6.3.1 Acute exposure

Four studies were provided for review. Table C10 below summarises these and other available results that were obtained from the literature, the US EPA Pesticide Database, or cited in the EPA Reregistration Eligibility Decision.

Diuron is rated as moderately to slightly toxic to rainbow trout for acute exposure, according to the DSEWPaC classification, and also for prolonged toxicity. From the non-reviewed results, the range of acute LC50s for diuron is from 0.71 to more than300 mg ac/L, corresponding to a rating of very slightly to highly toxic. In addition to the results presented below in Table C10, a report was reviewed showing diuron affects the livers of pink snapper (*Pagrus aratus*), measured using sorbitol dehydrogenase as the marker of hepatocellular (liver) damage, with a LOEC at 10 µg/L and NOEC of 5 µg/L. These results would appear to indicate that, although diuron is only moderately acutely toxic to fish, it can cause hepatocellular toxicity at considerably lower levels.

Table C10: Summary of acute fish toxicity results for diuron

TEST SPECIES	SYSTEM	96 h LC50 (mg ac/l) (95% CONFIDENCE INTERVALS)	REFERENCE
Bluegill sunfish	96 hours static; 28% ac	84.0 (68.3–103.3)	US EPA 2004
	96 hours static; 95% ac	3.2 (2.53–4.05)	US EPA 2004

	96 hours static; 95% ac	2.8 (2.3–3.3)	US EPA 2003
	96 hours static; 28% ac	>25 (NR)	Baer 1991b
Rainbow trout	96 hours static;	22.2 (10.6–46.3)	Zoltán 2001a
	96 hours static; 28% ac	23.8 (20–28.3)	US EPA 2004
	96 hours static; 95% ac	1.95 (1.5–2.54)	US EPA 2003
	96 hours static; 80% ac	16 (11–23)	US EPA 2004
	96 hours static; 80% ac	19.6 (NR)	US EPA 2004
	96 hours static; 80% ac	22.2 (Not calculated)	Baer 1991a
Fathead minnow	96 hours static; 98.6% ac	14.2 (13.4–15.0)	US EPA 2003
	10 days static renewal	27.1 (no CI)	Nebeker and Schuytema 1998
	7 days embryo/larvae	11.7 (10.1–13.5)	Nebeker and Schuytema 1998
Cutthroat trout	96 hours static; 95% ac	1.4 (1.1–1.9)	US EPA 2004
	96 hours static; 95% ac	0.71 (0.53–0.96)	US EPA 2003
Coho salmon	96 hours static; 95% ac	2.4 (NR)	US EPA 2004
Lake trout	96 hours static; 95% ac	2.7 (2.4–3.0)	US EPA 2004
	96 hours static; 95% ac	1.2 (0.9–1.6)	US EPA 2004
Striped mullet	96 hours static; 95% ac	6.3 (NR)	US EPA 2003
Sheepshead minnow	96 hours static; 99% ac	6.7 (3.6–10); NOEC = 3.6	Drottar 1986

The report for one study that tested acute toxicity of the metabolite m-CPDMU to rainbow trout was provided (Heintze 2002a). This test showed a 96-hour (static) LC_{50} of 28.7 mg ac/L (95 per cent confidence interval 22.1–39.8 mg ac/L), which indicates toxicity of this metabolite is not dissimilar to that of the parent compound to fish.

1.6.3.2 Reproductive and chronic exposure

Two studies were provided for review. Table C11 below summarises this and other available results that were obtained from the US EPA Pesticide Database or cited in the US EPA Reregistration Eligibility Decision. The reviewed study for sheepshead minnow indicates diuron is very slightly toxic, with a NOEC of more than 1 mg/L. However, the unreviewed study result for fathead minnow indicates moderate toxicity.

Table C11: Summary of chronic fish toxicity results for diuron

TEST SPECIES	SYSTEM	LOEC/NOEC (mg ac/l)	REFERENCE
Rainbow trout (*O. mykiss*)	14 days semi-static	LC50 8.8 (95% CI 7.9–9.8)	Zoltán 2001b
Fathead minnow	ELS, flow through; 60 days	LOEC = 0.0618 NOEC = 0.0264	US EPA Reregistration Eligibility Decision
Sheepshead minnow	ELS, flow through; 38 days	LOEC = 3.6 NOEC = 1.7	Ward and Boeri 1992a

1.6.4 Aquatic Invertebrates

1.6.4.1 Acute exposure

Several studies were provided for review. Table C12 below summarises this and other available results that were obtained from the US EPA Pesticide Database or cited in the US EPA Reregistration Eligibility Decision.

These results are indicative of slight to high toxicity to aquatic invertebrates through acute exposure.

Table C12: Summary of acute aquatic invertebrate toxicity results for diuron

TEST SPECIES	SYSTEM	EC50 (mg ac/l) (95% CONFIDENCE INTERVALS)	REFERENCE
Daphnia magna	48 hours static	12.8 (10.5–14.7)	Zoltán 2001c
	48 hours static; 80% ac	9.7 (8.6–10.6)	Baer 1991c
Daphnia pulex	48 hours static, 80% ac; 1st instar	1.4 (1.0–1.9)	US EPA 2003
	96 hours static	LC50 17.9 (14.2–22.6)	Nebeker and Schuytema 1998
	7 days static	LC 50 7.1 (5.8–8.8)	
Daphnid (*Simocephalus sp*)	48 hours static; 95% ac	2.0 (1.4–2.8)	US EPA 2004
Mysid shrimp	96 hours static, 99% ac	1.1 (0.9–1.3)	Boeri 1987
	96 hours static, 99% ac	1.2 (1.0–1.6)	US EPA 2004
Scud (Gammarus)	96 hours static; 95% ac	0.16 (0.13–0.19	US EPA 2003
Brown shrimp	48 hours flow through; 95% ac	1.0 (no confidence intervals)	US EPA 2003
Eastern Oyster	96 hours flow through; 96.8% ac	4.8; NOEC = 2.4	Ward and Boeri 1991
	96 hours flow through; 99% ac	3.2 (1.5–6.6); NOEC <1.3	Johnson 1986
	96 hours flow through; 96.8% ac	1.8 (no confidence intervals)	US EPA 2004
Amphipod (*H. azteca*)	96 hours static	LC50 = 19.4 (14.2–22.6)	Nebeker and Schuytema 1998
	10 days static renewal	LC50 = 18.4 (16.5-20.5)	
Midge (*C. tentans*)	10 days static renewal	LC50 = 3.3 (2.4–4.5)	
Worm (*L. variegatus*)	10 days static renewal	19.3 (no confidence interval)	
Snail (*P gyrina*)	10 days static renewal	8.2 (no confidence interval)	

One standard study testing toxicity of the metabolite m-CPDMU to *Daphnia magna* was provided (Heintze 2002b). This study showed a 48-hour EC_{50} of 67.4 mg ac/L (95 per cent confidence interval = 48.7–125 mg ac/L), indicating this metabolite is not as toxic to Daphnia as the parent compound.

1.6.4.2 Reproductive and chronic exposure—active constituent

Table C13: Summary of chronic aquatic invertebrate toxicity results for diuron

TEST SPECIES	SYSTEM	EC/LC50 (mg ac/l) (95% CI)	REFERENCE
Daphnia magna	21 days, static	21 day EC_{50} = 1.07 (0.844–1.44); NOEC = 0.432*; LOEC = 0.865	Samel 2006
Mysid shrimp (*Mysidopsis bahia*)	28 days, flow through	NOEC = 0.96; LOEC = 1.9	Ward and Boeri 1992b

** This study NOEC relates to adult survival. However, there appeared to be significant effects on survival of offspring with more than a 10 per cent reduction at all tested concentrations. Even at the lowest test concentration of 0.0572 mg/L, the mean number of live offspring were reduced by 14 per cent compared to the control.*

1.6.5 Benthic invertebrates

No data were provided for review and no information is available from the US EPA database.

1.6.6 Algae, diatoms and aquatic plants

1.6.6.1 Active constituent

Several studies on the toxicity of diuron to a range of algae were submitted for review. They are summarised in Table C14:

Table C14. Summary of algae and aquatic plant studies reviewed for diuron

TEST SPECIES	TEST DURATION	BIOMASS (µg ac/l)	GROWTH RATE (µg ac/l)	REFERENCE
TECHNICAL		EBC50	ERC50	
Selenastrum capricornutum	72 hours	-	11	Zoltán 2001d
	72 hours	18	22	Douglas and Handley 1988
	120 hours	2.3	>5.2	Blasberg et al. 1991
Scenedesmus subspicatus	96 hours	7.2	22	Heimbach 1991a
Synechococcus leopoliensis	72 hours	24.9	38.0	Dengler 2006a
Anabaena flos-aquae	72 hours	23.2	30.9	Memmert 1998
Navicula pelliculosa	72 hours	16.2	65	Dengler 2006b
Duckweed (*Lemna gibba*)*	7 days	15.7	26.9	Ferrell 2006

FORMULATED PRODUCT				
Selenastrum capricornutum	120 hours	14.9 (ac)	-	Monma 1998
Scenedesmus subspicatus	96 hours	4.8 (ac)	-	Heimbach 1991b
	72 hours	9.6 (ac)	-	Dengler 2003

** This study included a recovery period where it was demonstrated the effects on* Lemna gibba *were phytostatic rather than permanent with strong recovery shown in the highest test concentration group following cessation of exposure.*

In addition, several supplemental studies were available from the US EPA database as follows:

Table C15. Summary of aquatic toxicity studies with diuron—algae and diatoms available from the US EPA Reregistration Eligibility Decision (US EPA 2003). All studies were conducted to US EPA Guideline 122-2 except where indicated

SPECIES	COMMENTS	RESULTS (MG/L)
CHLOROPHYCEAE (GREEN ALGAE)		
Chlorella sp.	95% ac	72 hours EC50 = 19
Chlorococcum sp.	95% ac	72 hours EC50 = 10
Dunaliella tertiolecta	95% ac	240 hours EC50 = 20
Neochloris sp.	95% ac	72 hours EC50 = 28
Platymonas sp.	95% ac	72 hours EC50 = 17
Chlamydomonas sp	95% ac	72 hours EC50 = 37
BACILLARIOPHYCEAE (DIATOMS)		
Achnanthes brevipes	95% ac	72 hours EC50 = 24
Navicula incerta	95% ac	72 hours EC50 = 93
Nitzschia closterium	95% ac	72 hours EC50 = 50
Phaeodactylum tricornutum	95% ac	240 hours EC50 = 10
Stauroneis amphoroides	95% ac	72 hours EC50 = 31
Thalassiosira fluviatilis	95% ac	72 hours EC50 = 95
Cyclotella nana	95% ac	72 hours EC50 = 39
Amphora exigua	95% ac	72 hours EC50 = 31
RHODOPHYCEAE (RED ALGAE)		
Porphydriium cruentum	95% ac	72 hours EC50 = 24
PRYMNESIOPHYCEAE (HAPTOPHYTES MARINE ALGAE)		
Monochrysis lutheri	95% ac	72 hours EC50 = 18
Isochrysis galbana	95% ac	240 hours EC50 = 10

Diuron is rated as very highly toxic to algae according to the DSEWPaC classification. One study showed that diuron (technical) was considered to be algistatic rather than algicidal.

Some additional data have been obtained for aquatic vascular plants. There is an old scientific literature report showing EC_{50} values of 41 µg/L for *Lemna major* and 15 µg/L for *Lemna perpusilla*, which were determined graphically. These species are not currently the recommended test species although *L. perpusilla* is closely related to *Lemna gibba*, the standard test organism. A more modern literature report gives the IC50 (inhibition of growth) for *Lemna minor* as 25 µg/L. These results indicate that diuron can be rated as very highly toxic to duckweed, although algae are the most sensitive organisms to the effects of diuron.

1.6.6.2 Formulation

Reviewed algal toxicity data for formulated products are included above in Table C14.

The formulated products Karmex SC 500 (517 g ac/L) and Karmex DF (81.2 per cent ac) are very highly toxic to algae with 96 hour E_bC_{50} values of 29.8 (*Selenastrus. capricornutum*) and 11.8 (*Desmodesmus. subspicatus—formerly Scenedesmus subspicatus*) µg formulation/L respectively. Tests show that Karmex SC 500 was algistatic and not algicidal at 100 µg/L of test substance. For the green alga *Scenedesmus. subspicatus* and using the WP 80 formulation, the E_bC_{50} was 5.9 µg/L (corresponding to 4.8 µg ac/L). A recent report gives the 96-hour E_bC_{50} for *Raphidocelis subcapitata* as 0.7 µg/L of diuron using a formulated product (50 per cent WP). Although it is unclear from the report if this is for the active constituent or the formulation, DSEWPaC assumes that this result is for the active.

1.6.6.3 Metabolites

Table C16. Summary of algae studies for diuron metabolites

TEST ALGA	TEST MATERIAL AND PURITY	EBC50 (µg/l)	REFERENCE
Scenedesmus subspicatus	m-CPDMU (99.5%)	246 (72 hours)	Dengler 2002
	DCPU (99.0%)	5660 (72 hours)	Dengler 2006c
	DCPMU (99.9%)	18.4 (72 hours)	Dengler 2006d

The diuron metabolites DCPMU, mCPDMU and DCPU were rated as very highly toxic, highly toxic and moderately toxic to the green algae *D. subspicatus* respectively based on studies conducted to OECD Guidelines.

1.6.7 Mesocosm and microcosm studies

Knauert et al. (2008) report on an outdoor mesocosm study undertaken to evaluate if effects of a mixture of similar acting compounds on the photosynthetic activity of phytoplankton could be described by concentration addition. The test ran in outdoor mesocosms for a period of seven months and included a six week pre-exposure, five-week constant exposure and five-month post exposure period. In the diuron-only experiment, the test concentration for diuron was 5 µg/L. In addition, a third of this rate was tested. Within two days after application, exposure to diuron induced around 57 per cent inhibition of photosynthetic activity. Over the constant exposure period, the average inhibition of photosynthetic activity was 47.7 per cent. However, compared to control ponds, effects on photosynthetic activity had completely disappeared after 140 days. In this system, DCPMU was measured and was found at a maximum level of 15 per cent of the applied diuron.

Knauert et al. (2009) addressed the question of whether equitoxic concentrations of three herbicides (atrazine, isoproturon and diuron), and their equitoxic mixture resulted in similar effects on a phytoplankton community structure. Herbicide effects were evaluated using principal component analysis and principal response curve in addition to common community parameters, such as total abundance, number of species, diversity, dominance patterns (with respect to the level of classes), and dynamics of the most dominant species. The test concentration for diuron was 5 µg/L. The mesocosms were redosed twice on days 12 and 20. The phytoplankton community as well as herbicide concentrations were monitored for seven months, and the entire mesocosm experiment was thus subdivided into a six-week pre-exposure period, a five-week constant-exposure period, and a five-month post-treatment period.

During the five-week constant exposure, total abundance in the diuron treatment was reduced by a factor of approximately three. At the end of the experiment (day 173), total abundance in all treatments was significantly lower in the diuron mesocosms. However, principal response curve analysis indicated that communities in all treatments could recover within three to five weeks. In terms of number of different taxa, the number of taxa in the diuron treated mesocosms were comparable to the control during the period of constant exposure, and this remained during the post treatment phase of the study.

1.6.8 Other studies

1.6.8.1 Algae

Magnusson et al. (2008) provides a basis for comparing non-standard PAM chlorophyll fluorescence results with more traditional algae toxicity endpoints of growth and biomass. The study involved a 3-day (72 hours) exposure period using standard ecotoxicology test guidelines and two tropical benthic microalgae: *Navicula sp.* (Heterokontophyta) and *Nephroselmis pyriformis* (Chlorophyta). Replicate mother cultures for both organisms (n = 5) in exponential growth phase were dosed with a dilution series of seven concentrations of herbicide (diuron, hexazinone or atrazine) and a DMSO carrier control. The following results were obtained (Table C17).

Table C17: 72-hour growth rate (µ), biomass increase and effective quantum yield [Y(II)] values (µg/L)

	NAVICULA SP.			*NEPHROSELMIS PYRIFORMIS*		
FORMULATION	µ	BIOMASS	Y(II)	µ	BIOMASS	Y(II)
EC_{50}						
Diuron	7.8**	3.7	5.5	8**	5.8	5.9
Atrazine	130*	65	99	50	35	28
Hexazinone	27*	14	16	10	8.4	6.2
EC10						
Diuron	2.4**	0.5	1.0	5.2**	2.2	1.1
Atrazine	35*	26	19	23	11	6.8
Hexazinone	6.5*	3.4	3.3	4.8	3.8	2.1

** n=4; ** n=3; otherwise, n=5*

These results indicate that the PAM methodology would appear to give outcomes not dissimilar to the standard toxicity endpoints. Growth was less sensitive than reduction in quantum yield for both species and all chemicals tested, and this is important as the growth endpoint is the preferred one for reporting and use in the risk assessment of a standard regulatory assessment over results determined through biomass measurements. In this sense, use of PAM results may slightly overestimate toxicity compared to growth results, but nonetheless, the outcomes are in relatively good agreement.

In a study examining the synergistic effects of sedimentation and diuron on crustose coralline algae, three conditions were used: sediment alone (four sediments and three species), diuron in clean seawater, and diuron plus sediment. Based on the initial test, the most sensitive species and sediment that caused the greatest effects due to sedimentation were used. In the diuron-only experiment, the only concentration to reduce photosynthetic activity was the highest test concentration (about 22 µg/L) with around 65 per cent inhibition at the end of the exposure period. At the end of the nine-day recovery period, photosynthetic activity for this group was the same as control values. In the combined diuron–sedimentation experiment, at the end of the exposure period, all treatments (including the uncontaminated sediment treatment) showed similar reduction in photosynthetic activity (around 20 per cent of control values) indicating the stress was caused by sedimentation rather than diuron. However, during the recovery period, the uncontaminated sediment group showed stronger recovery and after nine days and had recovered to within about 75 per cent of control levels. Meanwhile, all the diuron treatment groups showed a statistically similar recovery and ranged from between 40 and 60 per cent of control values at the end of the recovery period. The implication of this is that while initial stress is caused by sedimentation, the occurrence of additional stress (in this case, diuron), can impede the recovery of crustose coralline algae, even though in this case, diuron did not cause any lasting adverse effects on the test organism when exposed in water alone up to 21 µg/L. These results cannot be used for regulatory purposes.

A literature study on the toxicity of diuron and other photosystem II (PSII) herbicides to reef-building corals, or more specifically to the unicellular algae (dinoflagellate) that live symbiotically in the coral organisms, has been reported using chlorophyll fluorescence techniques to examine changes in photosystem II. Two coral species were used: *Seriatopora hystrix* and *Acropora formosa*. The most sensitive dinoflagellate from *S. hystrix* gave an *in situ* EC_{50} for $\Delta F/F'm$ of 2.3 µg/L, NOEC <0.3 µg/L and LOEC = 0.3 µg/L. The other corals gave an EC_{50} for $\Delta F/F'm$ of 2.7 µg/L and NOEL and LOEC as above. These results suggest that coral dinoflagellates could be as sensitive as algae species in the standard algal toxicity tests (above). However, the endpoints used for the dinoflagellates were reduction in quantum yield and are not directly related to growth or mortality.

1.6.8.2 Corals

Another paper reported studies with diuron and four species of coral (the same as those above: *Seriatopora hystrix* and *Acropora formosa*, plus *Montipora digitata* and *Porites cylindrica*), again using chlorophyll fluorescence techniques. The measured EC_{50} values based on $\Delta F/F'm$ (maximum effective quantum yield: 10 hours exposures, 100 mmol quanta/m^2/s) were 5.1, 4.3 and 5.9 µg/L for *A. formosa, P. cylindrica* and *M. digitata* respectively. After 24 hours of exposure (at the end of a 14-hour dark period), Fv/Fm (maximum potential quantum yield) was significantly different to controls for the corals exposed to 1.0, 3.0 and 30 µg/L respectively. The dinoflagellate from *S. hystrix* was used to test the effect of light levels and there was a slight reduction in EC_{50} from 3.7 µg/L at 'normal' light levels to 2.9 µg/L at 75 per cent shading. The effect of reduced salinity was also examined (35 to 27 parts per thousand) but there was no significant interaction

between diuron and the reduced salinity levels. Exposure to higher concentrations of diuron (100 and 1000 µg/L) resulted in significant loss of symbiotic dinoflagellates, pronounced tissue retraction and bleaching of the corals.

The effect of diuron (and 2,4-D) on the hermatypic coral *Porites cylindrica* has been reported. The corals were exposed to three concentrations of diuron and effects were measured using a fluorometer (fluorescence measurements) and an oxymeter. All parameters measured were affected at 50 and 100 µg/L compared to controls. At 10 µg/L diuron caused significant reduction in all measured parameters except respiration (production of O_2 per m^2) and maximum florescence yield.

Coral colonies of *Acropora tenuis* and *Pocillopora damicornis* were exposed to diuron concentrations of 1 µg/L and 10 µg/L for 52 and 67 days respectively and compared to control colonies on the reef. Diuron caused photoinhibition in each species, with PAM measurements recording consistent declines in effective quantum yields of 20 per cent and 75 per cent at 1 and 10 µg/L respectively. *A. valida* and *P. damicornis* were both sensitive to this photoinhibition, becoming severely bleached at 10 µg/L. At 10 µg/L, *A. valida* sustained both partial and full colony mortality. However, *A. tenuis* was more resistant and neither bleached or sustained mortality at any treatment. Polyp fecundity was reduced by sixfold in *A. valida* and both *A. valida* and *P. damicornis* were unable to spawn or planulate following long term exposures to 10 µg/L diuron.

The effect of diuron on the early life stages (fertilisation, metamorphosis and symbiosis) of broadcast spawning and brooding corals was examined. Nominal concentrations were 0.1, 1, 10, 30, 100, 300 and 1000 µg/L, and solutions were renewed daily for the 96 hour exposures. Diuron did not affect fertilisation of the broadcast spawning species *Acropora millepora* and *Montipora aequituberculata* at concentrations of up to 1000 µg/L. Metamorphosis of symbiont-free *A. millepora* larvae was only significantly inhibited at 300 µg/L of diuron. *Pocillopora damicornis* larvae, which contain symbiotic dinoflagellates, were able to undergo metamorphosis after 24 hours of exposure to diuron at 1000 µg/L. Recruits were as sensitive as adults to effects of diuron on photosynthesis as measured by fluorescence using a PAM fluorometer, with effects at 1 µg/L. The recruits and adults recovered in uncontaminated seawater but *P. damicornis* was severely bleached at 10 µg/L of diuron or higher, and remained so after the recovery period.

1.6.8.3 Seagrasses

The effect of diuron on three species of seagrasses, collected from the wild and identified as *Halophila ovalis, Cymodocea serrulata* and *Zostera capricorni* has been studied. These were exposed to a single dose of diuron at 0.1, 1.0, 10 and 100 µg/L for a 5-day period and changes in chlorophyll fluorescence were measured daily using the PAM fluorometer. Average concentrations for each test concentration were 0.1, 0.9, 7.8 and 85 µg/L. After 5 days of exposure, the quantum yields for *H. ovalis* and *Z. capricorni* were depressed for all test concentrations and *C. serrulata* were depressed at the two highest test concentrations only. There was rapid recovery in all species following return to clean seawater, but recovery was not sustained as all species exhibited fluctuations in effective quantum yield over the 5-day recovery period. *H. ovalis* was the most sensitive species during the exposure, and the recovery period with the statistical analysis showing this species as significantly different to the other two and the quantum yield did not improve as much as the other two species. A statistically significant effect on the quantum yield of the three species of seagrass was concluded with diuron exposure at 10 µg/L in the water column. DSEWPaC calculated indicative (based on values read from graphs) 5-day EC50 (chrorophyll fluorescence) of 15.6 µg/L for *C. serrulata*; 7.6 µg/L for *H. ovalis*; and 27.7 µg/L for *Z. capricorni*.

In a study on the effect of antifouling herbicides on the seagrass *Zostera marina*, diuron and mixtures with Irgarol was tested. The effect of diuron alone and in mixtures with Irgarol on chlorophyll fluorescence (Fv:Fm) and leaf specific biomass ratio were examined after a 10-day exposure. The LOEC and NOEC for effect of diuron on *Z. marina* was 1.0 and 0.5 µg/L respectively based on reduction in fluorescence and the EC_{50} was 3.2 µg/L. The LOEC and NOEC for effect on growth (leaf biomass) was 2.5 and 1.0 µg/L respectively.

1.6.8.4 Mangroves

The results of some preliminary trials of the toxicity of PS II-inhibiting herbicides to four mangrove species have been reported (*Avicennia marina, Aegiceras corniculatum, Rhizophora stylosa* and *Cerios australis*— the first two species are described as 'salt excretors' and the others as 'salt excluders'). The seedlings of the four species were grown in pots and placed in tank units, which enabled high and low tide to be simulated. The toxicity of diuron (as well as ametryn and atrazine) was compared to an untreated control, at four treatment rates (4, 40, 400 and 4000 µg/kg dry weight of sediment), using herbicide dissolved in water to which 'commercially bought' clay was then added and mixed to simulate natural runoff conditions.

Diuron was the most toxic herbicide tested after 71 days (all responses refer to the maximum exposure concentration of 4000 µg/kg; lower concentrations were not statistically significantly different from the control) with *A. marina* as the most sensitive mangrove from photosynthesis measurements. All of the mangroves showed physical symptoms of injury (chlorosis and necrosis) and all the *A. corniculatum* plants were dead. Note that *A. corniculatum* and *C. australis* received the highest exposure to the herbicides as the roots and leaves were submerged during the simulated high tide whereas *A. marina* and *R. stylosa* were only exposed via the roots. *A. marina* had the highest measured concentrations of diuron in leaf tissues after 11 days of exposure, measured at about 340 µg/kg leaf (dry weight) and *A. corniculatum* was the second highest with about 230 µg/kg.

The research suggested that the salt-excreting mangrove species were more vulnerable to diuron and other herbicides than salt-excluding ones. On the basis of these preliminary experiments, diuron was judged likely to be the most toxic herbicide of the three tested due to its slow degradation rate and ability to affect more than one species.

Field studies

In areas where there was dieback of mangroves, there were measurable concentrations of diuron in the sediments (0–2 centimetres), ranging from 1.2 to 8.2 µg/kg. However, where there was no dieback, the concentrations of diuron measured were less than1.2 µg/kg in the sediments (0–2 centimetres). High levels of diuron in sediments and healthy *A. marina* mangroves were mutually exclusive in occurrence. Two other mangroves species were showing signs of stress, *Aegiceras corniculatum* (river mangrove) had dead branches and yellowing leaves in plots in the Pioneer River with the highest levels of diuron and while *Ceriops australis* (yellow mangrove) showed significant dieback in two small areas, this was not widespread and considered to be due to localised effects. The results of this small dataset indicated that diuron concentrations greater than >2 µg/kg in sediment may affect sensitive mangrove species.

The health of the mangroves in the Pioneer River estuary was studied during December 2004, before the wet started and after an extended dry period. There was evidence of previous dieback in many sites, but there was a noticeable absence of wilted yellow leaves that were noted between 2000 and 2002.

The levels of diuron in sediment declined compared to those found earlier but the levels at one site (Pioneer Fursden) were higher. The mangroves at this site did not appear to be affected by these levels. An index of stress for Avicennia mangroves was developed, but it did not correlate with diuron concentrations in sediment or with pore water concentration of diuron, that is, bioavailable diuron. (DSEWPaC notes that the index relates to total stress of the mangroves, not just that due to diuron exposure and diuron, is not the only stressor in the system).

The report stated that all the locations sampled had similar mineralogical composition and that heavy metals were within the ANZECC water quality guidelines.

In conclusion while there is some evidence (based on a weak statistical correlation) from an earlier study indicating that diuron can be correlated with the dieback in Avicennia in the Pioneer River estuary, this was not supported by laboratory studies or subsequent observations. The later observations were conducted at a time before diuron runoff would be expected to occur and during a prolonged dry period, and therefore the diuron measured may be 'older residues' with less biological availability; thus other stressors could be significant. It is noted that the estuary environment is very dynamic, and more so in the Mackay region due to the very large tidal movement (more than 6 metres between high and low tides), therefore showing clear and unchangeable cause and effect relationships is always going to be problematic.

It was concluded that there are uncertainties and the science is incomplete. At this stage there are insufficient data to categorically state that diuron has affected mangroves at Mackay.

1.6.9 Terrestrial invertebrates

1.6.9.1 Honey bees

Acute oral and contact exposure

One study was provided for review (Bocksch 2006). This showed through both contact and oral routes of exposure, diuron (80 per cent formulation) was, at worst, slightly toxic to honey bees: the oral 48-hour LD_{50} was more than 72.10 µg ac/bee and the contact 48-hour LD_{50} was more than 100 µg ac/bee.

1.6.9.2 Soil-dwelling invertebrates

Acute exposure

Only acute earthworm toxicity data with diuron metabolites have been provided (Table C18).

Table C18: Summary of acute soil dwelling invertebrate data

TEST ORGANISM	TEST SYSTEM	RESULT	REFERENCE
DCPMU METABOLITE			
Earthworms (*Eisenia foetida*)	14 d mortality	LC50 = 413 mg/kg dw NOEC = 178 mg/kg dw	Stäbler 2001
DCPU METABOLITE			
Earthworms (*Eisenia foetida*)	14 d mortality	LC50 = 801 mg/kg dw	Stäbler 2001

	NOEC = 668 mg/kg dw

While no data for diuron acute toxicity to earthworms was provided, one result is reported in the Pesticide Properties Database at <http://sitem.herts.ac.uk/aeru/footprint/en/index.htm>. i.e. a 14-day LD_{50} of more than 798 mg/kg to *Eisenia foetida*.

The Pesticide Properties Database is a comprehensive relational database of pesticide physicochemical, toxicological, ecotoxicological and other related data. The database has been developed by the Agriculture & Environment Research Unit based at the University of Hertfordshire, UK. It has evolved from a database that originally accompanied the Environmental Management for Agriculture software (also developed by Agriculture & Environment Research Unit), with additional input from the European Union-funded FOOTPRINT project (see <http://www.eu-footprint.org>). In the absence of registrant submitted data, the results from this database are considered acceptable.

Chronic exposure and reproductive studies

No data were provided. Given the focus of this review, these data were not requested. However, one result is reported in the Pesticide Properties Database i.e. a chronic 14-day reproduction NOEC of 14.4 mg/kg to *Eisenia foetida* is provided.

1.6.9.3 Non-target terrestrial invertebrates

Laboratory studies

Table C19. Summary of non-target terrestrial invertebrate data

TEST ORGANISM	TEST SYSTEM	RESULT	REFERENCE
Aphid parasitoid, (*A. rhopalosiphi*)	Adult mortality	No effect at 4 kg ac/ha	Schuld 2001
	Reproduction	36% effect at 4 kg/ha	
Predatory mite (*T. pyri*)	Adult mortality.	No effect at 4 kg ac/ha	Adelberger 2001
	Reproduction	4.5% effect at 4 kg//ha	

While two other results are available for non-target terrestrial invertebrates (lycosid spiders and rove beetle), they have not been used in the risk assessment as testing was performed with mixtures, and the actual cause of effects found in the studies is therefore not fully understood.

Specific field semi-field studies

No data were provided. Given the focus of this review, these data were not requested.

1.6.10 Microorganisms

1.6.10.1 Soil microorganisms

Table C20. Summary of diuron toxicity to soil microorganisms

TEST SUBSTANCE	TEST SYSTEM	RESULT	REFERENCE
Diuron	Carbon transformation	No significant effects up to 16 kg ac/ha	Raposo 2005a
Diuron	Nitrogen transformation		Raposo 2005b
DCPU	Carbon transformation	No significant effects up to 60 mg/kg	Kölzer 2001a
	Nitrogen transformation		
DCPMU	Carbon transformation	No significant effects up to 60 mg/kg	Kölzer 2001b
	Nitrogen transformation		

1.6.10.2 Microbial toxicity studies

No data were provided. Given the focus of this review, these data were not requested. A literature report has been reviewed (Tixier et al. 2001) considering the ecotoxicity of diuron and several metabolites using the Microtox test (effects on bioluminescent bacterium *Vibrio fischeri*). Several metabolites were considered including DCPMU and DCA (unfortunately, m-CPDMU was not tested). The results showed diuron (EC_{50} = 68 mg/L) was significantly less toxic than both these metabolites with DCPMU being almost four times as toxic (EC_{50} = 18 mg/L) and DCA being 140 times as toxic (EC_{50} = 0.48 mg/L). While such results cannot be used for regulatory decision-making, they do provide further reason for concern about the environmental toxicity of the relevant metabolites of diuron.

1.6.11 Terrestrial plants

Two studies were submitted for review. The first (McKelvey and Kuratle 1992) provided seedling emergence and vegetative vigour data for a standard suite of four monocots and six dicots. At the request of the US EPA, the second study (Heldreth and McKelvey 1995 re-evaluated the responses to five of the species. The following table summarises the most sensitive ER25 (and the NOECs that correspond to the ER25 effect measurement) from these two studies. The more detailed description of the test outcomes can be found in Volume 2. The results show that dicotyledons are generally more sensitive than monocotyledons, and thatplants are more sensitive in their active growth phase than during emergence.

Table C21. Summary of terrestrial plant toxicity studies with diuron.

SPECIES		ER25 (g/ha)	NOEC (g/ha)	EFFECT
COMMON NAME	TAXONOMIC NAME			
US EPA GUIDELINE 123-1A—SEEDLING EMERGENCE				
Corn	*Zea mays*	6384	840	Shoot height
Sorghum	*Sorghum bicolor*	907	840	Shoot height
Onion	*Allium cepa*	96.2	99.6	Shoot weight

Wheat	*Triticum aestivum*	2912	<840	Shoot height
Cucumber	*Cucumis sativus*	381	231	Shoot height
Rape	*Brassica napus*	102	211	Shoot weight
Sugar beet	*Beta vulgaris*	143	211	Shoot weight
Tomato	*Lycopersicon esculentum*	95	105	Shoot weight
US EPA GUIDELINE 123-1B—PLANT VEGETATIVE VIGOUR				
Corn	*Zea mays*	157	213	Root weight
Sorghum	*Sorghum bicolor*	31.4	<52.6	Shoot weight
Onion	*Allium cepa*	24.6	<51.5	Shoot weight
Wheat	*Triticum aestivum*	32.9	13.1	Shoot weight
Pea	*Pisum sativum*	4.5	5.6	Root weight
Soybean	*Glycine max*	12.3	12.3	Root weight
Cucumber	*Cucumis sativus*	3.8	5.6	Root weight
Rape	*Brassica napus*	4.3	12.3	Root weight
Sugar beet	*Beta vulgaris*	4.5	5.6	Root weight
Tomato	*Lycopersicon esculentum*	1.2	1.12	Root weight

1.7 Conclusions for environmental effects

Diuron is considered slightly toxic to bobwhite quail through both acute oral via gavage (LD_{50} = 1104 mg/kg body weight) and dietary exposure (LC_{50} = 1730 mg/kg diet). Diuron was shown to be practically non-toxic to three other bird species (mallard duck—acute oral and dietary; Ring neck pheasant—dietary; and Japanese quail—dietary). Bobwhite quail were less sensitive (NOEC = 100 mg/kg diet) than mallard duck in reproduction studies. The mallard duck NOEC was 10 mg/kg bw based on the effects on egg production. Four acute fish studies for diuron toxicity were provided, although several other non-reviewed results were also available. Results were variable both between species (range of acute LC_{50} values from 0.71 mg/L to cutthroat trout to more than 300 mg/L for bluegill sunfish), and where sufficient data exist, within species (bluegill sunfish results showed a range of 96-hour LC_{50} = 2.8–84 mg/L). Results generally resided in a 96-hour LC_{50} range of 1 to 25 mg/L (moderate to slight toxicity), although the most sensitive result is indicative of high toxicity. One subchronic (14-day) study was reviewed showing a 14-day LC_{50} of 8.8 mg/L to rainbow trout. Two chronic results give NOECs of 0.0264 mg/L (fathead minnow) and a NOEC of 1.7 mg/L to sheepshead minnow. Diuron is considered moderately to very slightly toxic to fish based on chronic exposure. The metabolite m-CPDMU was shown to be slightly toxic to rainbow trout with an acute 96-hour LC_{50} of 28.7 mg/L.

The acute toxicity of diuron to aquatic invertebrates was moderate (48-hour EC_{50} of 9.7 mg/L to *Daphnia magna)*. Several unreviewed results support a conclusion of moderate toxicity with EC_{50} values ranging from 1.0 mg/L (brown shrimp) to 8.4 mg/L (*Daphnia magna*). One more sensitive result was reported for the Scud

(*Gammarus*) with a 96-hour EC_{50} of 0.16 mg/L (high toxicity). Chronic toxicity data indicate slight toxicity with NOECs of 0.43 mg/L (based on adult survival) for *Daphnia magna* and 0.96 mg/L for mysid shrimp. The metabolite m-CPDMU was shown to be slightly toxic to *Daphnia magna* with an acute 48-hour LC_{50} of 67.4 mg/L.

No ecotoxicity test reports, or other data, were provided for benthic organisms when exposed through sediments.

Diuron is very highly toxic to algae and aquatic plants. Several test reports were reviewed. EC_{50} values based on growth rate ranged from 0.011 to 0.065 mg/L for five algae species (including diatoms). These results are supported by other unreviewed results showing EC_{50} values ranging from 0.010 to 0.095 mg/L for a range of algae species including green algae, red algae, a marine algae and several diatoms. A 7-day EC_{50} of 0.0157 mg/L was found for biomass in the aquatic vascular plant *Lemna gibba*, although at the maximum test rate of 0.079 mg/L, plants were observed to recover following cessation of exposure. Older results for several aquatic plants (*L. minor* and *L. perpusilla*) show diuron is highly toxic to these organisms with 7-day EC_{50}s of 0.015–0.041 mg/L.

Several non-standard test results are available for a range of aquatic plant species, including corals, seagrasses and mangroves. Generally, these data were not considered appropriate for use in the risk assessment, but the evidence indicates toxicity of diuron to them was not remarkably different from the more sensitive algae results obtained through standard test procedures, particularly for corals and seagrasses.

Two mesocosm studies from the literature measuring effects on photosynthetic activity and community effects showed phytoplankton communities recovered (five-week exposure period) as diuron levels in water diminished, however, this process was not rapid due to the persistence of diuron.

Very limited data were provided for diuron metabolite toxicity to algae with a single result for m-CPDMU and DCPMU being very highly toxic to the green alga *S. subspicatus* (72 ErC_{50} of 727 and 62.8 µg/L respectively), with DCPU showing much lower toxicity (72 ErC_{50} of 15 500 µg/L). A non-standard test with duckweed indicated that the toxicity of DCPMU is around 75 per cent that of parent diuron. Another non-standard test (Microtox test) showed several metabolites, including DCPMU, to be much more toxic than diuron in a.

Diuron is very slightly toxic to bees (an oral 48 -hour LD_{50} was more than 72.10 µg ac/bee). No diuron earthworm toxicity data were provided, but a 14-day reproduction NOEC of 14.4 mg/kg dry weight of soil was reported in the literature. The soil metabolites DCPMU and DCPU were not acutely toxic to earthworms (14-day LC_{50}s of 413 mg/kg dry weight and 801 mg/kg dry weight respectively). Diuron was not toxic to the aphid parasitoid (*Aphidium. rhopalosiphi*) or the predatory mite (*T. pyri*) up to 4 kg ac/ha. While there were no effects on the rove beetle (*Aleochara. bilineata*) up to 5.4 kg ac/ha, at this rate there was a 95 per cent reduction in reproduction; however, testing was performed with a mixture with amitrole, and effects can not be attributed solely to diuron.

There were no significant effects of Diuron on soil carbon or nitrogen cycles at soil concentrations up to 16 kg ac/ha, or of the soil metabolites DCPU and DCPMU at soil concentrations of 60 mg/kg.

Standard seedling emergence and vegetative vigour studies were reviewed. Diuron was more toxic to plants in their growth stage with vegetative vigour ER25 values ranging from 1.2 g/ha (tomatoes) to 157 g/ha (corn).

With the exception of corn, all vegetative vigour ER25 values were less than 35 g/ha, with half of these less than 10 g/ha.

C.6 ENVIRONMENTAL RISK ASSESSMENT

1.8 Preliminary comments

As a first tier, a deterministic approach was used to try and characterise the risk from diuron uses to the environment. With the deterministic risk characterisation, the primary outcome is the calculation of the risk quotient (RQ).

RQs were established for the different environmental organisms considered during the environmental effects assessment, that is, birds and terrestrial organisms and the various trophic levels in the aquatic ecosystem.

The risk quotient was interpreted through comparison with levels of concern (LOC) to analyse potential risk to non-target organisms and the need to consider further testing/refinement or regulatory action. Implicitly built into these LOCs are assessment factors to increase confidence in the risk assessment. For example, an acute LOC of 0.1 means the predicted environmental concentration (PEC) divided by either the LC_{50} or the EC_{50}, has an assessment factor of 10 built into the effects value.

For this diuron review, the aquatic risk assessment utilised a more quantitative approach using toxicity endpoints determined through a species sensitivity distribution, and using the large volume of monitoring data on concentrations in streams and coastal waters collected when assessing diuron runoff following application.

1.9 Predicted environmental concentrations

When assessing risk, not every case can be accounted for, so Australia follows an iterative process by considering:

- a ‘worst case’ exposure scenario, and if needed
- a series of refinements which account for other factors and results in setting more realistic scenarios at each step.

The worst case should identify the sensitive environmental compartment(s) most at risk from exposure to the chemical. If these environmental compartments are not at risk (i.e. the RQ-value is acceptable), then no further assessment is needed.

Exposure estimates are required for:

- birds and mammals – food
- soil dwelling arthropods, earthworms, soil microorganisms
- aquatic organisms, either from spray drift or runoff
- sediment (benthic organisms).

In addition, estimates of exposure to organisms such as bees, other non-target terrestrial arthropods and non-target terrestrial plants are based on the spray rate of the chemical.

For the initial exposure scenarios, a single application was initially assumed although for some cropping situations, more than one application per season can be applied. This was considered separately.

The exposure calculations and methodologies for the calculations are described below.

1.10 Application rates

The exposure calculations were dependent on diuron application rates. Diuron is used on a wide range of crops to control a range of annual broadleaf weeds and some annual grasses. The uses are on orchards, cereals, coffee, cotton, lucerne, lupins, perennial grass seed crops, pineapples, sugarcane, vineyards and rights-of-way. It is applied both pre- and post-emergent. Table C22 gives a broad summary of the rates for agricultural uses with the crops classified into orchards, broadacre (ie cereals, cotton, lucerne etc), sugarcane, non-agricultural uses (rights-of-way, commercial and industrial areas) and irrigation and drainage channels, together with some information on typical application equipment.

Table C22. Summary of diuron situations and application rates (not including antifouling)

AGRICULTURAL SITUATION	MIN-MAX RATES (kg ac/ha)	APPLICATION EQUIPMENT
Orchards	1.8–3.6	Ground rigs
Broadacre	0.45–3.6	Ground rigs
Rights-of-way, commercial and industrial areas	4–36 (initial treatment) 3.1–16 (re-treatment)	Ground rigs, spot spraying
Irrigation and drainage channels	10–75	
Sugarcane	1.8–3.6	Ground rigs, shielded sprayers

There are a number of mixed products on the market where diuron is used in combination with other herbicides, mainly hexazinone but also bromacil, thidiazuron and glyphosate. In these combination products, diuron is used at the lower rates as given in Table C22 above.

Specific predicted environmental concentrations (PEC) for different environmental compartments are detailed further below.

1.11 Ecotoxicity endpoints

Based on the ecotoxicity data assessed for diuron (both as the technical compound and in formulations), the following ecotoxicity endpoints were used for the risk characterisation:

Table C23: Ecotoxicity data endpoints for risk characterisation

ORGANISM	SPECIES	END POINT		UNITS
Birds, short term, dietary	Bobwhite quail	LC_{50}	1730	ppm diet

ORGANISM	SPECIES	END POINT		UNITS
Birds, chronic, reproduction	Mallard duck	NOEC	10	ppm diet
Aquatic organisms—fish and aquatic invertebrates*	95th percentile	NOEC	29.8	µg/L
	99th percentile (higher conservation areas)	NOEC	6.87	µg/L
Aquatic organisms—primary producers*	95th percentile	NOEC	1.56	µg/L
	99th percentile (higher conservation areas)	NOEC	1.19	µg/L
Sediment organisms	No available data for sediment exposure		No data	
Bees (oral toxicity)		48-hour LC_{50}	>72.10	µg/bee
Non-target terrestrial arthropods (Exposure through spray)		NOEC	4000	g ac/ha
Non-target terrestrial arthropods (Exposure through soil)		NOEC	No data	
Earthworms (based on soil concentration)	NOEC	14.4	mg/kg dw	
Soil microorganisms		NOEC	16000	g ac/ha
Non-target terrestrial plants (end point based on plant height data)		ER25	1.2	g ac/ha

** Considered representative for both freshwater and saltwater; Based on statistical approach.*

Given the amount of toxicity data on the toxicity of diuron to aquatic organisms, an SSD approach has been adopted. Methodology for generation of the endpoints is found in Appendix E. In summary, the data were separated between primary producers (algae and aquatic plants), and primary and secondary consumers (aquatic invertebrates and fish). For the algae data, where available, the preferred test endpoint of growth rate EC_{50} was used. Data were then transformed to chronic endpoints using an appropriate acute to chronic ratio.

There were several non-standard test results for the toxicity of diuron to coral species, which indicated that coral species may be similar in their sensitivity to algal species tested according to established test guidelines. Other data for seagrass species (non-standard endpoints) indicate EC_{50} values of 7.6–27.7 µg/L (chlorophyll fluorescence), with indications that diuron can affect photosynthesis of seagrasses at around 1.0 µg/L. While these data were based on non-standard endpoints, and cannot be used for regulatory purposes, (and consequently arenot included in the SSD dataset), they should not be ignored. The endpoints generated through the SSD approach are considered protective of these organisms.

1.12 Levels of concern

In order to characterise the risk, the RQ was compared to a LOC. In Australia, the following LOC values are used (that is, the RQ needs to be at or below the LOC for a risk to be deemed acceptable) (Table C24).

Table C24: Levels of concern for characterising environmental risk

ORGANISM	ACUTE LOC	CHRONIC LOC
Avian/mammals	0.1	1.0
Bees	1.0	
Terrestrial invertebrates	No set value	
Earthworms	0.1	1.0
Soil microorganisms	In the case of non-target soil microorganism exposure, an unacceptable risk is presumed in the event that nitrogen turnover or carbon mineralisation is affected by more than 25% over the course of the study. To mitigate this risk, it must be demonstrated there is no unacceptable impact on microbial activity under field conditions, taking account of the ability of microorganisms to multiply.	
Non target terrestrial plants	0.1 (for LC_{50} data—may be relaxed for EC_{25} data)	
Aquatic organisms (including sediment organisms)	0.1	1.0

Note that with respect to aquatic organisms, the view is taken that for acute LC_{50} or EC_{50} data, values of Q greater than 0.5 result in a 'presumption of unacceptable risk' to organisms, while if Q = 0.1–0.5, there is a 'presumption of risk that may be mitigated by restricted use', and Q being les than 0.1 indicates a low potential environmental risk. However, for this risk assessment, acute risk quotients have not been generated. A statistical approach has been taken to determine the toxicity endpoints for aquatic organisms (see Appendix E). This is considered a chronic value and is appropriate for a chemical with the potential persistence of diuron in the water column.

1.13 Risks arising from use

1.13.1 Avian

Birds and mammals may be exposed orally through food and water ingestion as well as other sources such as granules, baits and soil ingestion. At the Tier I level it was assumed that animals obtain all their diet from the treated area and the contaminated food was not avoided. Considerations differed depending on the use pattern, such as sprayed formulations compared with granules, baits or treated seed.

1.13.1.1 Spray formulations

For spray applications, DSEWPaC estimates pesticide concentrations in animal food items, focusing on quantifying the possible dietary ingestion of residues on vegetative matter and insects. Residue estimates are based on the updated Kenaga nomogram (Pfleeger et al. 1996) that relates food item residues to pesticide application rate. Residues are compared directly with dietary toxicity data or converted to an oral dose.

The residues and associated Q values to birds following a range of application rates are provided in Table C25.

Table C25: PECfood calculations and avian Q values

APPLICATION RATE	PECFOOD DIET A1	PECFOOD DIET B2	Q-VALUE	Q-VALUE
kg ac/ha	mg/kg	mg/kg ww	DIET A	DIET B
0.45	17.5	47.1	0.01	0.03
0.9	35.0	94.2	0.02	0.05
1.8	70.0	188.4	0.04	0.11
3.6	140	376.8	0.08	0.22
8	311	837.3	0.18	0.48
12	467	1256.0	0.27	0.73
16	622	1674.7	0.36	0.97
24	933	2512.0	0.54	1.45
32	1244	3349.3	0.72	1.94
36	1400	3768	0.81	2.18

= acute potential risk (0.1<Q<0.5)

= unacceptable acute risk (Q>0.5)

1) Residues based on 30% grain (same as long grass) and 70% insects—for example, mallard duck;

2) Residues based on 70% grain (long grass) and 30% insects— for example, bobwhite quail.

Acute avian risk quotients exceed and the LOC at higher application rates, particularly for birds with a diet based mainly on grain or long grass.

Two chronic bird toxicity studies were provided for review. Mallard duck were more sensitive than bobwhite quail with study NOECs of 100 and 10 ppm respectively. The bobwhite quail NOEC was based on slight effects on female adult body weights. However, based on actual reproductive effects, the study NOEC was 100 ppm.

There were definite reproductive effects in the Mallard duck study, primarily related to egg laying. At the study test concentrations of 10, 33, 100 and 160 ppm, the reduction in egg laying compared to control birds appeared to follow a dose–response relationship with reduction of 13, 28, 34t and 67 per cent respectively. Statistical analysis suggested that only the reductions at 100 ppm ($p > 0.05$) and 160 ppm ($p > 0.01$) were statistically significantly different to the control, although a reduction of almost 30 per cent at 33 ppm is of concern, and the study NOEC of 10 ppm based on egg laying appears appropriate.

For long term exposure, EFSA (2008) suggests a 21 day time-weighted average daily dietary dose. For this assessment, the initial residues were predicted using the Kenaga nomogram. EFSA (2008) recommends a default half-life for residues on food of 10 days, and assumes as an absolute worst case that half the diet is obtained by individuals from the treated area. Using these assumptions, and based on initial dietary residues in Table C25 above, 21 day time-weighted average concentrations and corresponding Q-values based on the study NOEC are predicted to be as listed in Table C26.

Table C26: 21 day TWA PECfood calculations and Q values for some bird breeding phases.

	APPLICATION RATE (kg ac/ha)	0.45	0.9	1.8	3.6
Exposure residues	21-day TWA, Diet A (mg/kg diet)	4.5	9	18	36
Q-values for:	Copulation/egg laying	0.45	0.9	1.8	3.6
Exposure residues	21-day TWA, Diet B (mg/kg diet)	12	24	49	97
Q-values for:	Copulation/egg laying	1.2	2.4	4.8	9.7

TWA = time-weighted average

The use of chronic NOECs means a Q-value of 1 or less is considered to represent acceptable risk. The above table shows a potential risk to birds at their copulation and egg laying stage at application rates above 0.9 kg ac/ha for Diet A, and at all application rates for Diet B. While this is the quail diet, the mallard duck NOEC is still used to cover sensitive species with this diet. Diuron is registered for application as a defoliant in cotton at 24 g ac/ha, and at this rate, the chronic risk to birds is acceptable (Q value = 0.06).

This long-term exposure assessment assumes the exposure duration required to cause NOAEL (or in this case, the study NOEC) effects is 21 days. Uncertainties exist in both directions, but most will tend to make the 'true' worst-case risk lower. Some species may be able to recover part or all of any lost reproductive output by re-nesting (EFSA 2008). However, given the potentially widespread use pattern for diuron with application at different times of the year, there are insufficient data to refine the risk quotient any further.

The rates modelled in Table C26 above reflect maximum rates for various uses. However, diuron is registered for lower application rates within certain uses. Application rates of 175 g ac/ha and 250 g ac/ha are registered for barley and wheat, while 250 g ac/ha is also registered for use in summer fallow, sugarcane and bananas. Table C27 shows the chronic bird Q-values for these rates:

Table C27: 21 day TWA PECfood calculations and Q values for avian reproduction, lower registered rates

	APPLICATION RATE (kg ac/ha)	0.175	0.25
Exposure residues	21-day TWA, Diet A (mg/kg diet)	1.75	2.50
Q-values for:	Copulation/egg laying	0.18	0.25
Exposure residues	21-day TWA, Diet B (mg/kg diet)	4.7	6.75
Q-values for:	Copulation/egg laying	0.47	0.68

TWA = time-weighted average

At these lower registered rates, the chronic risk to birds is considered acceptable.

The highest application rate that will allow a conclusion of acceptable chronic risk to birds is 370 g ac/ha. At this rate, the 21-day time-weighted average residues for birds with Diet B is 20 mg/kg diet, then assuming 50 per cent of their diet is taken from the treated area, this reduces to 10 mg/kg diet and gives in a Q-value of 1.

1.13.2 Aquatic

1.13.2.1 Preliminary Comments

Australia models output on a 3-metre wide water body with a depth of 15 centimetres. This means, for every 1 metre length of downwind field edge, an average 450 L of water receives drift (3 metres width by 1 metre length by 15 centimetres depth).

The exposure level below which aquatic primary and secondary consumers are not adversely affected by diuron (fish and aquatic invertebrates) is 29.8 µg/L, or 6.87 µg/L in high protection areas. For the LOC of 1 to not be exceeded, deposition to the water body therefore cannot exceed 4,470 µg/m^2 (1,031 µg/m^2 for high protection areas).

Due to the much higher sensitivity of aquatic primary producers (algae and aquatic plants), the exposure level below which these organisms are not adversely affected by diuron is 1.56 µg/L, or 1.19 µg/L in high protection areas. For the LOC of 1 to not be exceeded, deposition to the water body therefore cannot exceed 234 µg/m^2 (179 µg/m^2 for high protection areas).

1.13.2.2 Spray drift

A spray drift risk assessment considering downwind buffer zones for protection of both non-target aquatic and terrestrial areas is reported separately in Section 8.5.6.

1.13.2.3 Runoff

There are large uncertainties involved in predicting runoff, and levels of chemical in runoff will be dependent on many site specific parameters including soil characteristics, slopes, distances between edge of field and receiving waters and types of buffers in between areas (for example, vegetative filter strips, bare ground, grassed buffers).

For this assessment, one of the main focuses of the review relates to runoff of diuron. The chemical has been detected routinely in surface waters and is attributed to off-farm runoff. Two Australian field studies showed diuron loading in single runoff events accounted for up to 0.2 per cent of the diuron applied, although the result from the more recent study was only for around 25 per cent of the runoff event and the actual diuron loading could have been around 0.5 per cent. International data showed up to 4.4 per cent of the applied diuron could be found in runoff (even higher where ground was compacted). Runoff of 0.5 per cent from a 1 ha field at an application rate of 3.6 kg/ha into a 1-hectare, 15-centimetre deep pond results in a water concentration of 12 µg/L. This level gives corresponding Q-values of less than 1 for fish and aquatic invertebrates (acceptable risk) in normal protection areas, although a Q of 1.4 for fish and aquatic invertebrates occurs for high protection areas (unacceptable risk). Q-values of 7.7 and 10.1 are calculated for algae/aquatic plants based on normal and high protection status respectively. While application rates could be lower, runoff values could easily be higher. The relatively limited data in this area, and the unacceptable Q-values based on this simple modelling make a more detailed assessment necessary.

Since the release of the PRF in 2005, DSEWPaC has established an in-house model for undertaking screening level runoff exposure estimates, and this model is described in Appendix E.

Broadacre agricultural uses; sugarcane; orchards

This issue of diuron in runoff from farms was of particular concern, as described in the scoping document for this review. In addition to this, there are several reports providing monitoring data for diuron in river systems that can be attributed to runoff. This allows a comparison of modelled values to measured values in the environment to check the chosen value for its relevance.

The approach and reasoning behind the runoff values chosen for this assessment is described in Appendix E. While there is a range of application rates in broadacre agriculture from 0.45 kg/ha (wheat) to 3.6 kg/ha (several uses), the most reliable monitoring data available come from Queensland water catchments where the most likely use rates are between 0.9 and 1.8 kg/ha, primarily to sugarcane crops (based on current knowledge of uses in these areas).

The DSEWPaC runoff model estimated peak field runoff concentrations that were supported by available data. However, due to the extent of the monitoring data, they have been used to determine a representative value in primary streams as they allowed better consideration of spatial and temporal aspects of runoff exposure that is not available from the model. Similarly, monitoring results were used for determining representative runoff concentrations of diuron in secondary rivers and coastal waters due to greater confidence in the data than from modelling alone. Consideration has also been given to the lower application rates (0.45 and 0.9 kg/ha).

For this assessment, several environmental monitoring values were chosen in order to characterise risk of diuron to the aquatic compartment following off-farm movement through runoff. As explained in Appendix E, these assume an average catchment application rate of 1.35 kg/ha. These values are in Table C32.

Table C32: Water concentrations (µg/L) from runoff events with diuron to be used in the risk characterisation

	CONCENTRATION (µg/l)	BASED ON
Primary streams	13	Monitoring
Secondary streams	1.9	Monitoring
Coastal discharge	0.28	Monitoring

For algae and aquatic plants, the ‘normal’ protection level (95th percentile of the species sensitivity distribution) is 1.56 µg/L while the ‘high’ protection level (99th percentile) is 1.19 µg/L. Based on these exposure concentrations, the following Q values have been calculated (Table C33)

Table C33: Risk quotients (Q values) associated with water concentrations from diuron runoff

TROPHIC LEVEL	FISH AND AQUATIC INVERTEBRATES		ALGAE AND AQUATIC PLANT	
PROTECTION LEVEL	NORMAL	HIGH	NORMAL	HIGH
Primary streams	0.44	1.89	8.33	10.9
Secondary streams	0.06	0.28	1.22	1.60
Coastal discharge	0.01	0.04	0.18	0.24

Lower broadacre application rate uses

The problems with modelling runoff exposure concentrations are discussed in Appendix E. Consequently, good quality monitoring data was relied on for the runoff assessment above. However, these values were considered indicative of average use rates around 1.35 kg/ha within a catchment area. To consider the potential risks from low application rates (for example, 0.45 kg/ha in wheat or a lowest application rate of 0.9 kg/ha in other broadacre uses such as sugarcane or cotton), levels predicted in Appendix E and provided above in Table C32 will need to be extrapolated. This is a screening level approach as there were no monitoring data available that could be related to specific application rates. There is evidence from field studies that diuron loading in runoff waters can be in excess of 4 per cent of what was applied (international data) with recent Australian information showing up to 0.5 per cent being possible in a 1-hour runoff event.

Exposure concentrations for the two lower application rates will be considered only for primary and secondary rivers as the risk assessment has already shown an acceptable risk in coastal waters even at the higher rates.

As demonstrated in Appendix E the modelled values in secondary streams tended to overpredict water levels when compared with monitoring results. There were obvious uncertainties here as there was no indication of mean application rates that contributed to the monitoring levels, and the modelled values were based on a single contribution of 20 per cent of streamflow values from runoff waters. However, in the absence of other information, it was assumed that the mean application rates contributing to runoff waters was 1.35 kg/ha (see Appendix E), and a pro-rata exposure rate was used from the monitoring data relating to both primary and secondary rivers for 0.9 (67 per cent of monitoring value from Table C32) and 0.45 kg/ha (33 per cent of monitoring value from Table C32).

Table C30: Water concentrations (µg/L) from runoff events with diuron used in the risk characterisation

	CONCENTRATION (µg/L)				
	0.175	0.25	0.45 KG/HA	0.9 KG/HA	BASED ON
Primary streams	1.7	2.4	4.3	8.7	Monitoring
Secondary streams	0.25	0.35	0.63	1.3	Monitoring

Based on these exposure concentrations, the following Q values have been calculated for algae and aquatic plants using the 95th percentile protection level of 1.56 µg/L (Table C31).

Table C31: Algae and aquatic plant Q values associated with water concentrations from diuron runoff at lower broadacre application rates

	CONCENTRATION (µg/L)			
	0.175	0.25	0.45 kg/ha	0.9 kg/ha
Primary streams	1.1	1.54	2.76	5.58
Secondary streams	0.16	0.22	0.40	0.83

These data indicate an unacceptable risk to algae and aquatic plants in primary streams even at the lower 95 per cent protection level for broadacre uses as low as 0.45 kg/ha. Diuron is also registered for lower application rates within certain uses. Application rates of 175 g ac/ha and 250 g ac/ha are registered for barley and wheat, while 250 g ac/ha is registered for use in summer fallow, sugarcane and bananas. Even at these rates, the risk to algae and aquatic plants in primary streams from runoff remains unacceptable. The unacceptable risk to primary streams at the lower application rate is important. It is appreciated that in many areas where this rate will be used (for example, the wheat belt), primary streams are often dry. However, the persistence of diuron means it will be available for runoff for a long time after application. Further, when runoff can occur in some drier areas, the runoff itself may constitute almost the entire streamflow in primary streams, and consequently, the actual diuron levels in the runoff could be more concentrated.

The highest application rate that will allow a conclusion of acceptable chronic risk to algae and aquatic plants in primary streams as a result of runoff is 160 g ac/ha. At this rate, the predicted concentration, as a function of the percentage of observed values which were assumed to be based on an average application rate of 1.35 kg ac/ha, would be 1.54 µg/L, resulting in a risk quotient of 0.99. The uncertainties of extrapolating the measured values used for exposure estimates to lower application rates is discussed above.

Mitigation and refinement of aquatic risk outcomes associated with runoff

Refinement of exposure estimates

An unacceptable risk was identified above at all rates to algae and aquatic plants for both normal and high protection areas in primary and secondary streams. Based on current knowledge, the risk to these organisms in high protection coastal waters has been deemed acceptable. The Q-value is based on 90th percentile measured data from flood plumes when concentrations would be expected to be at higher levels, and would also be expected to dissipate, thereby not leading to prolonged exposure at such elevated levels. Information on more ambient concentrations of diuron in coastal waters suggested a lower value of 0.02 µg/L (Q value 0.017 to algae and aquatic plants, high protection value).

With regard to the unacceptable risks identified for non-coastal fresh waters, namely, primary and secondary streams, it was difficult to further refine the exposure endpoint. It could reasonably be argued that these levels will not be constant, and for the majority of the time, exposure levels would be significantly less. However, the following salient points need to be considered:

1. Diuron can be persistent in water and while the half-life is expected to be variable, it has been shown to be as long as two months in laboratory systems and 1.5 months in outdoor mesocosm systems. Therefore, where quiescent or low-flow conditions exist, exposure to sensitive primary producers could be prolonged. However there are no relevant toxicity data to consider such effects.
2. Based on very limited information, the main metabolite of diuron in soil, DCPMU, appears persistent and shows a similar toxicity to algae and duckweed as the parent compound, and may be as mobile based on Koc data. This metabolite has been found in Australian sediments in a stream in the Burnett Catchment in Queensland (see Stork et al. 2008) at levels higher than parent diuron. Therefore, conversion of diuron to this metabolite does not allow mitigation of exposure based on degradation of the parent compound.
3. Based on very limited information, the main metabolite of diuron in water (which also occurs from anaerobic metabolism), m-CPDMU, is very highly toxic to algae, although not as high as DCPMU, and

also has demonstrated persistence (see Sarff 2007b; and Sarff 2007c;). Therefore, conversion of diuron to this metabolite does not allow mitigation of exposure based on degradation of the parent compound.

4. Algae and aquatic plants have been shown to recover following cessation of exposure through the water column. However, diuron can be very persistent under field conditions, for example, within the soil or under trash blankets, where it remains available for future runoff. Therefore, release of diuron to receiving waters may be a low levels, but over an extended period of time. There are currently no toxicity data available that consider the effects such 'pulse' exposures.

The issue of persistence makes use of time weighted average concentrations difficult to apply, particularly as exposure could continue at elevated levels for periods of time much longer than the duration of most available toxicity tests. This is a problem common to persistent compounds in general.

Eliminating aquatic exposure resulting from runoff (through collection and retention of irrigation or rainfall tailwaters) is the only way of mitigating the risks determined here based on current knowledge.

On the issue of methodology, DSEWPaC does not have a range of Q-values where the risk may be mitigated when chronic endpoints are used. The risk is considered acceptable where the risk quotient is 1 or less, and unacceptable where it is more than 1. In the case of the lower application rates of 175 and 250 g ac/ha, the risk quotients exceed 1, but are only marginally greater at 1.1 and 1.5 respectively. However, this does not take into account the presence of metabolites in the run off water, of which at least one, DCPMU is of similar toxicity to algae as diuron is, as also noted above, there are still unanswered issues relating to exposure of algae and aquatic plants from sediment pore-water following accumulation in the sediments of diuron and DCPMU

Sugarcane

DuPont has submitted high level modelling data indicating significant reductions in water concentrations resulting from runoff through altering management practices. The two most significant, and implementable practices, were to reduce the per hectare application rate through complete use of band spray (reduction in application rate of 50 per cent with a corresponding reduction in runoff estimated at around 50 per cent), and through altering the timing of application to allow application so that it did not occur during the wetter months. Combining these two management practices resulted in a predicted average decrease in maximum water concentrations of around 80 per cent.

Since the provision of this modelling, DSEWPaC was advised that the main two assumptions relating to application practices are hard to sustain. The window concept (altering the timing of application) does not allow a practical risk-based approach to the application of herbicides. It does not take into consideration local weather conditions or seasonal weather patterns. The wet season in Queensland is variable and setting a window provides no scope to choose an application time when the risk is low for application based on conditions within a practical timeframe. Secondly, the crop cycle in cane is variable and dependent on the seasonal conditions. The crush may finish anywhere between October and January, and crops either planted or ratooned after the harvest period would be disadvantaged as row closure (DuPont has proposed to limit use to this stage) does not occur intil 120–150 days after harvest (potentially up to the end of April) which would be outside the proposed application window.

In relation to reducing the application rate by 50 per cent to account for band spraying, diuron-based products are reported to be applied as both band and full cover with the exclusion of the plant line area. In situations where cane is more advanced and there are concerns about crop safety, then directed application is used. This is effectively applying in a band with sprays being applied on the furrow to base of the plant. DuPont Australia estimates that 70-85 per cent of the band area would be covered, not the 50 per cent assumed in the modelling.

Essentially, this does not allow very much mitigation, particularly where full cover application is used. In the event band spraying is used, it appears the effective application rate may be reduced by 15–30 per cent. Assuming 20 per cent, the revised water concentrations would be 10.4 µg/L, 1.52 µg/L and 0.22 µg/L in primary streams, secondary streams and coastal discharge respectively. Corresponding Q-values would be 6.7. 0.97 and 0.18 respectively. This still results in an unacceptable risk to primary streams, and while the risk is acceptable for secondary streams, it is very close to the LOC of 1.0.

Further, the modelling, and available monitoring data used for comparison and validation consider only parent diuron with no account of metabolites formed or their levels in the envrionment.

Refinement of the aquatic toxicity endpoint

The 95th and 99th percentile protection levels have been determined using a statistical approach using as much of the available data as considered appropriate for a regulatory assessment. However, there are still uncertainties about these levels. The algae and aquatic plant endpoints used were EC_{50} values, extrapolated to chronic values using acute to chronic ratios. This resulted in a most sensitive 'chronic' endpoint around 1.56 µg/L for *Navicula sp.* and the aquatic vascular plant *Lemna gibba*. These extrapolated results were more sensitive than the actual values for NOEC and EC_{10} in the study. However, there is concern about marine plant species in the Great Barrier Reef, and the available non-standard test data for some of these species indicates they can be relatively sensitive to diuron exposure. Therefore, such an approach is still considered protective.

An important factor to consider, however, was the issue of recovery. The most sensitive algal species for which standard test data are available is the green alga *Selenastrum capricornutum*, where a 120-hour ErC_{50} of 22 µg/L was determined, and a corresponding study NOEC of 10 µg/L. After the end of the 5-day exposure period during which, cultures were exposed to 80 and 160 µg/L reculturing the algae in clean media (no diuron) resulted in regrowth.

In a recent *Lemna gibba* study submitted, the 7-day EC_{50} was 15.7 µg/L (study NOEC around 2.5 µg/L). However, following seven days of exposure, plants at test concentrations exhibiting more than 50 per cent inhibition were transferred to clean medium, and strong frond recovery was observed. For example, in the highest exposure group of 79 µg/L, there was a sevenfold frond growth during the 7-day recovery period compared to 1.3-fold in the control group.

Both these tests indicate that the effects of diuron are algistatic rather than algicidal, and following exposure for 5 to 7 days, it can be argued the NOAEC is much greater than the study NOECs of 2.5–10 µg/L, and it could be as high as 80 µg/L.

Higher tier mesocosm studies available in the literature also demonstrated reversibility of effects at a community level, although at a slow rate. In these studies, the exposure of the mesocosms was to diuron at

concentrations around 5 µg/L. In one of these studies evaluating effects of mixtures of similar acting compounds on the photosynthetic activity of phytoplankton, initial inhibition of photosynthetic activity was around 48 per cent with recovery observed to correspond to decreasing diuron concentrations in the water. After around 140 days following cessation of exposure, inhibition was reduced to levels not statistically significantly different from the controls (the corresponding diuron concentration at this time was about 1.2 µg/L based on values read from a graph). In the second mesocosm study considering effects on phytoplankton community structure, from days 12 to 40, differences in species composition between the control and treated mesocosms were observed. However, during the post treatment period, the communities treated with diuron recovered and were similar to the control communities. The time for recovery was estimated to be between three and five weeks.

The recovery times in these mesocosm studies appears long and given the potential for pulse exposure in the environment repeat exposures may occur prior to plant communities recovering from previous exposure. However, the exposure periods were five weeks at 5 µg/L. Monitoring data shows such extended exposures are unlikely to occur in nature with monitoring data indicating elevated diuron levels are unlikely to continues for more than a few days. Further, the mesocosms were still water bodies, so there was no recharge of clean water as would be found in streams in the environment.

When the available monitoring data used to establish water concentrations for the risk assessment were considered, the 95th percentile protection concentration (1.56 µg/L) was exceeded more than 10 per cent of the time using all observations, or around 12 per cent of the time when only positive detections were used. Factoring this along with the ability for exposed plants to recover from any inhibition in growth observed during exposure to diuron, and noting the revised Q-values through refinement of the exposure estimates above, it can be reasonably argued that the risk of long lived adverse effects on algae and aquatic plants in primary and secondary streams is acceptable, provided management practices are put in place to reduce the likelihood of diuron runoff resulting in acceptable levels in the water column.

For this risk assessment, it was difficult to determine a more refined endpoint. The available recovery data (discounting the mesocosm studies) were performed for single exposure periods with exposure only through water (no sediment available in the test systems). Impacts from pulse exposure, particularly where follow-up exposures occur prior to recovery being complete, are not understood. Further, effects resulting from the likely prolonged exposure through sediment pore water concentrations of diuron and its metabolites to rooted vascular plants and other sediment fauna (discussed below) are not understood.

Summary of risk mitigation

In attempting to mitigate the risks identified to the aquatic environment through runoff of diuron, both exposure and environmental effects have been considered. While it is theoretically possible to reduce estimated exposures, for example, through refining exposure calculationsn the persistence of diuron and its metabolites makes this difficult to apply. More appropriately, the risk assessment should consider total residues given the toxicity of the main metabolites. Further, while recovery of diuron affected aquatic plants through water exposure may occur, it is difficult to determine a more refined ecotoxicity endpoint for use in the risk assessment, particularly when factors for which there are no data such as pulse exposure and prolonged exposure through sediment pore water from diuron and its metabolites are considered. Finally while some management actions have been proposed and demonstrate significant reductions in runoff, the risk to primary streams is still unacceptable (and to secondary streams is in the mitigable range).

Use under the Reef Protection Legislation

Under the Queensland Government initiative on Reef Protection Package, comprehensive guidelines on chemical use have been prepared. A copy of the ReefWise Farming 'Sugarcane Grower's Guide to Chemical Use under the Reef Protection Legislation' (see <http://www.reefwisefarming.qld.gov.au/pdf/sugarcane-guide-chem-use.pdf>) was provided to the APVMA by DuPont. This guide applies to all sugarcane properties in the Wet Tropics, Burdekin Dry Tropics and Mackay Whitsunday catchments regulated under the *Environmental Protection Act 1994 (Qld)*. The document provides a number of mandatory requirements when using diuron (and some other herbicides), based on the use of a 20-metre No-Spray Zone OR a 5-metre effective vegetated treatment area (EVTA).

For runoff, mandatory requirements under the Queensland reef protection legislation for diuron use include:

- 'do not use within 20 metres of all down slope water bodies, or maintain a 5 metre EVTA between the edge of the down slope water body and any point where low flow runoff exits the inter-row furrow'
- 'do not prepare them at a place susceptible to runoff into a water body or within 20 metres of a water body'

When using diuron, conduct and follow a Rainfall Runoff Risk Assessment

- 'do not irrigate to the point of runoff within 48 hours of application'

For spray drift, mandatory requirements for diuron under the reef protection legislation use include:

- 'do not apply within 30 metres of a water body unless using a shielded sprayer; or applying below the level of the canopy; or the water body is upwind of the application site'
- 'use a shielded sprayer or another device that allows application below the level of the canopy, with no smaller than medium spray droplets; but use with another type of device (should be) with no smaller than coarse droplet size'

The requirements also include 'do not apply more than 1.8 kg of "active diuron" per ha per calendar year'.

DSEWPaC has not been involved with these requirements and is not aware of the basis for these restrictions. The effectiveness of the Queensland initiatives remains to be demonstrated. DSEWPaC has considered the use of vegetative buffer strips in assessments in the past and has failed to find convincing data to include the use of such tools in its risk mitigation recommendations to date. Further, the basis for the prescribed spray drift buffer zone of 30 metres is not known, and where shielded sprayers are not used, modelling using standard APVMA parameters indicates this may not be sufficiently protective.

High application rate uses

Diuron can be used at rates up to 36 kg/ha for rights of way, commercial and industrial areas, and up to 75 kg/ha for irrigation and drainage channels. The runoff values used above are not considered applicable for such use patterns. The following table provides revised modelled exposure values (based on the model described in Appendix E based on a range of application rates for these use patterns and their

corresponding Q values for primary streams. Q values are based on the 95 per cent protection level (Table C36).Table C36: Q-values calculated for high application rate use patterns

USE PATTERN	APPLICATION RATE (kg/ha)	WATER CONC. (µg/L)	Q VALUE	
			FISH/AQUATIC INVERTEBRATES	ALGAE/AQUATIC PLANTS
Rights of way; commercial; industrial	6	69.5	2.33	44.6
	12	139	4.66	89.1
	24	278	9.33	178
	32	370	12.4	237
Irrigation channels/ drainage ditches	35	405	13.6	260
	70	810	27.2	519

These results show an unacceptable risk to all aquatic organisms in the event of water receiving runoff following application at these high rates of diuron. While actual areas being exposed to such high rates would be small by comparison to areas under broad acre farming, the Q values are very high, especially for algae and aquatic plants. These Q values are based on the 95 per cent protection level, and would be higher if high protection areas wre exposed (99 per cent protection level).

Based on current knowledge, and for the reasons described above, it would be difficult to mitigate these identified risks.

Diuron levels in sediment – implications for aquatic organisms

Diuron has been detected in Australian sediments. Sediment monitoring results (Section A1.5.1.4,) show levels up to 10 µg/kg sediment in estuarine environments with much higher concentrations in irrigation ditches (up to 340 µg/kg from cotton use and 120 µg/kg from sugarcane use). A recent Australian field study measured diuron levels in stream sediment where the stream was located below a sugarcane catchment (Stork et al. 2008,). In this study, diuron was detected in all measured sediment samples at concentrations between 3 and 19 µg/kg while DCPMU was found (again in all samples) at concentrations of 4 to 31 µg/kg. Based on values read from a graph, the mean concentration of diuron (10 samples) was about 15.1 µg/kg while that for DCPMU was about18.2 µg/kg.

Diuron is not a strongly bound chemical. It is possible to estimate the likely water column diuron levels based on known sediment levels using equilibrium partitioning (EqP). As explained in Di Toro et al. (1991), the sediment concentration (Cs) and free dissolved pore water concentration (Cd) share the following relationship:

Cs/Foc = Koc X Cd, or conversely, Cd = Cs/(Foc X Koc).

If it is assumed that sediment has a fraction of organic carbon (Foc) of 2 per cent, and based on the lowest definitive Koc of 418, the following porewater concentrations for a range of sediment concentrations can be predicted (see Table C37).

Table C37: Predicted pore water concentrations (µg/L) and algae and aquatic plant Q-values based on measured sediment concentrations

SEDIMENT LEVEL (µg/kg)	EXAMPLE AS MEASURED	PREDICTED PORE WATER CONCENTRATION (µg/L)	Q-VALUE, 95% PROTECTION LEVEL
10	Sub-tidal sediment	1.2	0.77
15	Stream sediment	1.8	1.15
33	Stream sediment*	4.2	2.69
100	Irrigation ditch	11.2	7.18

** In stream monitoring (Stork et al. 2008), mean levels of diuron were about 15.1 µg/kg and the metabolite DCPMU were about 18.2 µg/kg. Given the very toxic nature of the metabolite, consideration of total residues is important. While metabolite levels were not measured in other monitoring results available, the level of 33 µg/kg is used as a possible 'total residue level' in inland streams where runoff waters containing diuron occur.*

These results show that pore water concentrations resulting from measured diuron residues in Australian sediments could well be at levels resulting in an unacceptable risk to algae and aquatic plants. While this is a pore water concentration and not likely to be reflected in the overlying water concentration, they are potentially risky to rooted vascular plants or benthic algae where exposure could predominantly be through the pore water.

1.13.3 Leaching

Leaching potential can be easily predicted using a nomogram based on the mobility and persistence, (Gustafson 1989). Use of laboratory data for persistence (laboratory half-lives in soil of 20–372 days) and sorption (Koc 418–1666) gives ground ubiquity scores (GUS) of 1.0 to 3.5 and places diuron mainly in the transitional class (short half-life), extending into the probable leacher range (longest half-life and lowest Koc).

The field lysimeter data showed only limited leaching, which was confirmed in the field studies. Those studies conducted in Europe showed very limited leaching of diuron with no evidence of movement below 20 centimetres depth. The US data also showed limited leaching with no detections below 30 centimetres, except at one sandy site in California where diuron showed leaching down to 60 centimetres (Tweedy 1999, Stevenson 1990). In Australia field studies, conducted in sugarcane at Bundaberg, diuron was detected in ground water at a maximum concentration of about 6 µg/L (Simpson and Hargreaves 2001). This is higher than would be expected from the overseas studies, possibly due to the low organic matter in the Australian soils and could indicate that diuron has higher mobility in Australian soils.

Diuron was also found in the Murrumbidgee Irrigation Area in tile drain water at levels up to 28 µg/L (Bowmer et al. 1998). The tile drains in the Murrumbidgee Irrigation Area are porous pipes installed at approximately 2 metres depth and are designed to keep the watertable below the root zone. In the Murrumbidgee Irrigation Area, diuron is mainly used in citrus or in drains, and as citrus is grown on well draining soils, predominately sandy soil, diuron appears to be leaching in these well draining sandy soils.

It is concluded that Australian field data show that diuron can leach and is found in groundwaters in several areas. This is contrary to overseas field lysimeter studies and general field studies showing that diuron is not

likely to leach in most circumstances and that only limited leaching occurs in sandy soils to 60 centimetres deep.

1.14 Antifouling use

1.14.1 Overseas action and assessment

The use of diuron on vessels longer than 25 metres or on all vessels has been revoked in the UK, Denmark and the east coast of Sweden (Kevin et al. 2002). The use of diuron in antifouling paints has also been banned in Bermuda due to the toxicity of diuron to corals (Carbery et al. 2006). The Netherlands specifies a maximum permissible concentration for diuron of 430 ng/L in surface waters (Warmer and van Dokkum 2002).

Diuron has been found in a high proportion of seawater samples obtained in sampling programs in New Zealand in 2003 and 2006 (NRC 2003, 2006). In 2003, concentrations were 130 and 230 ng/L in two Northland marinas, 110 ng/L in Tutujaja Bay and 30 ng/L in Whangarei Estuary. Concentrations averaged 273 ng/L in Marlborough Sound samples, with a maximum concentration of 830 ng/L measured at a site near the base of a marina slipway. Results of monitoring in 2006 were broadly consistent with these results. Thus levels detected were comparable to mean levels in open marinas and estuaries in the UK and most results were below the maximum permissible concentration in the Netherlands. The evaluators determined that the risks associated with diuron use were largely limited to marinas, and that even the marina samples exceeded only the most conservative (UK) guideline values (presumably the predicted no effect concentration used for risk assessment—see below). They concluded that the use of diuron as an antifouling co-biocide was not resulting in unacceptable risks to the marine environment in New Zealand, but that continued monitoring of diuron in coastal waters was advisable.

The UK Advisory Committee on Pesticides reviewed use of diuron as an antifoulant and took the decision to revoke the use of diuron on all vessels due to environmental and human health concerns (ACP 2000; ACP 2001; ACP 2002). This was based on significant levels of diuron being detected in water and sediment throughout UK estuary and coastal sites as well as freshwater sites. Chronic exposure data endpoints were selected as more appropriate for the purpose of a marine risk assessment for the use of antifoulant booster biocides such as diuron. The endpoint used for risk assessment of diuron was a predicted no effect concentration of 0.038 or 0.19 µg ac/L using 50-times or 10-times assessment factors and a chronic NOEC of 1.9 µg ac/L derived from a study of marine periphyton communities in Norway (Molander and Blank, 1992—this study was not reviewed by DSEWPaC). The measured levels in open marinas, more typical of Australian marinas, ranged from less than 1 to 613 ng/L with an average of 170 ng/L, whereas higher levels were recorded in marinas where water is trapped by lock gates (Table A1.44, Appendix I).

Modelling of diuron use for antifouling using the UK REMA (Regulatory Environmental Modelling of Antifoulants) program predicted diuron concentrations in water (PECwater) in open marinas and estuaries of 2254 ng/L and 1272 ng/L, respectively (100 per cent of all boats using diuron antifoulant paints, ASTM/ISO leaching rate = 3.3 µg/cm^2/day). When a lower leaching rate was considered (flume leaching rate = 0.8 µg/cm^2/day), predicted concentrations in open marinas (546.4 ng/L) and estuaries (308.3 ng/L) in the UK were more comparable with measured values. Predicted concentrations in sediment (PECsediment) were 50 µg/kg in open marinas and 6.6 µg/kg in estuaries at the higher leaching rate and 7.1 µg/kg and 1.6 µg/L,

respectively, with the lower leaching rate. While these estimates were based on use on 100 per cent of pleasure craft in the marina, usage at the time in the UK was 52 per cent.

Based on risk quotients calculated using measured concentration data with an assessment factor of 10 to arrive at a predicted no effect concentration, use of diuron as an antifoulant was considered to pose an unacceptable risk to enclosed marinas in all seasons (the measured concentration exceeds the predicted no effect concentration for at least 50 per cent of the data). While not themselves considered to be ecologically relevant sites, enclosed marinas were considered indicative of potential effects on enclosed areas such as freshwater lakes. For the inlet marina and open marina scenarios, which are considered to be environmentally relevant, during the boating season at least 14.3 per cent of the sample points indicated an unacceptable risk from diuron. For estuary data, at least 6 per cent of the sample points indicated an unacceptable risk. However, the risk was acceptable at all inlet marina, open marina and estuary sample points during winter. Based on predicted rather than measured concentrations, and assuming 100 per cent use on pleasure craft (again with assessment factor of 10), the risk was unacceptable both in estuaries (58.3 per cent of sites exceeding an acceptable level of risk) and open marinas (85.7 per cent exceedance).

From this evaluation of measured data and predicted data for 100 per cent pleasure craft use, the UK review recommended that approvals for all antifouling products should be revoked in that jurisdication.

1.14.2 Predicted concentrations—Australian use

It is difficult to characterise release in a manner that is representative of the range of marinas found in Australia. The OECD publishes emission scenario documents for specific industries, and has recently published one for antifoulants (OECD 2005). The emission scenario documents are for use by OECD member countries where country specific information is not available, and the emission scenarios described for antifoulants are considered appropriate to use as a screening level surrogate for Australia. Predicted concentrations of diuron under the OECD-European Union default marina and harbour scenarios described in the OECD Emission Scenario Document for Antifouling Products (OECD 2005; van Hattum et al. 2002) were modelled using the default settings for these scenarios and for diuron provided in the MAMPEC model (Version 2.0) and the CEPE/MAMPEC default steady state leaching rate of 2.5 µg/cm^2/day.

The MAMPEC model takes into account emission factors (e.g. leaching rates, shipping intensities, residence times, ship hull underwater surface areas), compound-related properties and processes (e.g., Kd, Kow, Koc, volatilisation, speciation, hydrolysis, photolysis, bacterial degradation), and properties and processes related to the specific environment (e.g. currents, tides, salinity, dissolved oxygen content and suspended matter load). In modelling water exchange the model takes account of three mechanisms:

- filling and emptying by the tide
- the horizontal eddy generated in the harbour entrance by the passing main flow
- vertical circulation currents in the marina/harbour generated by density differences between the water inside and outside the marina or harbour basin.

The model can also consider the extra effects of a water discharge through the marina or harbour basin to the estuary or sea, but this was set to zero in the scenarios used. The model considers the steady state release rate and does not consider inputs from application or maintenance of the treated vessels. The

OECD_European Union default marina scenario considers release from vessels at berth, while that for a commercial harbour also considers release from moving ships.

Results from the modelling are summarised in Table C38. Both scenarios assume use on 90 per cent of the craft present, with model settings including the following:

- Marina: 141.5 x 141.5 metres, 4 metres deep, 100 metre wide mouth, flow velocity past mouth 1 m/s, tidal difference 1.5 m, maximum density difference 0.1 kg/m^3, 500 craft 1–50 metres long with an average wetted surface area of 30.7 m^2.
- Harbour: 1000 x 1000 metres, 15 metres deep, 2500 metres wide mouth, flow velocity past mouth 1 m/s, tidal difference 1.5 m, maximum density difference 0.4 kg/m^3, 24 craft in various size classes (50–100 metres long to 250–300 metres long, average wetted surface areas 1163-15,640 m^2).

Table C38. Predicted concentrations of diuron arising from use of antifoulant paints containing diuron in the OECD-European Union default marina and harbour scenarios

AVERAGE CONCENTRATION OF DIURON	OECD-EU MARINA	DEFAULT MARINA 400 METRES POORLY FLUSHED	OECD-EU COMMERCIAL HARBOUR
Total (µg/L)	0.323	1.04	0.0732
Dissolved (µg/L)	0.322	1.04	0.0730
Suspended matter (µg/g dw)	0.023	0.074	0.0052
Sediment after 10 years (µg/g dw)	0.011	0.056	0.0026

1.14.3 Comparison of predicted concentrations with measured levels

There are no Australian data for levels of diuron in marinas. Measured concentrations of diuron in open marinas in the UK (up to 630 ng/L) and marinas in New Zealand (30–830 ng/L) were comparable to the levels predicted above with the MAMPEC model and the OECD-European Union default marina scenario, although no detections were found at the highest predicted concentration of 1040 ng/L for the poorly flushed marina above. Levels in a locked marina in the UK did exceed this value with an average of 1439 ng/L (range 112–6742 ng/L) while levels in three other locked marina sites, also in the UK, were considerably less than this (4–334 ng/L). This indicates that the modelled values above are conservative, although not unrealistic as a worst case.

The Australian data for levels of diuron in marine sediments and seagrasses (Haynes et al. 2000) showed positive detections in areas not closely associated with sugarcane: the subtidal sediments outside of the Fitzroy River (0.9 mg/kg) and in intertidal seagrass at Pallarenda (0.8 mg/kg dw). However, the Fitzroy River and Pallarenda sites are near large metropolitan centres (Rockhampton and Townsville) where there could be diuron used on rights-of-way and commercial areas as well as antifoulant uses in marina and ports. In addition, the Fitzroy River has a substantial area of the catchment (2790 km^2, and 2 per cent of catchment) is used for horticultural crops (GBRMPA 2001)).

1.14.4 Risk quotients

Chronic Q-values for aquatic life in marinas, based on the 95th percentile protection concentrations (noting that marinas are not high protection sites) have been calculated for the water column to be 0.01, 0.03 and 0.002 for the default marina, the poorly flushed marina, and the commercial harbour respectively for aquatic primary and secondary consumers (aquatic invertebrates and fish), indicating an acceptable risk to these species.

Chronic Q-values for aquatic primary producers (algae and aquatic plants) have been calculated to be 0.21, 0.67 and 0.05 for the default marina, the poorly flushed marina and the commercial harbour respectively. While these Q-values are still indicative of acceptable risk, it is apparent that poorly flushed marinas may contain sufficient diuron levels to pose a risk to algae and aquatic plants (Q value approaching 1).

1.14.5 Release from marinas to receiving waters

The 'in marina' concentrations above will dilute on release from the marina to receiving waters. Given risk quotients have been shown to be acceptable within the marina, it follows that once discharged to receiving waters, the risk will remain at acceptable levels.

There are no coastal water measured concentrations that can be attributable simply to use of diuron as an antifoulant. However, the coastal water predicted concentration described earlier in this report of 0.28 µg/L (flood plume concentrations) resulted in an acceptable risk to aquatic organisms. While it is unclear (and data do not allow an estimation) of the level of contribution of diuron from antifoulant use to total levels found in marine waters, more realistic ambient concentrations of 0.05 µg/L or less from a small dataset of coastal water concentrations is likely to include diuron from all sources including from use as an antifoulant. This level results in an acceptable risk to algae and aquatic plants, even in high protection areas.

1.14.6 Risks from application and maintenance

In addition, there is a potential hazard from localised environmental exposure during paint application and during washdown or preparation of existing surfaces for repainting. Application of diuron containing marine paints to pleasure craft is unlikely to occur in commercial slipways or shipyards with well-controlled procedures to minimise environmental exposure during application, maintenance and removal (for example, collection of waste material from bunded areas of the slipways and dry-docks involved and appropriate disposal to approved landfill facilities). Rather, such paints will generally be applied by professional applicators in facilities with more limited controls, or by 'DIY' (do-it-yourself) boat owners. The nature of facilities varies widely, but users are expected to comply with relevant state environmental regulations and local government requirements, though controls vary between jurisdictions and are less comprehensive than for drydocks handling large ships.

Release of diuron during application and maintenance operations is likely to be localised to areas such as slipways and drain outlets in facilities lacking good control measures. Releases would be expected to be relatively intermittent in nature, as not all vessels are treated at the same time or with the same product. However, paint flakes may accumulate in sediment near the release points and any remaining diuron would be released slowly and potentially affect algae or seagrasses in the immediate vicinity.

A Code of Practice has been developed by the ANZECC (Australia and New Zealand Environment and Conservation Council) for the use of antifoulant paints, which has been published (ANZECC 2000). Appropriate guidance for the application and maintenance of vessel antifoulant coatings is also available from state environmental agencies (eg NSW EPA 1999; Vic EPA 1998). Release of paint residues to the environment during cleaning, application and maintenance procedures should be minimised as far as possible.

1.15 Sediment organisms

Diuron has been detected in river and coastal sediments in Australia. However, no toxicity data exist for sediment flora or fauna when exposed through the sediment. Some data were obtained for benthic organisms exposed through the water phase. In terms of risk characterisation, these organisms were included in the primary and secondary consumers (fish and aquatic invertebrate) dataset and consequently, the risk quotients above in Table C33 would apply to sediment organisms where exposed through the water column.

1.16 Terrestrial invertebrates

Exposure to bees is determined for spray applications based on the maximum application rate. This rate is converted to a rate of chemical (ac) per square centimetre (PECsurface) on the assumption that a honeybee is approximately 1 cm^2 in surface area (Davis and Williams, 1990).

One study provided showed both contact and oral routes of exposure to honey bees resulted in values of 48-hour LD_{50} exceeding 100 µg ac/bee and 72.1 µg ac/bee respectively. Based on contact toxicity, more than 10 kg/ha of diuron would need to be applied for Q-values to bees to approach unacceptable levels.

This suggests an acceptable risk to bees through all broadacre, orchard and sugarcane uses of diuron. However, application rates can exceed this level for rights-of-way, commercial and industrial areas and irrigation and drainage channels. In such situations, application is likely to be restricted, that is, unlike broadacre uses, only small areas will be treated thereby significantly reducing exposure to bees.

Exposure to other arthropods (for example, predators, parasites and ground dwelling organisms) is determined for spray applications based on the maximum application rate in kg/ha.

The exposure calculations for soil organisms such as earthworms, soil dwelling arthropods and soil microorganisms are based on the application rate of the chemical. With regard to these situations, the concentration in soil is predicted based on uniform mixing within the top 10 centimetres using a soil density of 1500 kg/m^3 (PECsoil). There are no data for non-target terrestrial arthropods with exposure through soil. However, there are data based on spray rates. A tier I risk assessment was performed in this case based on the methods outlined in ESCORT 2 (Candolfi et al. 2000). Both in-field and off-field risk were considered. However, the methodology for off-field risk was modified from ESCORT 2. This document refers to ground drift estimates based on data not used by the APVMA. Consequently, spray drift was estimated using AGDRIFT, with a downwind terrestrial deposition width of 3 metres, with drift, estimated at 0 metres downwind from the edge of the field. For off-field exposure, ESCORT 2 suggests using a vegetation distribution factor to account for the likelihood that off-field areas are vegetated rather than having the bare ground characteristics used in generating drift data (thereby trapping drift and lowering exposure). They also

recommend a correction factor be applied to the ecotoxicity endpoint to account for expected higher diversity of species found off-field. A factor of 10 is suggested for both these corrections. As these cancel each other out in the formula, they were not used for this assessment.

At the edge of the field, AGDRIFT estimated a drift fraction of 0.1827 of the application rate.

The following table provides these PEC calculations for a range of application rates.

Table C39: PECsoil based on different application rates of diuron

APPLICATION RATE (kg/ha)	0.45	0.9	1.8	3.6	8	16	75
PECsoil (mg/kg)	0.3	0.6	1.2	2.4	5.3	11	50
In-field PEC (g ac/ha)	450	900	1800	3600	8000	16000	75000
Off-field PEC (g ac/ha)	82.2	164	329	658	1460	2920	13700

1.16.1 Earthworms and soil microorganisms

Table C23 above provides the ecotoxicity data endpoints used for risk characterisation. The endpoint for earthworms is a NOEC of 14.4 mg/kg dry weight, and that for soil microorganisms is 16000 g ac/ha. Assuming uniform mixing in the top 10 centimetres soil with soil density of 1500 kg/m^3, this equates to a NOEC of 11 mg/kg soil. Based on the PECsoil for the different application rates, the following Q-values were found for earthworms and soil microorganisms (Table C40).

Table C40: Q-values for earthworms and soil microorganisms

APPLICATION RATE (kg/ha)	0.45	0.9	1.8	3.6	8	16	75
Q-value, earthworms	0.021	0.042	0.083	0.17	0.37	0.77	3.47
Q-value, soil microorganisms	0.027	0.054	0.11	0.22	0.48	1	4.5

Due to the use of a chronic NOEC for earthworm risk characterisation, Q-values are acceptable at application rates up to 16 kg ac/ha.

At 16 kg ac/ha, the Q-value to soil microorganisms was 1 (one). Levels of concern are not applied to soil microorganism data to quantify risk. Instead, an unacceptable risk is presumed in the event that nitrogen turnover or carbon mineralisation is affected by more than 25 per cent over the course of the study. To mitigate this risk, it must be demonstrated there is no unacceptable impact on microbial activity under field conditions, taking account of the ability of microorganisms to multiply. Maximum application rates in soil microorganism testing were 16 kg ac/ha, and at this level, no long-term adverse impacts on soil microorganisms were expected.

The primary soil metabolite, DCPMU, was found at up to 35 per cent the concentration of parent diuron in soil metabolism studies. This metabolite showed an acute LD_{50} = 413 mg/kg dw soil, which equates to an application rate of around 600 kg/ha if distributed in the top 10 centimetres of soil. Therefore, the risk to earthworms from this metabolite is acceptable. Neither DCPU nor DCPMU had any long-term impacts on soil

respiration or nitrogen cycle activities up to 60 mg/kg dry weight (indicative application rate of 90 kg/ha), and the risk to soil microorganisms from these metabolites was acceptable.

1.16.2 Non-target terrestrial invertebrates

Table C23 provides the non-target terrestrial arthropod endpoint as a NOEC = 4000 g ac/ha. The following Q-values are obtained for in-field and off-field exposure.

Table C41: Q-values for non-target terrestrial arthropods

APPLICATION RATE (kg/ha)	0.45	0.9	1.8	3.6	8	16	75
In-Field Q-Values	0.11	0.22	0.45	0.90	2	4	18.8
Off-Field Q-Values	0.02	0.04	0.08	0.16	0.36	0.73	3.42

Australia has no set level of concern for characterising risk to terrestrial arthropods based on these Q-values. However, ESCORT 2 does provide methodology in this regard, where risk quotients of less than 2 are considered indicative of low risk. The tier 1 risk assessment is based on risk quotients to two species, *Aphidius rhopalosiphi* and *Typhlodromus pyri*, which conforms with the available data for this assessment.

Applying an acceptable Q-value of below 2, the above table indicates that there is a low risk to off-field habitats at application rates up to 16 kg ac/ha, however, diuron may present a risk to the in-field habitat at application rates of 8 kg ac/ha and higher.

1.17 Terrestrial plants

The risks to non-target terrestrial plants is considered in terms of exposure through spray drift. A spray drift risk assessment to recommend downwind buffer zones to both aquatic and terrestrial non-target areas is reported separately.

The ecotoxicity endpoint used in the risk assessment for non-terrestrial plants is the most sensitive ER25 of 1.2 g ac/ha for tomatoes; A level of concern of 0.1 may be relaxed where EC25 data are used. Ordinarily, the level of concern would be set at 0.5 in the case of ER25 data, meaning the risk quotients can not exceed 0.5 without a presumption of risk. However, for this assessment the level of concern is being relaxed further to 1.0 for the following reasons:

1. The endpoint has been set based on vegetative vigour data, which showed all plants are much more sensitive in this test than in seedling emergence test systems.
2. Tomato plants had both the most sensitive ER25 and NOEC values for all ten plant species tested.
3. There were several occasions where the ER25 was in fact more sensitive than the NOEC (sorghum, onion, pea, cucumber and sugar beet). This is not uncommon in terrestrial plant studies, but given that pea, cucumber and sugar beet were the most sensitive plants after tomato, it supports a less conservative LOC as technically, the ER25 would be more protective in these cases than the NOEC.
4. The ratio of NOEC/ER25 for tomato was 0.93 which indicates the use of the NOEC would not be much more protective than that for the ER25.

5. Finally, a statistical distribution of the ER25 values (n = 10) and defined NOECs (n = 8) from the vegetative vigour studies result in a 95 per cent protection value of 1.51 g ac/ha and 1.43 g ac/ha respectively using the BurrilOz software. Both these are less protective than the tomato ER25 value.

Consequently, the terrestrial deposition for diuron to non-target terrestrial plants where risk is acceptable was set at 1.2 g ac/ha or less.

1.18 Spray drift risk assessment

A spray drift risk assessment was conducted for diuron use as a cotton defoliant; it is the only use where aquatic risks are considered acceptable.

Buffer zones were established through modelling as outlined in the APVMA Operating Principles in Relation to Spray Drift (APVMA 2008). The modelling predicts deposition of the chemical based on application rates at distances away from the edge of the treated field, which is compared to the representative ecotoxicity value for the different environmental organisms to provide a Q value. The downwind distance from the spray zone considered acceptable is that resulting in sufficiently low deposition to give a Q-value (ratio of PEC to toxicity endpoint), which is compared to a pre-determined level of concern (LOC).

Computer modelling was used to quantify the spray drift and risks arising from the drift. Aerial spray drift was assessed using the AGDISP model. Input parameters have been standardised by the APVMA. A summary of the model input data for fixed wing aircraft (Aerial Agricultural Fixed Wing - Average Applications) and helicopter (Aerial Agriculture Helicopter) can be obtained from the relevant APVMA website <http://www.apvma.gov.au/use_safely/spray_drift/scenarios.php>. These input data remained constant with the exception of changes to application rates, droplet sizes and wind speeds.

An important component of the AGDISP model relates to the fraction of non-volatiles in the tank mix. It is important to differentiate between the fraction of non-volatiles in the formulation as opposed to the tank mix. All formulations have been reviewed, and any ingredient, active or inert, was considered non-volatile unless it is water. The fraction of non-volatiles in the tank mix is a function of the application rate (which dictates the amount of product formulation needed per hectare) along with the amount of non-volatile components in the product formulation. For solid formulations (granules, wettable powders), the formulation consists of 100 per cent non-volatile components. For liquid formulations, it is assumed all formulations have a specific gravity of 1.0. Where products contain water, the fraction of non-volatile components in the formulation therefore becomes 1 minus the fraction of non-volatile components in the formulation.

Spray drift from ground application was performed according to the AGDRIFT model (APVMA 2008). This model is limited in the parameters that can be changed. The downwind limit for this model is 300 metres, and cannot be extended. The following provides a summary of the set values used in the modelling:

- Tier Tier 1 Agricultural
- Boom height High/Low—identified individually below
- Swath width 13.72 metres
- Number of swaths 20

While the model does not allow for changes in droplet size, DSEWPaC and the APVMA have adopted the following parameters to 'adjust' for different droplet sizes:

AGDRIFT SPRAY QUALITY	BOOM HEIGHT	DATA PERCENTILE	ASSUMED DROPLET SIZE
Very fine to fine	High	90	Fine
Fine to medium/coarse	High	90	Medium
Fine to medium/coarse	High	50	Coarse

For modelling very coarse and extremely coarse droplets, a later ground model (Hewitt 2010) was supplied by the APVMA to DSEWPaC. This model is yet to be made publicly available, but has been used for this assessment.

Final buffer zone recommendations for the different droplet sizes have been derived based on the calculations and applying the APVMA standard no-spray zone increments.

Interrogation of PUBCRIS (last checked 4 April 2011) showed there were many diuron products registered as an algaecide (22 products) or as an antifoulant (19 products), which are outside the scope of a spray drift risk assessment. This assessment was limited to those registered for herbicide use with registered application rates below 370 g ac/ha. PUBCRIS revealed a total of 64 registered products for which a spray drift risk assessment was required (4 April 2011). These products have been broadly grouped either by diuron concentration and formulation type for the products, or their registered use pattern. These groupings are shown below in Table C38.

Table C38: Summary of diuron product numbers and groupings for spray drift risk assessment

GROUP	CONCENTRATION	PRODUCT	USES
3	60 g/L	59120	Cotton defoliants
		59134	
		61371	
		65131	
	120 g/L	59777	

There are five products in this group. All are co-formulated with thidiazuron, and the maximum application rate is 24 g ac/ha for diuron. There are slight differences between products in this group. Four of the five contain diuron at 60 g/L while one contains it at 120 g/L. The application rates are the same, so the fraction of active constituent in the tank mix is the same for all four. All five products require the addition of a spray adjuvant. The spray adjuvants specified on the labels have been checked, and four of the five require this to be added at a rate of 1 L/ha while one requires addition at 2 L/ha. This impacts the level of non-volatiles in the tank mix and so has been taken into consideration in modelling the buffer zones.

The nature of use of these products requires thorough penetration, so use of very and extremely coarse droplets is unlikely. For these products, fine, medium and coarse droplet sizes were modelled.

This assessment is for diuron. These products, being co-formulated with thidiazuron, should take combination toxicity into account (see

<http://www.apvma.gov.au/morag_ag/vol_3/part_07_environment.php>). While thidiazuron has not been reviewed in Australia, the US EPA reregistration eligibility document provides a most sensitive aquatic toxicity value of a NOEC of 110 µg/L to the marine diatom *Skeletonema costatum* (US EPA 2005). This value is 70 times higher than the diuron endpoint in this assessment, so for aquatic toxicity, it is reasonable to assume that diuron will be the limiting substance in aquatic risk.

However, it is not so clear for terrestrial plants. The most sensitive EC25 in the US EPA report is a vegetative vigour EC25 of 1.2 g ac/ha for lettuce and a corresponding NOEC of about 0.06 g ac/ha. The EC25 is the same as that for diuron, but thidiazuron is present at twice the level. Therefore, in the absence of any combination or formulation toxicity, it must be recognised that the following terrestrial buffer zones are for diuron only, and product specific terrestrial buffer zones cannot be recommended.

Table C45: Fixed wing aircraft, Group 3 Products 59120, 59134, 59777 and 65161

			AQUATIC			TERRESTRIAL		
RATE			WIND SPEED (km/hour)			WIND SPEED (KPH)		
(G AC/HA)	F_{ACTIVE}	F_{NV_TANK}	8	14	20	8	14	20
Fine Droplets								
24	0.0012	0.0536	129	164	168	231	366	436
Medium Droplets								
24	0.0012	0.0536	20	28	36	52	69	77
Coarse Droplets								
24	0.0012	0.0536	8	12	17	18	28	36

Table C46: Helicopter, Group 3 Products 59120, 59134, 59777 and 65161

			AQUATIC			TERRESTRIAL		
RATE			WIND SPEED (KPH)			WIND SPEED (KPH)		
(G AC/HA)	F_{ACTIVE}	F_{NV_TANK}	8	14	20	8	14	20
Fine Droplets								
24	0.00048	0.0214	98	119	98	184	290	253
Medium Droplets								
24	0.00048	0.0214	18	27	32	45	56	57
Coarse Droplets								
24	0.00048	0.0214	12	18	23	18	27	34

Table C47: Fixed wing aircraft, Group 3 Product 61371

RATE			AQUATIC			TERRESTRIAL		
			WIND SPEED (KPH)			WIND SPEED (KPH)		
(g ac/ha)	F_{ACTIVE}	F_{NV_TANK}	8	14	20	8	14	20
Fine Droplets								
24	0.0012	0.1036	106	152	174	174	280	371
Medium Droplets								
24	0.0012	0.1036	20	29	38	50	69	82
Coarse Droplets								
24	0.0012	0.1036	8	12	17	19	29	37

Table C48: Helicopter, Group 3 Product 61371

RATE			AQUATIC			TERRESTRIAL		
			WIND SPEED (KPH)			WIND SPEED (KPH)		
(g ac/ha)	F_{ACTIVE}	F_{NV_TANK}	8	14	20	8	14	20
Fine Droplets								
24	0.00048	0.0414	90	129	112	153	246	309
Medium Droplets								
24	0.00048	0.0414	19	28	34	46	60	60
Coarse Droplets								
24	0.00048	0.0414	12	18	24	18	28	35

Table C49: Ground application, Group 3 Products

RATE (g ac/ha)	AQUATIC			TERRESTRIAL		
	FINE	MEDIUM	COARSE	FINE	MEDIUM	COARSE
24	7	1	1	14	2	2

1.19 Conclusions from the risk assessment

Based on available information, application rates indicative of broadacre use (up to 3.6 kg ac/ha) result in an acceptable acute risk to birds. However, at higher rates as used for rights of way, industrial and commercial uses, and for weed control in irrigation channels and drainage ditches, the acute risk to birds is considered unacceptable. Based on current knowledge, these high application rate use patterns should be discontinued due to unacceptable risk to birds. With the exception of application as a defoliant in cotton (24 g ac/ha), the chronic risk to birds was deemed unacceptable at all application rates in excess of 370 g ac/ha based on risk quotients from the Mallard duck study (NOEC = 10 ppm).

Risks to aquatic organisms resulting from spray drift with broadacre uses can be controlled through use of buffer zones. The limiting factor in the aquatic risk assessment was risk to primary streams resulting in runoff. The spray drift risk assessment was therefore driven by use rates below that shown to be a risk to algae and aquatic plants following runoff. Only one agricultural use pattern remained acceptable therefore, which was use as a cotton defoliant at 24 g ac/ha. These products are co-formulated with thidiazuron. This active constituent has not yet undergone a spray drift risk assessment. Buffer zones for aquatic protection are considered acceptable for the products. However, terrestrial buffer zones are only diuron specific and individual product buffer zones cannot be recommended without combination and formulation toxicity data.

Diuron's persistence in the terrestrial environment, and its demonstrated mobility, means that risks to aquatic organisms from off-farm runoff are potentially high. This concern is heightened by the demonstrated persistence and very high toxicity of the main metabolites (based on a very small dataset) to algae and aquatic plants. The persistence of diuron in the aquatic environment makes mitigation of such exposures difficult to apply unless runoff can be prevented through collection and retention of tailwaters resulting from irrigation or rainfall.

Higher tier modelling of different management practices in sugarcane (band spraying leading to half the hectare being treated, and adjusting the application time away from the wet season) shows that runoff can be reduced significantly, by an average of 80 per cent. However, limiting application to a window before the wet season starts (October onwards) will severely restrict the use of diuron. Currently most sales are from October to December, and canopy closure (the growth stage at which DuPont proposed to limit application) occurs up to the end of April (120–150 days after planting or ratooning which occurs up to January). Further more current practice is that band spraying involves between 70–85 per cent of the treatment area. Therefore such labelling amendments would be impractical and unlikely to be complied with.

There are limited toxicity data available for the main diuron metabolites, which may be equally as persistent and as toxic as diuron itself. This means there is unlikely to be any net gain to the environment even if diuron degrades to these metabolites. Despite this, higher tier mesocosm studies did show recovery of phytoplankton communities correlated to a decrease in diuron concentration, and in this regard, the organisms in the mesocosm would have been exposed to the mixture of parent diuron and its metabolites, although, in the aquatic system tested, the DCPMU metabolite did not contribute to more than 15 per cent of the initial diuron levels.

The risk assessment showed that risk to algae and aquatic plants in primary streams (freshwater habitats) is unacceptable at all registered broadacre applications rates, including the lowest currently registered rate of 175 g ac/ha to barley and wheat. The lowest application rate that was deemed to result in an acceptable risk to algae and aquatic plants in primary streams was 160 g ac/ha. Therefore, the only agricultural use pattern currently registered for which risk to algae and aquatic plants in primary streams is considered acceptable is as a cotton defoliant at 24 g ac/ha. The contribution of diuron and it main toxic metabolites (particularly DCPMU) in sediments to algae and aquatic plant risk indicated an unacceptable risk to these organisms when exposed through the pore water based on measured sediment levels in irrigation ditches, streams and estuaries in Australia.

The risk to coastal waters was deemed acceptable due to dilution of diuron in the ocean. Nonetheless, diuron is routinely detected in coastal waters. The persistence in water and very high toxicity of diuron makes the its presence undesirable.

The risk to aquatic organisms through high application rate uses (rights-of-way and weed control in irrigation channels and drainage ditches) is unacceptable for all trophic levels based on runoff and uses involving the high rates should be discontinued.

Risk to aquatic organisms through use as a marine antifoulant has been shown to be acceptable, although again, diuron's properties of persistence in water and very high toxicity make its presence in coastal waters undesirable.

The risk to bees is considered acceptable up to application rates of 10 g ac/ha. The risk to earthworms and soil microorganisms is considered acceptable up to 16 kg ac/ha. The risk to soil organisms from the soil metabolites DCPU and DCMPU is considered acceptable. The risk assessment for non-target terrestrial arthropods indicates there is a low risk to off-field habitats at application rates up to 16 kg ac/ha, however, diuron may present a risk to the in-field habitat at application rates of 8 kg ac/ha and higher.

Diuron is very toxic to non-target terrestrial plants. For this assessment, buffer zones were only ascertained for cotton defoliation. Based on the sensitive nature of terrestrial plants, ground buffer zones of 30 metres or less have been calculated while aerial buffer zones of about 550 metres (coarse droplets) to 100 metres (extremely coarse droplets) have been calculated. Higher application rates would result in larger buffers. For example, buffer zones required to protect downwind stands of vegetation in excess of 300 metres are required for ground application to broadacre fields unless drift reducing technology is used at application.

C.7 CONTROLS AND LABELLING

Given the outcomes of the risk assessment demonstrated unacceptable risk to a number of environmental concerns, the following labelling recommendations for spray drift buffer zones are only for products with registered use rates below 160 g ac/ha (continuing use rates). At this stage, no minimum spray quality is found on product labels. For each product containing registered use rates below 160 g ac/ha, several different spray qualities have been modelled. The recommended buffer zones provided below will depend on which spray quality is included on the individual product labels.

Preceeding these buffer zones on labels, the following instructions should appear:

1.20 Mandatory no-spray zones

> DO NOT apply when there are aquatic and wetland areas including aquacultural ponds or surface streams and rivers downwind from the application area; or non-target terrestrial vegetation downwind from the application area; and within the mandatory no-spray zone shown in the table below.

Currently, the cotton defoliant product labels do not specify a minimum spray quality for application. Consequently, several different spray droplet sizes have been modelled and buffer zones recommended accordingly. A range of fine to coarse droplets have been modelled, rather than the medium to very coarse for other products. The reason for this is it is unclear how fine the droplets need to be for these products to be efficacious.

These products are all co-formulated with thidiazuron. This active constituent has not yet undergone a spray drift risk assessment. Buffer zones for aquatic protection are considered acceptable for the products. However, terrestrial buffer zones are only diuron specific and individual product buffer zones cannot be recommended without combination and formulation toxicity data. The following buffer zones are based on diuron alone.

1.21 Fine droplets (according to ASAE S572 definition)

The following applies to product numbers 59120, 59134 and 59777:

FOR AERIAL APPLICATION—TERRESTRIAL VEGETATION PROTECTION		
WIND SPEED RANGE AT TIME OF APPLICATION	DOWNWIND RISK AREA	
	FIXED WING AIRCRAFT	HELICOPTER
3 to 8 kilometres per hour	250 metres	180 metres
9 to 14 kilometres per hour	350 metres	300 metres
15 to 20 kilometres per hour	450 metres	300 metres
FOR GROUND APPLICATION—TERRESTRIAL VEGETATION PROTECTION		
WIND SPEED RANGE AT TIME OF APPLICATION	DOWNWIND RISK AREA	
3 to 20 kilometres per hour	15 metres	

FOR AERIAL APPLICATION—AQUATIC PROTECTION		
WIND SPEED RANGE AT TIME OF APPLICATION	DOWNWIND RISK AREA	
	FIXED WING AIRCRAFT	HELICOPTER
3 to 8 kilometres per hour	120 metres	100 metres
9 to 14 kilometres per hour	160 metres	120 metres
15 to 20 kilometres per hour	160 metres	120 metres
FOR GROUND APPLICATION—AQUATIC PROTECTION		
WIND SPEED RANGE AT TIME OF APPLICATION	DOWNWIND RISK AREA	
3 to 20 kilometres per hour	10 metres	

The following applies to product numbers 61371 and 65161:

FOR AERIAL APPLICATION—TERRESTRIAL VEGETATION PROTECTION		
WIND SPEED RANGE AT TIME OF APPLICATION	DOWNWIND RISK AREA	
	FIXED WING AIRCRAFT	HELICOPTER
3 to 8 kilometres per hour	180 metres	160 metres
9 to 14 kilometres per hour	300 metres	250 metres
15 to 20 kilometres per hour	350 metres	300 metres
FOR GROUND APPLICATION—TERRESTRIAL VEGETATION PROTECTION		
WIND SPEED RANGE AT TIME OF APPLICATION	DOWNWIND RISK AREA	
3 to 20 kilometres per hour	15 metres	

FOR AERIAL APPLICATION—AQUATIC PROTECTION		
WIND SPEED RANGE AT TIME OF APPLICATION	DOWNWIND RISK AREA	
	FIXED WING AIRCRAFT	HELICOPTER
3 to 8 kilometres per hour	100 metres	100 metres
9 to 14 kilometres per hour	160 metres	120 metres
15 to 20 kilometres per hour	180 metres	120 metres
FOR GROUND APPLICATION—AQUATIC PROTECTION		
WIND SPEED RANGE AT TIME OF APPLICATION	DOWNWIND RISK AREA	
3 to 20 kilometres per hour	10 metres	

1.22 Medium droplets (according to ASAE S572 definition)

The following applies to product numbers 59120, 59134, 59777, 61371 and 65161:

FOR AERIAL APPLICATION—TERRESTRIAL VEGETATION PROTECTION		
WIND SPEED RANGE AT TIME OF APPLICATION	DOWNWIND RISK AREA	
	FIXED WING AIRCRAFT	HELICOPTER
3 to 8 kilometres per hour	60 metres	60 metres
9 to 14 kilometres per hour	80 metres	60 metres
15 to 20 kilometres per hour	80 metres	60 metres
FOR GROUND APPLICATION—TERRESTRIAL VEGETATION PROTECTION		
WIND SPEED RANGE AT TIME OF APPLICATION	DOWNWIND RISK AREA	
3 to 20 kilometres per hour	5 metres	

FOR AERIAL APPLICATION—AQUATIC PROTECTION		
WIND SPEED RANGE AT TIME OF APPLICATION	DOWNWIND RISK AREA	
	FIXED WING AIRCRAFT	HELICOPTER
3 to 8 kilometres per hour	20 metres	20 metres
9 to 14 kilometres per hour	40 metres	40 metres
15 to 20 kilometres per hour	40 metres	40 metres
FOR GROUND APPLICATION—AQUATIC PROTECTION		
WIND SPEED RANGE AT TIME OF APPLICATION	DOWNWIND RISK AREA	
3 to 20 kilometres per hour	5 metres	

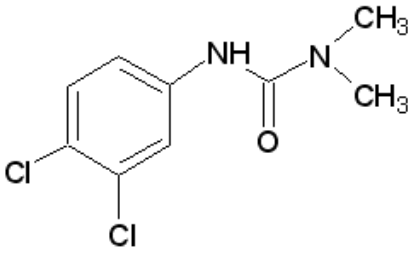
1.23 Coarse droplets (according to ASAE S572 definition)

The following applies to product numbers 59120, 59134, 59777, 61371 and 65161::

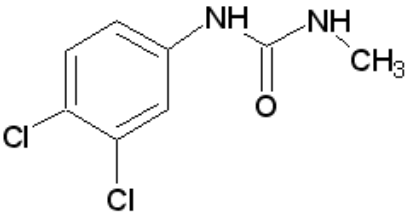
FOR AERIAL APPLICATION—TERRESTRIAL VEGETATION PROTECTION		
WIND SPEED RANGE AT TIME OF APPLICATION	DOWNWIND RISK AREA	
	FIXED WING AIRCRAFT	HELICOPTER
3 to 8 kilometres per hour	20 metres	20 metres
9 to 14 kilometres per hour	40 metres	40 metres
15 to 20 kilometres per hour	40 metres	40 metres
FOR GROUND APPLICATION—TERRESTRIAL VEGETATION PROTECTION		
WIND SPEED RANGE AT TIME OF APPLICATION	DOWNWIND RISK AREA	
3 to 20 kilometres per hour	5 metres	

FOR AERIAL APPLICATION—AQUATIC PROTECTION		
WIND SPEED RANGE AT TIME OF APPLICATION	DOWNWIND RISK AREA	
	FIXED WING AIRCRAFT	HELICOPTER
3 to 8 kilometres per hour	20 metres	20 metres
9 to 14 kilometres per hour	20 metres	20 metres
15 to 20 kilometres per hour	20 metres	40 metres
FOR GROUND APPLICATION—AQUATIC PROTECTION		
WIND SPEED RANGE AT TIME OF APPLICATION	DOWNWIND RISK AREA	
3 to 20 kilometres per hour	5 metres	

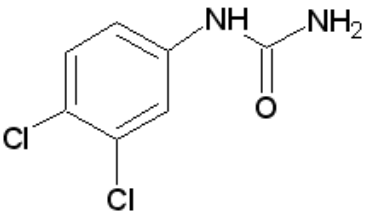
APPENDIX A—CHEMICAL STRUCTURES OF DIURON, ITS METABOLITES AND RELEVANT METABOLLIC PATHWAYS



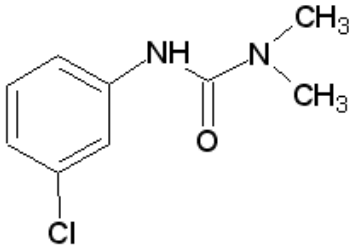
Diuron



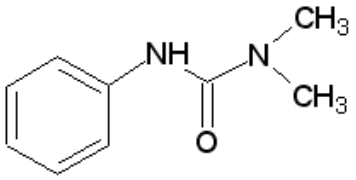
DCPMU



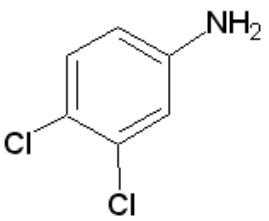
DCPU



m-CPDMU

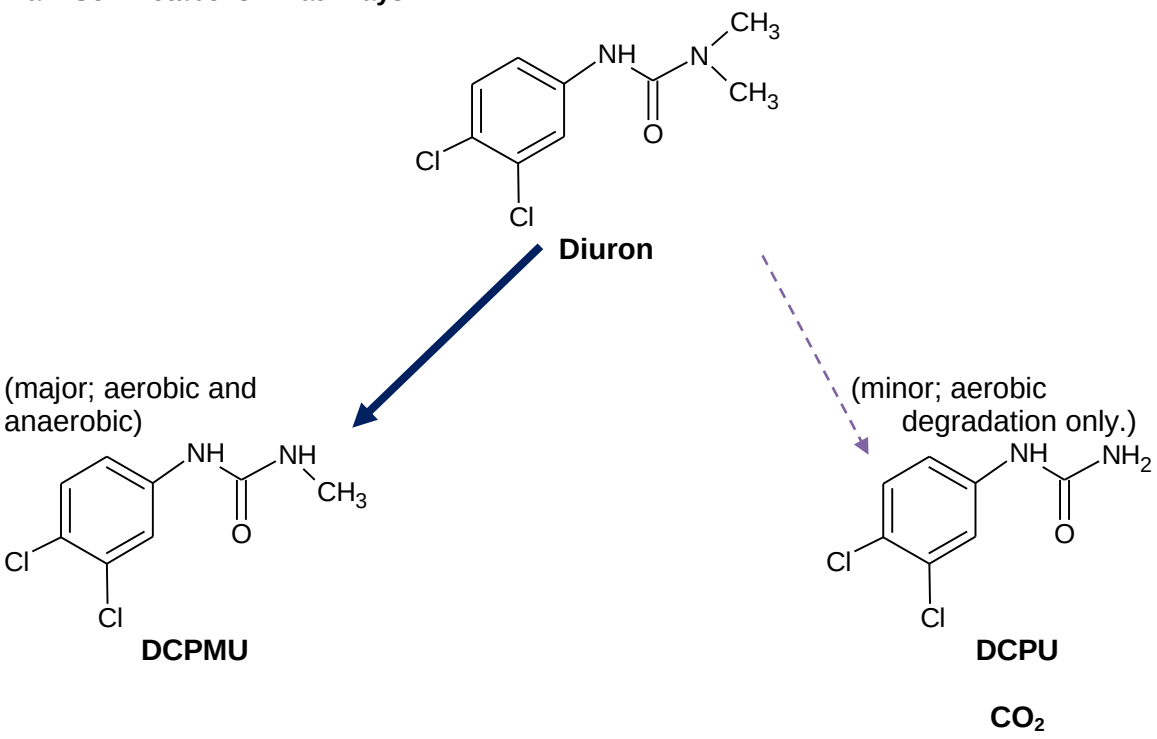


PDMU (Fenuron)

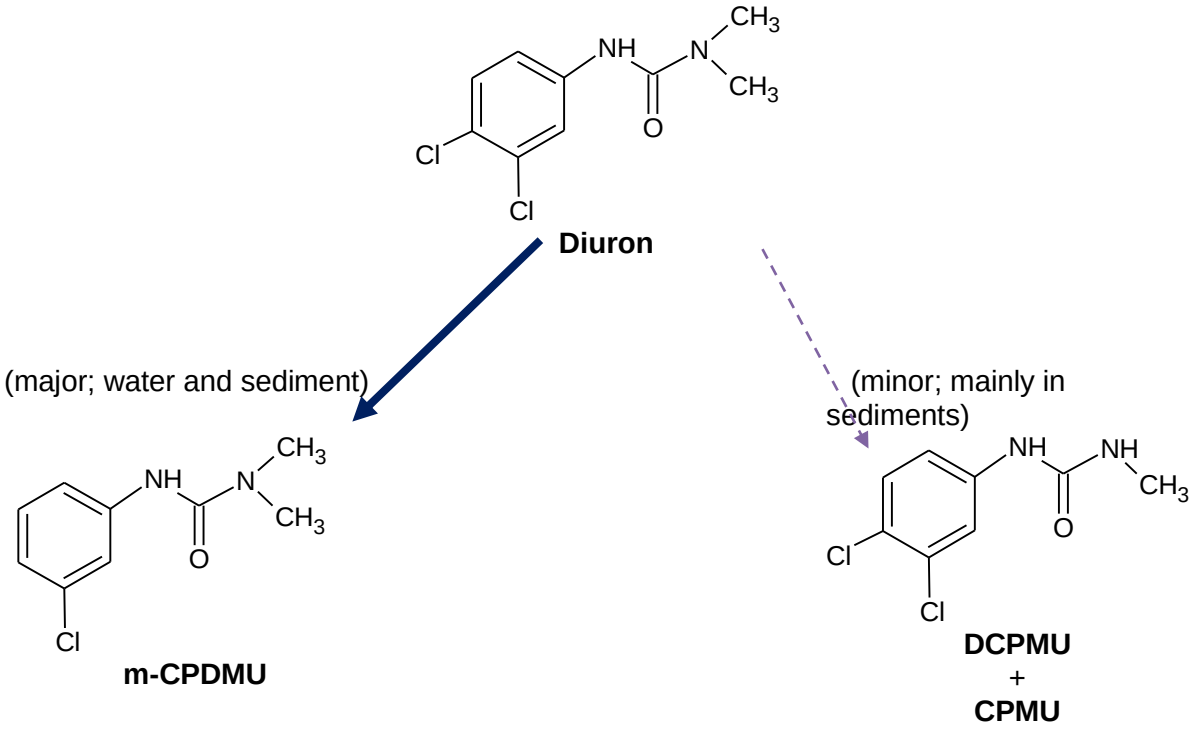


DCA

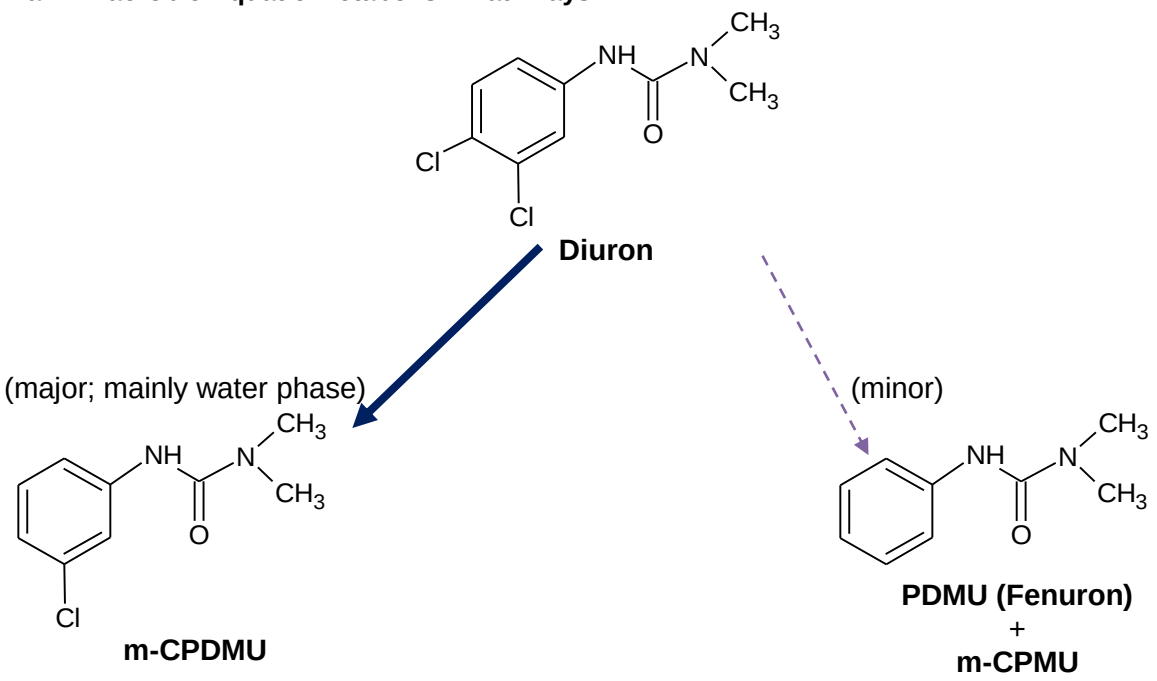
Main Soil Metabolism Pathways



Main Aerobic Aquatic Metabolism Pathways



Main Anaerobic Aquatic Metabolism Pathways



APPENDIX B —REFINEMENT OF AQUATIC TOXICITY ENDPOINT

In order to use the full range of data, DSEWPaC has compiled a species sensitivity distributions for the available toxicity data based on standard endpoints. The software used by DSEWPaC is BurrliOZ v1.0.14, developed by CSIRO (see <http://www.cmis.csiro.au/envir/burrlioz/>).

In deciding on input values for generating the SSDs, where multiple results existed for a single species:

1. Results with the active constituent were preferred over formulated product.
2. Where multiple results existed for an active constituent but the test results were comparable (for example, same duration), the geometric mean was taken.
3. Where multiple results existed for an active constituent, but the test results were different, the lowest result was taken (for example, *Selenastrum capricornutum*).
4. Where measured chronic endpoints were available (fathead minnow, sheepshead minnow, *Daphnia magna* and mysid shrimp), these were used in preference to transformed acute data.

To convert acute results to chronic NOECs, acute results were divided by 10. The following input data were obtained (tables E1 to E4).

Table E1: Summary of acute fish toxicity results for diuron

TEST SPECIES	96 H LC50 (µg/L)	RESULT USED	ACCEPTED VALUE (µg/L)	CHRONIC VALUE (= ACUTE RESULT/10)
Bluegill sunfish	84000 3200 2800 25000	No, 28% ac. Yes Yes No, 28% ac; threshold value	3000 (geometric mean)	300
Rainbow trout	22200 23800 1950 16000 19600 22200	No, result uncertain No, 28% ac Yes No, 80% ac No, 80% ac No, 80% ac	1950	195
Fathead minnow	14200 27100 11700	No. Measured chronic NOEC available for this species.	-	-
Cutthroat trout	1400 710	Yes Yes	1000 (geometric mean)	100
Coho salmon	2400	Yes	2400	240
Lake trout	2700 1200	Yes Yes	1800 (geometric mean)	180

TEST SPECIES	96 H LC50 (µg/L)	RESULT USED	ACCEPTED VALUE (µg/L)	CHRONIC VALUE (= ACUTE RESULT/10)
Striped mullet	6300	Yes	6300	630
Sheepshead minnow	6700	No, Chronic NOEC used	-	-

Table E2: Summary of chronic fish toxicity results for diuron

TEST SPECIES	CHRONIC NOEC (µg/L)	RESULT USED	ACCEPTED VALUE (µg/L)
Rainbow trout	14-day LC_{50} = 8800	No (only sub-chronic test)	
Fathead minnow	26.4	Yes	26.4
Sheepshead minnow	1700	Yes	1700

Table E3: Summary of acute aquatic invertebrate toxicity results for diuron

TEST SPECIES	LC/EC50 (µg/L)	RESULT USED	ACCEPTED VALUE (µg/L)	CHRONIC VALUE (= ACUTE RESULT/10)
Daphnia magna	12800 9700	No. Chronic NOEC available.	-	-
Daphnia pulex	1400 17900 7100	Yes No—lowest value used No—lowest value used	1400	140
Daphnid (*Simocephalus sp*)	2000	Yes	2000	200
Mysid shrimp	1100 1200	No. Chronic NOEC available.	-	-
Scud (Gammarus)	160	Yes	160	16
Brown shrimp	1000	Yes	1000	100
Eastern oyster	4800 1800 3200	Yes Yes Yes	3024 (geometric mean)	302
Amphipod (*Hyalella azteca*)	19400 18400	No—lowest value used Yes	18400	1840
Midge (*Chrionomus tentans*)	3300	Yes	3300	330
Worm (*Lumbriculus variegatus*)	19300	Yes	19300	1930

Snail (*Physa gyrina*)	8200	Yes	8200	820

Table E4: Summary of chronic aquatic invertebrate toxicity results for diuron

TEST SPECIES	CHRONIC NOEC (µg/L)	RESULT USED	ACCEPTED VALUE (µg/L)
Daphnia magna	432	Yes	432
Mysid shrimp	960	Yes	960

For algae studies, the preferred observational endpoint is the growth rate inhibition because it is not dependent on the test design, whereas biomass depends both on growth rate of the test species as well as test duration and other elements of test design. Therefore, in the reviewed studies (Table E5) where both a biomass and growth rate EC_{50} are available, the growth rate value has been used. If the endpoint has not been specified (results in Table E6), then for this exercise these values have been interpreted as an equivalent endpoint.

The following results for algae tests are considered to be chronic. This is because, even though results are generally for 72 hours, this is still quite long in terms of the life cycle of algae, and during this period, algae multiply several times. To convert these chronic EC_{50} values to a chronic NOEC, a factor of 5 has been used (Warne 2001). Results for algal tests using formulated products were not used in the SSD where results were also available for the test species using the active constituent, so are not reported in the Table E5. Study NOECs have not been used here as the large number of algae results that have been used from the US EPA report did not provide NOECs. From the acute to chronic conversions reported in Table E5 below, this approach both overestimated and underestimated the NOECs obtained through the studies.

Table E5: Summary of reviewed algae toxicity results for diuron

TEST SPECIES	EC50 (µg/L)	RESULT USED	ACCEPTED VALUE (µg/L)	CHRONIC NOEC (= ACUTE EC50/5)
Selenastrum capricornutum	11	Yes	15.6	3.12
	22	Yes		
	>5.2	No, <50% reduction in test		
Scenedesmus subspicatus	22	Yes	22	4.40
Synechococcus leopoliensis	38	Yes	38	7.60
Anabaena flos-aquae	30.9	Yes	30.9	6.18
Navicula pelliculosa	65	Yes	65	13.0

In addition, several supplemental studies were available from the US EPA database as listed in Table E6.

Table E6. Summary of aquatic toxicity studies with diuron—algae and diatoms available from the US EPA Reregistration Eligibility Decision (US EPA 2003)

TEST SPECIES	EC50 (µg/L)	RESULT USED	ACCEPTED VALUE (µg/L)	CHRONIC NOEC (= ACUTE EC50/5)
CHLOROPHYCEAE (GREEN ALGAE)				
Chlorella sp.	19	Yes	19	3.8
Chlorococcum sp.	10	Yes	10	2
Dunaliella tertiolecta	20	Yes	20	4
Neochloris sp.	28	Yes	28	5.6
Platymonas sp.	17	Yes	17	3.4
Chlamydomonas sp	37	Yes	37	7.4
BACILLARIOPHYCEAE (DIATOMS)				
Achnanthes brevipes	24	Yes	24	4.8
Navicula incerta	93	Yes	93	18.6
Nitzschia closterium	50	Yes	50	10
Phaeodactylum tricornutum	10	Yes	10	2
Stauroneis amphoroides	31	Yes	31	6.2
Thalassiosira fluviatilis	95	Yes	95	19
Cyclotella nana	39	Yes	39	7.8
Amphora exigua	31	Yes	31	6.2
RHODOPHYCEAE (RED ALGAE)				
Porphydriium cruentum	24	Yes	24	4.8
PRYMNESIOPHYCEAE (HAPTOPHYTES MARINE ALGAE)				
Monochrysis lutheri	18	Yes	18	3.6
Isochrysis galbana	10	Yes	10	2

In addition, two more recent results are available (Magnusson et al. 2008) for two tropical benthic microalgae, *Navicula sp*. (Heterokontophyta) and *Nephroselmis pyriformis* (chlorophyta). These species were tested in a 3-day (72-hour) exposure time frame for endpoint comparison and determination of EC_{50} concentrations following standardised ecotoxicology test guidelines (US EPA 1996; OECD 2006), so the results are considered acceptable for inclusion in the SSD. The ErC_{50} values were reported and used in the SSD as follows (Table E7).

Table E7: Summary of reviewed algae toxicity results for diuron

TEST SPECIES	EC50 (µg/L)	RESULT USED	ACCEPTED VALUE (µg/L)	CHRONIC NOEC (= ACUTE EC50/5)
Navicula sp.	7.8	Yes	7.8	1.56
Nephroselmis pyriformis	8	Yes	8.0	1.6

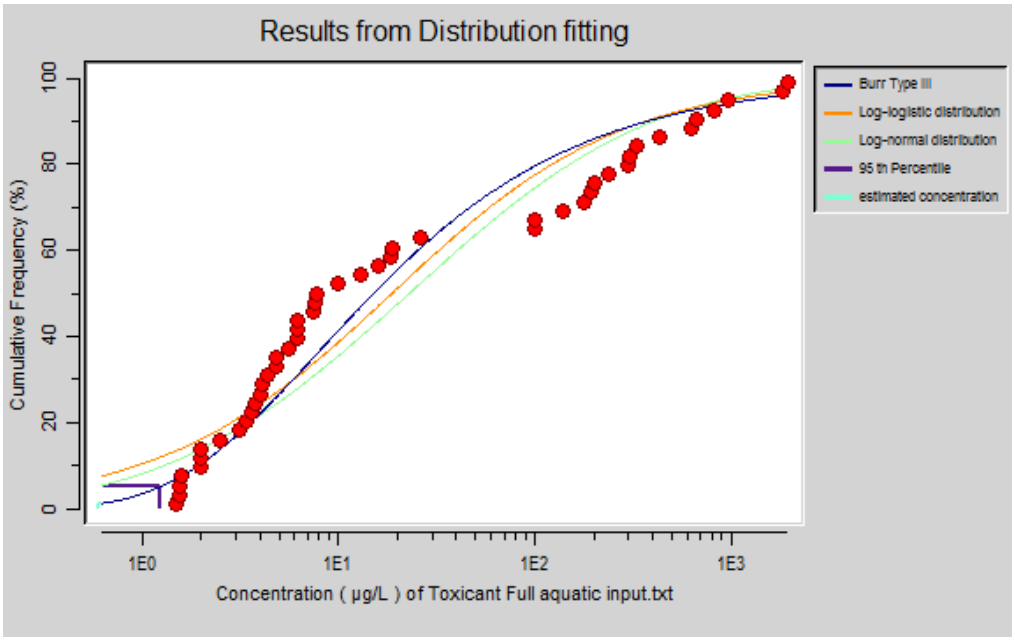
One study assessing diuron toxicity to the duckweed *Lemna gibba* was reviewed. This result is reported below along with other literature results obtained for aquatic vascular plants (Table E8).

TableE8: Summary of acute aquatic plant toxicity results for diuron

TEST SPECIES	LC/EC50 (µg/L)	RESULT USED	ACCEPTED VALUE (µg/L)	CHRONIC VALUE (= ACUTE RESULT/10)
Lemna gibba	15.7	Yes	15.7	1.57
Lemna minor	25	Yes	25	2.5
Lemna major	41	Yes	41	4.1
Lemna perpusilla	15	Yes	15	1.5

The following SSD was generated using the full dataset (Figure E1).

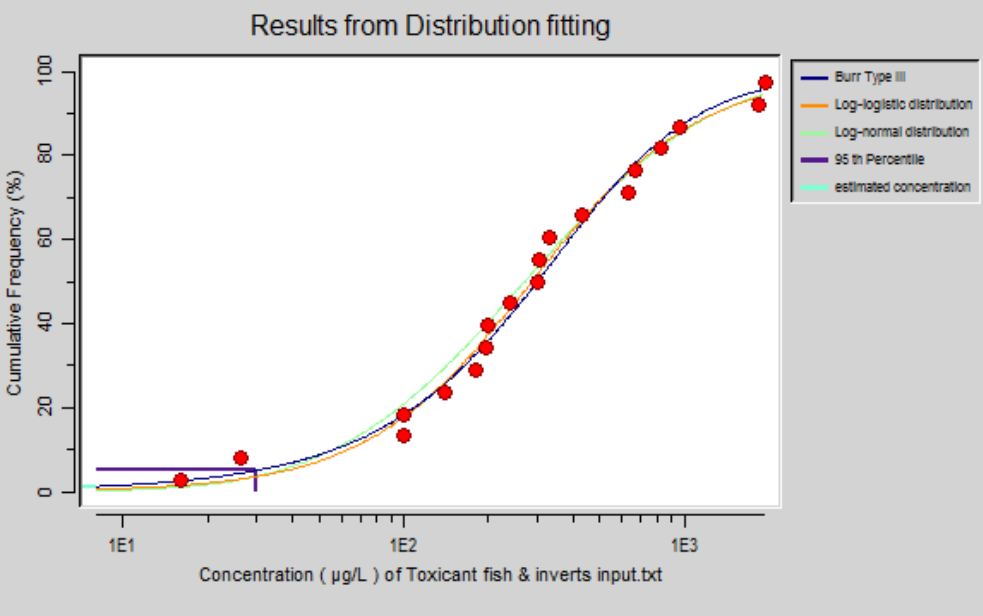
Figure E1: SSD generated from the full dataset



The distribution for the whole dataset (47 observations) provides a 95 per cent protection level of 1.24 µg/L and a 99 per cent protection level of 0.60 µg/L.

For diuron, the sensitivities of primary producers (algae and aquatic plants) is generally much higher than that for primary consumers (aquatic invertebrates) and secondary consumers (fish). Consequently, the total data above do not show a particularly good fit to the distribution. There are arguments for and against separating taxa in undertaking a SSD (Suter II et al. 2002), and given the relatively large dataset for diuron, DSEWPaC has separated the SSD into primary and secondary consumers, and primary producers. The following results were obtained (Figure E2).

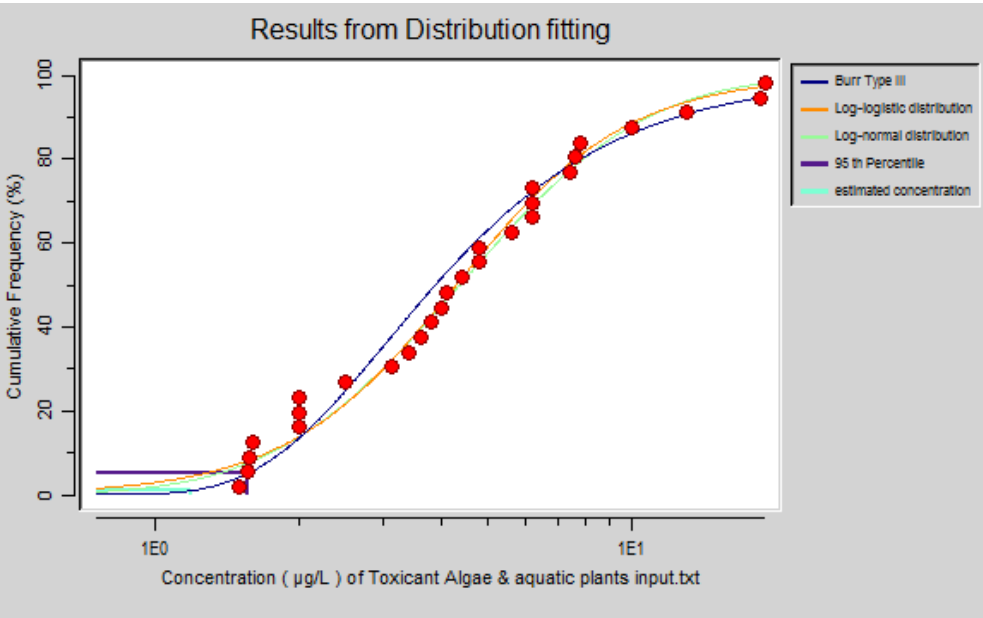
Figure E2: Primary and secondary consumers (aquatic invertebrates and fish)



The data here provide a much better fit to the distribution, and show how aquatic fauna (based on available data) are less sensitive to diuron than the whole dataset tends to indicate.

The distribution for the fish and aquatic invertebrate dataset (19 observations) provides a 95 per cent protection level of 29.8 µg/L and a 99 per cent protection level of 6.87 µg/L (Figure E3).

Figure E3: Algae and aquatic plants



The data for algae and aquatic plants show a relatively good fit to the distribution and the dataset (28 observations) provides a 95 per cent protection level of 1.56 µg/L and a 99 per cent protection level of 1.19 µg/L.

1.24 Final values for use in the risk assessment

Based on the above analysis, the following final values were used in the risk assessment.

Table E9: Final values to be used in the risk assesment

TROPHIC LEVEL	95% PROTECTION LEVEL (µG/L)	99% PROTECTION (µG/L)
Fish and Aquatic Invertebrates	29.8	6.87
Algae and Aquatic Plants	1.56	1.19

The 95 per cent protection level was applied as a general protection to surface waters, and the 99 per cent protection level was applied to waters of higher protection value (notably, the Great Barrier Reef Marine Park). For all aquatic exposure estimates, a level of concern of 1 or less was considered to be an acceptable risk.

APPENDIX C—RUNOFF VALUES FOR USE IN THE RISK ASSESSMENT

There are large uncertainties involved in predicting runoff, and levels of chemical in runoff depend on many site-specific parameters including soil characteristics, slopes, distances between edge of field and receiving waters and types of buffers in between (for example, vegetative filter strips, bare ground, grassed buffers). Since the last iteration of the aquatic risk assessment performed following the release of the PRF (2005), DSEWPaC has established an in-house model for undertaking screening level runoff exposure estimates. This model is described briefly below.

An estimation of the amount of diuron in runoff water was calculated using a sub-model of the REXTOX model proposed by the OECD (Probst et al. 2005); this modelhas been adopted as a working model by DSEWPaC. The model considers rainfall and runoff water, topography of the land (slope), degradation of the pesticide, mobility of the pesticide and buffer zones. In addition to the REXTOX sub-model DSEWPaC considers heterogeneity of fields, interception and retention of the pesticide by crops/weeds and sediment transport of the pesticide.

The model is based on the following equations:

$$L\%runoff = (R/P) \times Crsoil\_surface \times f1slope \times f2bufferzone \times f3foliar\_application \times heterogeneity\_factor \times 100 + suspended\_pesticide \quad (1)$$

Where L% runoff is the percentage of application dose available in runoff water as dissolved substance, R is the quantity of runoff water (mm/day), P is the daily precipitation (mm/day), an Crsoil-surface is the concerntration on soil following degradation and partitioning. Currently DSEWPaC considers a rainfall event of 100 mm with 20 mm of runoff water in its worst-case scenario. On a hectare basis, the assumption of 100 mm rainfall with 20 per cent running off results in a runoff water volume of 200 m^3 per hectare, or 200 000 litres of water.

Topography especially slope is an important consideration in assessing runoff. The model predicts the effect of slope according to

$$f1slope = 0.02153 \times slope + 0.001423 \times slope2 \text{ for slope } <20\%$$
$$\text{Where slope } \geq 20\%;\ f1 = 1. \quad (2)$$

In order to take into account the many topographical situations in which a pesticide may be applied, DSEWPaC generally considers the worst case for two scenarios. Most cropping is expected to be performed on gentler slopes of 12.5 per cent or less (7º), although some crops may be grown on slopes steeper than 12.5 to more than 20 per cent (7º–11º). Solving equation 2 results in a value of ≤0.5 for f1slope with a slope of 12.5 per cent or less, and 1.0 for a slope of 20 per cent. Therefore, with all other factors equalling 1, f1slope will range from 0.5 to 1.0, and results in a prediction of 10 per cent applied chemical in runoff from a 12.5 per cent slope and 20 per cent applied chemical in runoff from a 20 per cent slope based on equation 1. For this exercise, f1slope will be set at 0.5.

The 10 per cent of the applied pesticide in runoff water is likely to be high as this value assumes all areas contribute to runoff. DSEWPaC estimated that less than half of an area effectively contributes to runoff in most realistic circumstances (based on Dunne and Black 1970). Accordingly, Equation 1 is multiplied by 0.5

to reflect the heterogeneity of real fields. This correction lowers the initial estimated amount of chemical in runoff water to 5 per cent as a first tier approach.

The model is further refined by considering the fate of the pesticide. The model assumes that in a worst case, the runoff event occurs three days after the application of the pesticide. The mobility of the pesticide is also taken into account. The fraction of the pesticide available for runoff is estimated by the equation:

Crsoilsurface = e(-3 ln2/DT50) X (1/(1+Kd) for three days of degradation. (3)

The two critical input values, apart from application rate, in the DSEWPaC model are the degradation half-life and the Koc (or preferably, Kd where values are available). The model is more sensitive to sorption than half-life. For example, laboratory soil half-lives range from 20 days to 372 days. Keeping Kd constant in the model, the difference between edge-of-field concentration at the longest half-life is around 10 per cent more than using the shortest half-life. For this exercise, the geometric mean (79 days) was used, and in fact, this only resulted in a reduction of around 2 per cent of the predicted edge of field concentration from using the longest laboratory half-life.

The choice of Kd will have the largest impact in the DSEWPaC model. Measured Kd values from laboratory studies (n = 7 soils with measured Kd values) range from 2.9 mg/kg to 28 mg/kg. Keeping the half-life constant, the difference in predicted concentration at the lowest Kd is almost 7.5 times higher than the predicted concentration using the highest Kd. For this exercise, the geometric mean Kd (9.75 mg/kg) will be used, and this results in a predicted edge of field concentration (all other things being equal) around 2.8 times lower than if the lowest Kd was used.

Applying these values to equation (3) gives: Crsoil_surface = 0.09.

For pesticides applied to crops a portion is retained (Fret) by the crop and not available for runoff during the event. CAS estimates that half of the intercepted (Fint) pesticide is retained based on Linders et al. (2000 citing Willis et al. 1994). The value of f3foliar_application is equal to (1-Fret), where Fret = Fint × 0.5. For weeds and bare soil Fret = 0 and f3foliar_application is consequently =1. The value of suspended_pesticide = 0 for pesticides with water solubility ≥1 mg/L. Pesticides in solution is the major form of transportation, with only chemicals with a water solubility of <1 mg/L being transported primarily by sediment (Grover 1989). This is due to the volume of runoff water greatly outweighing the mass of sediment transported in a runoff event (Grover 1989; Afyuni et al. 1997). For this modelling exercise, due to pre-emergent use of diuron, no crop interception was assumed.

The concentration of pesticide in the worst-case ‘edge of field’ runoff water may be calculated by considering the amount runoff water and amount of pesticide on a hectare basis. The input values, as described for equation 1 above, were as follows:

R = 20 mm
L = 100 mm
Crsoil_surface = 0.09
f1slope = 0.5
f2bufferzone = 1 (default value)
f3foliar_application = 1 (bare ground, pre-emergent uses)

heterogeneity factor = 0.5
suspended pesticide = 0

Therefore, for an application rate of 450 g ac/ha, equation 1 predicted a percentage runoff of 0.45 per cent if the runoff event occurred three days after application. This equates to 2.02 g of diuron per hectare in 200 000 L water/ha, or a concentration of 10 µg/L.

Applying the DSEWPaC model with an estimated soil half-life of 79 days and a soil Kd of 9.74 mg/kg, the following predicted edge of field concentrations were calculated for different application rates (Table F1).

Table F1: Predicted runoff concentrations for different application rates

Application rate (kg/ha)	0.45	0.90	1.8	3.6
Runoff concentration (µg/L)	10	20.4	40.8	81.6

If the higher slope values were used in the DSEWPaC model, the above values would be predicted to increase by a factor of two (2). This will obviously increase exposure to streams taking the first flush in the event these are on steeper slopes. In terms of catchment-wide runoff, it is not expected that average slopes will exceed 12.5 per cent, so for this exercise, the values in Table F1 were used.

The runoff concentrations in Table F1 above best represents the concentration in first flush waters, that is, they are the peak concentration prior to entry into receiving waters. This concentration would occur at the edge of the field or in drainage channels prior to entering streams and rivers.

The concentration of diuron in receiving waters will be dependent on the volume of the receiving water prior to runoff, and the contribution the runoff then makes to the overall water volume (Table F2). In the case of streams and rivers, deeper and wider rivers will result in lower overall concentrations than shallower and narrower rivers. A representative receiving stream concentration has been derived based on the assumption that runoff from diuron use areas comprises 20 per cent of the streamflow during such an event with the remainder of streamflow being from areas of the catchment or the runoff area not treated with diuron. This example is representative of the total area of sugarcane in the Pioneer River catchment.

Table F2: Predicted stream concentrations based on runoff contribution to stream flow

APPLICATION RATE kg/ha	CONTRIBUTION TO STREAMFLOW (%)				
	10	20	30	40	50
0.45	1.0	2.0	3.1	4.1	5.1
0.9	2.0	4.1	6.1	8.2	10.2
1.8	4.1	8.2	12.2	16.3	20.4
3.6	8.2	16.3	24.5	32.6	40.8

Canegrowers, the peak industry body representing canegrowers presented additional information on use of diuron in sugarcane (Wrigley 2005). A considerable difference in the use rates for diuron was observed, especially for grasses and broadleaf weeds. The rate range reported was from 0.45 to 1.8 kg ac/ha, considerably less than 1.8 to 3.6 kg ac/ha given on the currently registered labels. The majority of rates

appeared to be 0.9 to 1.8 kg ac/ha. For the purpose of runoff modelling, both these rates and their mean (1.35 kg ac/ha to consider possible averages over a catchment basis) were considered. These rates are assumed to be representative for all broadacre agricultural uses for this runoff assessment.

Once streams discharge to the ocean (for example, the Great Barrier Reef Marine Park), an initial dilution of 10:1 is assumed.

Based on these considerations, the final concentrations in runoff water have been modelled for use in the assessment (Table 54).

Table F3: Modelled Peak Concentrations (µg/L) from Runoff Events with Diuron.

APPLICATION RATE (kg ac/ha)	0.9	1.35	1.8
Primary streams	20.4	30.6	40.8
Secondary streams	4.1	6.1	8.2
Coastal discharge	0.41	0.61	0.82

1.25 Comparison with measured concentrations

To gain a better understanding of the relevance of modelling for use in the risk assessment, modelled values can be compared to monitoring data where available. Fortunately, for diuron, there is significant monitoring information available. The data have generally been generated for catchments discharging to the Great Barrier Reef, and cover large areas different land uses including grazing, forestry and agriculture (primarily sugarcane growing). Other data are available for NSW and include cotton growing areas, and rivers within the Murrumbidgee Irrigation Area. In general, the findings from Queensland and NSW are comparable with diuron levels in river systems, where detected, being found at mainly less than 10 µg/L (but sometimes around 20 µg/L).

The more recent Queensland data are considered most useful for this comparative exercise. Monitoring was performed for a range of ambient and flow events, and monitoring was performed following main times of diuron application (monitoring in January) and therefore is expected to largely capture ‘first flush’ events. Monitoring was also often performed later in the year (e.g. April) and comparisons can therefore be drawn between likely first flush concentrations and those found later in the cycle. While some of the monitoring stations were in areas unlikely to be impacted by agricultural runoff, a high proportion of monitoring stations were located in the agricultural use areas.

1.26 Primary streams

For this assessment, primary streams may include smaller creeks or brooks, and such watercourses may often be found closest to farm lands and receive the first ‘edge of field’ water from runoff events. Monitoring data for such watercourses are not as common as data for secondary streams (considered in this report as rivers and larger streams receiving inflows from primary streams). However, data are available and discussed in more detail in Volume 2.

These data show that concentrations can be very high (including in farm drains). Possibly, the most relevant data for primary streams comes from NSW monitoring. During the four years from July 1997 to June 2001, water monitoring of drainage water at 15 sites in the Murrumbidgee Irrigation Area was undertaken and showed several detections of moer than 20 µg/L. From a total of 548 samples, the 75th, 90th, 95th and 99th percentile values were reported as 0.4, 0.9, 2.26 and 12.6 µg/L respectively. More recent data (2004–06) at these sites gave similar results, although the highest level detected was 13.2 µg/L.

DSEWPaC accepts that farm drains are part of the agricultural landscape and should not necessarily be considered as natural waterways. However, for this assessment, these data wre considered a surrogate for situations where first flush runoff waters can enter small tributary streams and creeks. The measurements appear to be of the drainage waters, not measurements within actual farm drains or irrigation ditches that themselves may have been treated with very high rates of diuron, so were considered comparable for use as surrogate values in primary streams (NSW DEC 2005).

The monitoring data indicate that the modelled peak values reported in Table F3 may be overly conservative. The peak concentration from the modelling is predicted to be 30.6 µg/L (using an average rate of 1.35 kg ac/ha) compared to maximum detections in the dataset described above only approaching half this level, although limited monitoring of sugarcane drains has levels of 26 and 36 µg/L.

As a screening tool, the DSEWPaC model appears to be acceptable, particularly where there are no 'real-world' data to base runoff estimates on. However, for this exercise, the extensive available monitoring data was given priority, primarily because they can help provide a temporal and special context to the data. While peak concentrations are one aspect, the duration of such concentrations, and the consistency of such levels should be considered if possible. It appears from the available data that peak concentrations, or levels approaching them, in primary streams may not be common or long-lived because there is a relatively large difference between the 95th and 99th percentile values reported above (2.26 and 12.6 µg/L respectively). Conversely, there is more uncertainty associated with primary streams given that they can have a wide range of characteristics (water volumes, flow rates), with many possibly being dry for much of the year. To try and accommodate this added uncertainty, this assessment used the 99th percentile concentration of the 548 samples of drainage waters in the Murrumbidgee Irrigation Area from 1997 to 2001 described above (about 13 µg/L). In doing so, it is recognised that some peak concentrations would be likely to exceed this level, but it is also expected that levels in any given area of an exposed stream would be very much less than this for most of the time.

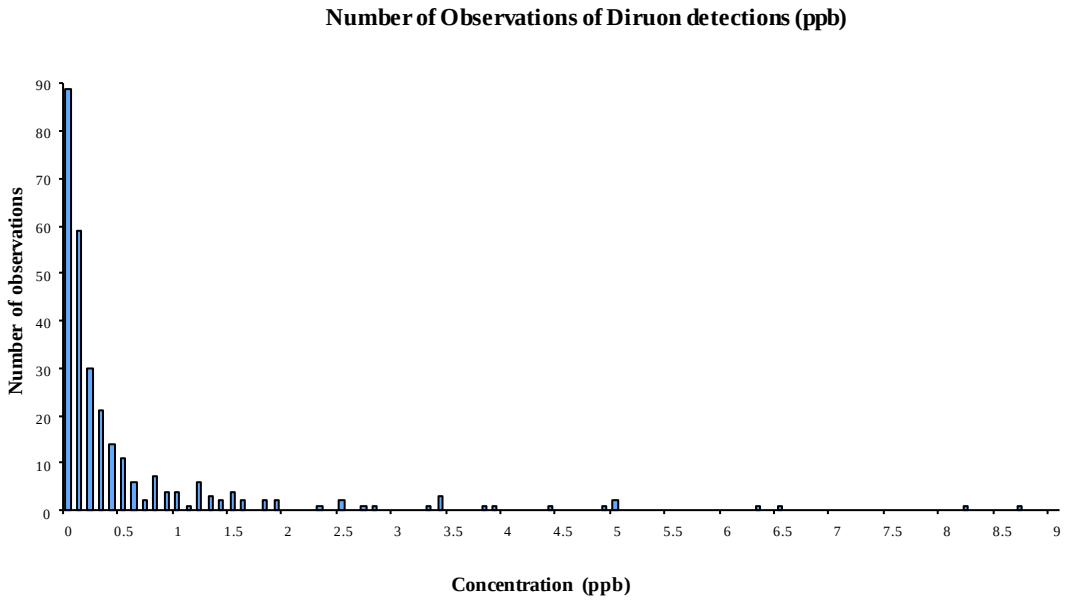
1.27 Secondary streams—Queensland

For a more detailed analysis of monitoring data, DSEWPaC used raw data for streams (not counting drainage channels where these were monitored) from Rohde et al. 2006 (Mackay Whitsunday Region – 2004/2005), Lewis et al. 2007 (lower Burdekin and Don River catchments, 2005–07) and Faithful et al. 2007 (Tully–Murray Rivers Region, Queensland). These reports were chosen as they provide recent data of good quality. In all, some 288 data points were available for consideration. While the predominant agriculture around sampling stations were from cane growing areas, other land uses were also considered (including grazing, forestry, urban, bananas).

General observations of the data indicated that higher levels were associated with cane growing (although positive detections were found with other land uses as well) and the first flush concentrations were,

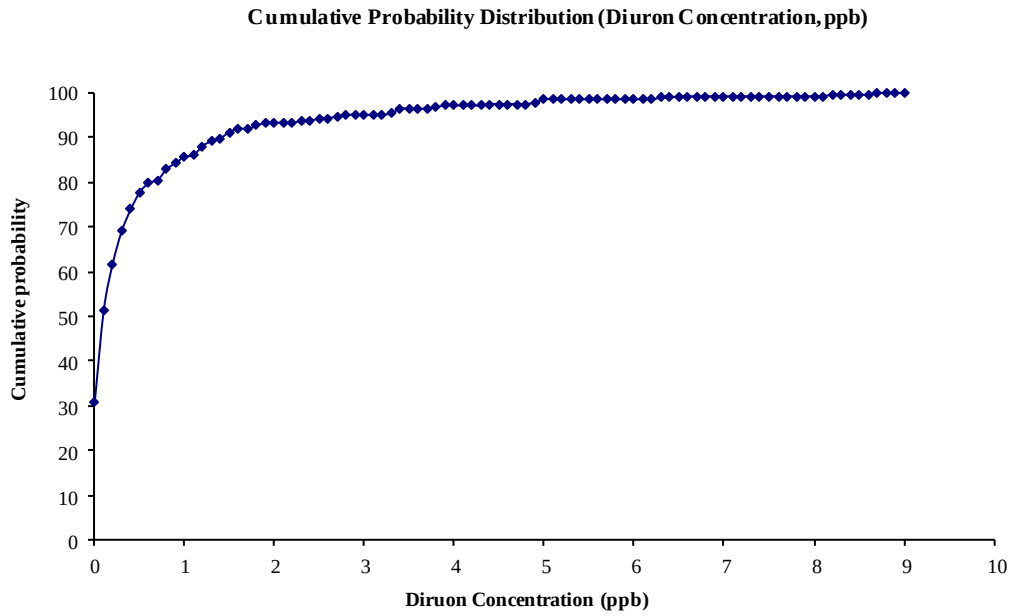
unsurprisingly, at the higher end of the concentration distribution. Where observations were made at the same sampling station with several data points over a period of time (for example, over several days during a flow event), it was apparent that, while there was a steady decline in residues, they could remain at relatively elevated levels for a period of days. Because of the timing of observations, this has the effect of increasing the number of observations found at the higher end of the distribution, and thereby increasing the conservativeness of any endpoint associated with these data.

The following graph summarises the observations for the whole dataset used in this analysis:



The data had a range of less than 0.01 µg/L (about 31 per cent of observations) to 8.7 µg/L. Around 51 per cent of observations were lower than 0.1 µg/L and around 85 per cent of observations were at 1 µg/L or less. One observation of 19 µg/L was reported (Faithful et al. 2007). However, this value is uncertain as it is more than twice the value of any other level reported over several years. It appears more indicative of a level expected in drainage channels or primary streams adjoining fields of application; hence it was not used in the secondary streams assessment.

The cumulative probability distribution of these data is shown below:



Based on the distribution of the above monitored data, the 50th and 90th percentile concentrations (calculated by EXCEL) were 0.075 and 1.4 µg/L respectively. The distribution of positive only values (0.01 µg/L or greater) was also considered and resulted in 50th and 90th percentile concentrations of 0.26 and 1.9 µg/L respectively. These values are considered more conservative for use in assessing risk from runoff as they are based on observed values more likely to be found within diuron use areas. However, it should be noted that more than 93 per cent of all observations in the full distribution described above were found at levels exceeding 1.9 µg/L.

Data from Lewis et al. (2007) were further analysed between ambient measurements (41 observations) and flow event measurements (82 observations). The data showed that 'flow' events (for example, daily discharge greater than 10000 megalitres) did not result in larger water concentrations. In fact, the opposite was true based on the dataset considered with a 90th percentile water concentration of 1.1 µg/L in flow events and 1.8 µg/L under ambient conditions. This is despite around 40 per cent of ambient observations having 0.1 µg/L or less compared to 26 per cent in flow events. These data indicate that the 90th percentile of 1.9 µg/L found for analysing the full dataset of positive values should be representative of both ambient and flow conditions. It must also be remembered that runoff can occur under 'ambient' conditions as defined within the monitoring programs. Rainfall may be sufficient to generate runoff, but still not generate enough runoff to constitute a 'flow event'. In such cases, higher concentrations may not be surprising as there will be significantly less dilution.

A more detailed description of Australian and international monitoring data for diuron are found in Section 6.5.2 of the report. Other values described in this section for river and stream systems for other agricultural areas are generally within the range of data used here.

1.28 Secondary streams—NSW

The NSW Department of Land and Water Conservation (NSW DLWC), Central and Northwest Regions Water Quality Program routinely monitored the major rivers in the central and northwest of NSW for pesticides from 1991 to 1999 in the major cotton growing valleys in NSW. This monitoring program was terminated in 2000 (coinciding with the year of uptake of Cotton Australia's Best Management Practice Manual commenced), but undertook more limited monitoring up to 2004–05. In their submission to an earlier version of the DSEWPaC diuron assessment, Cotton Australia (2006) provided the relevant monitoring data from 1991 to 2004–05. DSEWPaC undertook an assessment of these data including consideration of monitoring from 1991 to 1998; monitoring from 1999 to 2005; monitoring in rivers only from 1999 to 2005; monitoring in creeks/brooks only, 1999 from 2005. The following table summarises these statistics.

Table F4: Summary of monitoring data for diuron in the riverine systems of the Namoi, Gwydir and Border river valleys, 1991-2005.

	N	% DETECTION	MAX (µg/l)*	90th % (µg/l)*	50th % (µg/l)*
Whole data, 1991–1998	2259	12	82.1	5.9	0.4
Whole data, 1999–2005	2248	12	19.5	1.93	0.3
Rivers, 1999–2005	1346	8.4	8.4	1.3	0.3
Creeks, 1999–2005	902	17.2	19.5	2.6	0.3

** from the range of positive detections*

The data generally show that levels detected decreased significantly from 1999, with the 90th percentile of the 1999–2005 data of 1.93 µg/L being in good agreement with that from Queensland streams above. However, the number of non-detections (noting that the detection limit was 0.1 µg/L in the NSW data compared with 0.01 µg/L in the Queensland data) was significantly greater in NSW (88 per cent of observations) compared to Queensland (about 51 per cent of observations were less than 0.1 µg/L), which is possibly the result of many NSW farms having the ability to retain tailwaters.

Further analysis of the 1999–2005 data showed that in rivers, frequency of detections were much lower than creeks (8.4 per cent compared to 17.2 per cent respectively), and levels found were generally lower. With the creek data, one creek in particular (Thalaba Creek at Merrywinebone) was found to have consistently higher levels of diuron than other creeks. Removal of this creek from the dataset resulted in creek detections of 13 per cent of observations with a 90th percentile of 1.7 µg/L.

The Thalaba Creek data were useful in gauging times of the year when detections were mainly observed. In the hotter months of the year (October through March, averaged from 1999–2005), detections were more common (56 per cent of observations compared with 41 per cent in the colder months), but levels were lower (90th percentile of 2.2 µg/L compared to 11.7 µg/L in the colder months). Note that these representative of other creeks or rivers in this area being monitored. However, what they help to illustrate is that detections arise from several use situations. For example, the cotton season from September to March may not contribute as much as other situations such as winter cereals or non-crop uses at other times of the year.

Another important consideration with these data is their representativeness for other diuron use areas both within NSW or other parts of the country. It is known that in the area of sampling, many farms are equipped

with the ability to retain stormwater runoff. This may be one reason that so many samples from surface waters showed no detections (88 per cent). However, it may not be accurate for other diuron use areas.

Other monitoring data are available from the Murrumbidgee Irrigation Area. The last three years of compliance data as reported by Murrumbidgee Irrigation Limited (2005, 2006, 2007) were considered. These data are based on monthly samples from 14 different surface water areas. Drought conditions meant limited flows, so many samples were not taken (in times of 'no flow'). Also, as the data are taken monthly, detections are unlikely to represent peak concentrations where found. However, some useful information can be obtained. Based on the 2005–07 data, the highest levels found (for example, where maximum levels are more than 2 µg/L) occur in the cooler months (April through August). Analysis of these months showed diuron (0.1 µg/L or higher) in 60.6 per cent of samples (n = 137), and where detected, the 90th percentile was 2.1 µg/L. The maximum level detected was 13.2 µg/L. Eleven per cent of samples exceeded 1 µg/L. In the warmer months (taken as September through March), diuron was found (0.1 µg/L or higher) in 36.2 per cent of samples (n = 185), and where detected, the 90th percentile was 0.54 µg/L. The maximum level detected was 1.1 µg/L. Some 1.1 per cent of samples exceeded 1 µg/L.

A further point of interest regarding these monitoring data was raised in Hyne and Aistrope (2006). The Murrumbidgee Irrigation Limited (MIL) data above are based on monthly grab samples. Hyne and Aistrope report results of field measurements using the cellulose membrane passive samples deployed over a period of 7–22 days from mid-October to mid-November 2004, at two sites also sampled by MIL receiving runoff from citrus and rice fields. The average daily diuron concentrations at both sites were all between approximately 1.5 to 4.5 µg/L, reflecting the more typical diuron water concentrations at these sites for that period, rather than the low concentrations measured in the grab samples collected each month by MIL (values were all less than 1 µg/L). This shows that exposure in surface waters could be at elevated levels for extended periods of time, but such periods at elevated levels are unlikely to be detected in long-term monitoring programs due to time between sampling.

1.29 Coastal discharge

Queensland monitoring data can be used to assess likely coastal water concentrations. In a 2007 flood plume produced from the Haughton River and Barratta Creek (Burdekin area), diuron concentrations were measured in the range of less than 0.01 µg/L to 0.08 µg/L, and it was found in 12 of a total of 14 samples (Lewis et al. 2007). More than 85 per cent of the observations were below 0.04 µg/L. A flood plume from 2005 (reported in Rohde et al. 2006) detected diuron at much higher levels with a range of less than 0.01 to 0.44 µg/L. Diuron was detected in 9 of 11 samples. Combining these two datasets (25 samples), the 50th and 90th percentile values were 0.03 and 0.28 µg/L respectively. These values are very conservative as they relate to plume levels and not ambient concentrations. Some data are available for coastal waters as presented in Section 6.5.2 of the report that indicate levels mainly up to 0.02 µg/L (20 ng/L: see 'Marine waters' below). In any event, the coastal discharge level of 0.61 µg/L (application rate of 1.35 kg ac/ha) based on modelling above appears too conservative, possibly by an order of magnitude for ambient conditions.

1.30 Marine waters

More details for detection of diuron in marine waters are found in Volume 2.

Souter (2009) provides information on pesticide monitoring of the inshore Great Barrier Reef by the Reef Quality Marine Monitoring Program. These data show diuron being detected up to 35 kilometres off-shore. Mean concentrations were low with average wet-season concentrations from 2005 to 2008 ranging from 0.171 ng/L at Pixies Garden (35 kilometres off-shore) to 5.41 ng/L at High Island (about 4.5 kilometres off-shore).

Kapernick et al. (2007) describe results from routine passive sampling from 10 of the same inshore reef sites where sampling continued throughout the wet and dry seasons of 2006–07. Average dry season concentrations were much lower than wet season concentrations, with average levels of 0.07–1.8 ng/L. During this sampling period, average wet season concentrations ranged from 0.59 ng/L at Pixies Pinnacle to 17 ng/L at the Outer Whitsunday (about 12 km off shore).

1.31 Choice for water concentrations for use in the risk assessment

Expected water concentrations have been discussed above for both calculated and monitored levels. These levels are considered with respect to runoff only (drift values are discussed separately), and in the case of monitoring data, given the timing of monitoring compared to likely application of diuron, the levels found are more likely to be the result of runoff rather than spray drift.

Comparison of calculated *versus* observed levels shows a general agreement in the case of primary streams (including some drainage channel data), and for peak concentrations in secondary streams. Calculated values for coastal areas are higher by more than an order of magnitude than those available from monitoring data.

For the risk characterisation, the value with the highest confidence should be used. In the case of primary streams found adjacent to fields of use, potential peak concentrations from modelling are supported by the available monitoring data. For the risk assessment, the 99th percentile of a large dataset (548 observations) of drainage waters was used to represent exposure concentrations in primary streams, namely 13 µg/L.

For secondary streams, a value of 1.9 µg/L was used. This value represents the 90th percentile value described above from all positive values from the more recent Queensland data, and also from the 1999-2005 NSW data from the major cotton growing valleys. Confidence in this value is high given the large dataset that has been compiled over recent years for several different catchment areas. This value remains conservative, as it didn't include the large number of non-detections (at concentrations below 0.01 µg/L). However, in using this value, it must be recognised that there will be occasions when higher levels will occur. Also, analysis of the data shows other areas of concern that must be accommodated within this choice of value, as follows:

- The Queensland data allow with some confidence in the conclusion that much of the observed diuron levels in rivers is due to sugarcane farming. However, no such clear observation from land use can be made from NSW data where diuron detections appeared to increase in number and concentration in cooler months, suggesting several crop and non-crop uses could be contributing.
- The main monitoring data from NSW were in the major cotton growing valleys of NSW where a large proportion of farms are known to have tail water retention facilities, which possibly increased the very high proportion of non-detections from sampling. These tailwater retention facilities are unlikely to represent surface waters in other diuron use areas where no such facilities exist.

- Some evidence is available showing average daily levels of diuron can be much greater than levels found during long-term monitoring programs, and such elevated levels can exist for long periods of time (weeks). Such information is not discernible from longer term monitoring where significant periods of time can exist between samples.

For coastal waters, the modelled concentrations ranged from 0.4 to 0.8 µg/L (0.9–1.8 kg ac/ha). These were well in excess of measured coastal concentrations found under ambient conditions, and in reasonable agreement with those found following flood plume events (90th percentile 0.28 µg/L). This may indicate that relevant elimination processes were not considered in the modelled value, or probably more likely, the dilution factor is underestimated. In this case, the measured data are considered to represent the higher likely concentrations given they were measured during flood plumes, and would therefore be higher than ambient levels. However, available monitoring data for coastal waters still remain relatively limited. Therefore, for use in the risk assessment, the 90th percentile of 0.28 µg/L described above was used, and uncertainties associated with this value will be explored further in the risk characterisation. In summary, the following values were used in the risk characterisation (Table F5).

Table F5: Water concentrations (µg/L) from runoff events with diuron to be used in the risk characterisation

	CONCENTRATION (µg/l)	BASED ON
Primary streams	13	Monitoring
Secondary streams	1.9	Monitoring
Coastal discharge	0.28	Monitoring

While there are obvious uncertainties associated with any value that will be applied within a national assessment, these uncertainties are considered manageable. It is quite possible that actual peak concentrations in any of the above water situations may exceed the value used in Table F5 for the risk assessment. However, the extensive nature of the available monitoring data indicates that such concentrations will not be found extensively, or last for extended periods of time. Therefore they are considered reasonable for risk assessment.

APPENDIDIX D - ENVRIONMENTAL FATE

1. ABIOTIC DEGRADATION

1.1 Hydrolysis

Study 1 – US EPA/OECD/EU guidelines

The hydrolysis of diuron, uniformly ^{14}C-labelled in the phenyl ring, was studied in darkness at an initial concentration of approximately 1 ppm in sterile pH 4, 5, 7, and 9 buffered aqueous solutions (Williams, 1995a). The study was conducted according to US EPA guideline 161-1, OECD Guideline 111 and EU data requirements.

The solutions were incubated at two temperatures of approximately 25 and 50°C and then analysed at various time intervals for 30 days by HPLC to determine the amount of parent and the identity and distribution of radiolabelled degradation products. Preliminary studies showed that there was no loss of radioactivity from the glass vials after 48 hours, taken to indicate that the test substance did not adsorb to glass or was volatile.

At 25°C there was no observable degradation at pH 7 and 9 and only slight degradation at pH 4 and 5 with calculated half-lives of 798 and 313 days respectively. However, as the fit to first order was poor and the half-lives are significantly longer than the experimental duration, these are not reliable.

At 50°C hydrolysis was more pronounced for pH 4, 5 and 9 with half-lives of 26, 56 and 109 days at pH 4, 5 and 9 respectively. As the fit to first order was good for pH 4 and 5 (r^2 of 0.963 and 0.906 respectively) these results are considered reliable. At pH 7, there was insufficient degradation for the determination of a reliable half-life.

There were 2 degradation products noted in the HPLC, only one of which was >10% of applied radioactivity (AR). The major degradate reached maximum concentrations at 50°C of 52.5, 34.3, 9.7 and 20.8% of applied radioactivity (AR) for pH 4, 5, 7 and 9 respectively and was identified as 3,4-dichloroaniline (DCA) by co-chromatography. The recovery for all samples was good and ranged from 92.5 to 121.6% of the initial radioactivity and averaged 97.9-106.5% of the initial radioactivity for each test solution over the study. Microbial plate counts (bacterial and fungal) at the start and on termination (0 and 30 days) showed that sterility was maintained.

Study 2 – US EPA guidelines

The hydrolytic stability of diuron, uniformly ^{14}C-labelled in the phenyl ring, was studied in darkness at an initial concentration of approximately 10 ppm in sterile pH 5, 7, and 9 buffered aqueous solutions (Hawkins, Kirkpatrick and Shaw, 1989). The study was conducted according to US EPA guideline 161-1 requirements.

The solutions were incubated at approximately 25°C and then analysed at various time intervals for 30 days by TLC to determine amount of parent and distribution of radiolabelled degradation products. The identity of degradates were determined by TLC co-chromatography and confirmed by HPLC.

There was only limited degradation of 1-2% at all pH values and while a half-life was calculated, it was not considered meaningful. It was concluded that the half-life was greater than 500 days. There were 3 minor

degradates detected with 2 identified as N'-(3,4-dichlorophenyl)-N-methyl urea (DCPMU) and 3,4-dichloroaniline (DCA), the third degradate was not identified.

1.2 Aqueous photolysis

Study 1 – US EPA guidelines

Diuron, uniformly ^{14}C-labelled in the phenyl ring, was irradiated with simulated sunlight at 25±1°C in aqueous buffers (pH 5, 7 and 9) and purified water (Williams, 1995b). The simulated sunlight was approximately the intensity of natural sunlight at the equinox 40° N. The study was conducted according to US EPA guideline 161-2 and to satisfy EU data requirements (Point 2.9.2 and 2.9.3 of Directive 94/37/EU) using continuous irradiation for 24 hours. The dark controls were maintained in darkness in the same buffers as part of the aqueous hydrolysis study above. The photolysis and dark solutions were analysed at various time intervals by HPLC to determine the identity and distribution of radiolabelled degradation products.

A preliminary study was conducted to estimate the half-lives, determine the sampling schedule, estimate the direct and indirect photolysis half-lives, and to check the proposed analytical method. During the preliminary study it was shown the indirect photolysis (using acetone as the sensitizer) was very fast with half-lives estimated as 0.195, 0.488, 0.184 and 0.313 hours (11.7, 29.3, 11.0 and 18.8 minutes) for pH 5, 7, 9 and purified water respectively.

In the definitive study, the photolysis of diuron followed first order kinetics and was pH-dependent with degradation at pH 7 slower that at pH 5 or 9. There was little degradation in the dark controls (half life >200 hours). The half-lives were 7.8, 16.3, 8.9, and 16.9 hours for pH 5, 7, 9 and purified water respectively. Using data from the measured light intensity, the quantum yield for diuron was calculated and used to determine the half lives under environmental conditions (blue skies and undisturbed surface) with varying seasons and latitude, the results of which are given in Table A1.1 for the latitudes relevant for Australia.

Table A1.1. Degradation half-lives (hours) in natural sunlight at various seasons and latitude.

	Spring			Summer			Autumn			Winter		
Latitude, °N	20	30	40	20	30	40	20	30	40	20	30	40
Purified water	12.0	12.3	13.1	11.4	11.2	11.2	14.6	17.0	21.3	17.4	22.4	33.3
pH 5	6.85	7.01	7.40	6.48	6.36	6.34	8.25	9.55	11.9	9.77	12.5	18.4
pH 7	16.3	16.7	17.6	15.5	15.2	15.1	19.6	22.6	28.0	23.1	29.4	43.1
pH 9	7.52	7.69	8.12	7.11	6.98	6.96	9.06	10.5	13.1	10.7	13.7	20.3

After irradiation, 11 photolysis products were observed, 4 of which were major degradates and present in concentrations of >10% each. The major degradates were not identified, a significant weakness in the study (the report states that identification of these degradates will be conducted in a supplemental report but this has not been presented to DEWHA). Two minor peaks in the HPLC were identified, one tentatively identified as either 3-(4-chlorophenyl)-1,1-dimethyl urea (CPDMU) or 3,4-chlorophenyl urea (maximum of 4.9% of AR) and another as 3,4-dichloroaniline (<1.5% of applied) by comparison with authentic samples. The recoveries averaged 89.6 to 99.4% of AR and individual measurements ranged from 83.0 to 100.6%. The pH 5 buffered solution showed the highest losses and could be due to $^{14}CO_2$ as there were no gas traps used. There were also high losses of applied radioactivity in the preliminary study for the sensitized systems at pH 5 and the purified water, but not in the pH 7 and 9 buffered systems (formation of carbonate ion?).

The buffered solutions were sterile at the start, determined by bacterial and fungal plate counts with no colony forming units found, and at test termination.

The report concludes that photodegradation appears to be a likely removal mechanism for diuron in the environment.

Study 2 - US EPA guidelines

Diuron, uniformly ^{14}C-labelled in the phenyl ring, was irradiated with simulated sunlight at 25±1°C in aqueous buffers (pH 7) at 10 mg/L (Hawkins *et al*, 1989). The simulated sunlight was 1.8 times the intensity of natural sunlight at the equinox 40° N over the UV wavelength range 290-400 nm. The study was conducted according to US EPA guideline 161-2 using continuous irradiation for 15 days. The dark controls were maintained in the same buffer. The photolysis and dark solutions were analysed at various time intervals by TLC to determine the identity and distribution of radiolabelled degradation products. Volatile and evolved gases were trapped.

The photolysis of diuron followed first order kinetics and the half-life was determined as 9.0 days (r^2 = 0.975; all duplicate data), equivalent to about 43 days under natural (latitude 30-40°N) sunlight assuming 12 hours of sunlight. There was little degradation in the dark controls. Volatiles as carbon dioxide amounted to 16.4% of applied radioactivity. The TLC analyses showed that major degradates were more polar than diuron, none of which were >10% of applied and were not identified. Recoveries ranged from 86.7 to 100.2% of applied radioactivity.

Study 3 – calculated half lives

The photolysis of diuron under natural sunlight was calculated from the quantum yield and measured UV absorption spectrum of diuron over the 290-400 nm range in 5 nm steps and from 400 in 10 nm steps according to ECETOC procedures (Hellpointner, 1991). These stepwise quantum yields were then used in either the GC-SOLAR program (US EPA) or by the published method of Frank and Klöpffer (1985, not sighted by DEWHA). The results of these calculations are given in Table A1.2.

Table A1.2. Half-life of diuron calculated for photolysis under environmental conditions.

Season	Half-life period, days		
	GC-SOLAR		
Latitude	30°N	40°N	50°N
Spring	2.5	2.9	3.5
Summer	2.2	2.3	2.5
Fall	3.7	5.1	8.3
Winter	5.4	9.2	20.4
	Frank and Klöpffer*		
Month	minimal	mean	maximal
April	2.8	5.1	21
June	2.5	3.7	12
October	7.7	15	67
December	23	48	220

*In central Europe, 50°N

1.3 Soil photolysis

The photo-degradation of diuron on soil, uniformly ^{14}C-labelled in the phenyl ring, was studied according to the US EPA Guideline 161-3 using a silt loam soil (Stevenson, 1990a). The soil used is the same as was used for the aerobic and anaerobic metabolism studies.

Soil plates were prepared using water to give 1 mm deep soil and was dried slowly over 6 days before being dosed at 9.7 kg ac/ha (8.69 lb/A) and then irradiated with a xenon lamp (which has similar spectral energy distribution and an intensity of 76% of natural sunlight) for 30 days with a 12 hour on/off cycle per day. Soil temperature was maintained at 25°C. Gas traps were used to trap possible volatiles. Samples were taken throughout the photolysis period and analysed by LSC and TLC.

The study material balance was good and the mean recovery was 106.2% of AR.

Degradation in light exposed samples was relatively slow with 89.8% of the applied diuron recovered after 30 days of irradiation. N'-(3,4-dichlorophenyl)-N-methyl urea (DCPMU) was the main degradate noted by TLC reaching 3.6% of applied. There was no appreciable degradation in the dark samples and these samples were not analysed further. There were no volatiles trapped in the gas traps. The half-life of diuron was 173 days using first order kinetics.

The study clearly indicates that soil photolysis is very slow and unlikely to be a significant contribution to environmental degradation of diuron.

2. METABOLISM

2.1 Aerobic soil metabolism

Study 1 – US EPA guidelines

The metabolism of diuron (^{14}C labelled in the phenyl ring) was studied in an agricultural soil according to US EPA Guideline 162-1 (Hawkins *et al*, 1990). The soil used, a silt loam (Keyport soil) from Newark, Delaware, was treated with diuron at 19.5 mg/g soil (dry weight basis), with sufficient water added to give 75% of 0.33 bar before being aerobically incubated for 12 months in the dark at 25°C. The soil used was microbially active and remained so during the incubation with bacteria, bacterial spores, fungi and actinomycetes showing acceptable counts (colony forming units) on days 0, 180 and 365. In addition, sterile samples were prepared by autoclaving the soil and preparing the soil as before under sterile conditions and using sterile water. Each sterile soil received the radiolabelled diuron at 20.3 mg/g soil (dry weight). The sterile soil remained sterile throughout the study. Table A1.3 gives the characteristics of the soil.

Table A1.3. Soil characteristics of soils used to determine the half-life of diuron.

Soil origin	Soil texture	sand	silt	clay	om	pH
Newark, Delaware	Silt loam	22	59	19	3.7	4.6
Keyport soil (anaerobic)	Silt loam	14.0	59.2	26.8	1.3	6.6
Uppsala, Sweden	Loamy sand	84.21	5.71	10.11	1.36*	7.3
Falkenberg, Sweden	Sand	90.91	7.81	2.11	1.64*	5.8
Mogenstrupvej, Denmark	Sandy loam	58.21	24.11	17.71	2.24*	6.0
Speyer 2.1, Germany	Sand	88.41	9.81	1.91	1.08*	5.9

1) From European data: sand =63-2000 mm; silt 2-63 mm clay <2 mm. * organic matter = 1.74 X organic carbon

At the end of the incubation period, extracted radioactivity accounted for 81.0% of the radioactivity applied to non-sterile soil with 14.9% remaining in the soils and 3.36% as CO_2 (determined by precipitation with barium chloride). Total recoveries ranged 99.1 to 103.3% of AR. Results are in Table A1.4.

Table A1.4. Recoveries of radioactivity to various fractions as total of applied from Newark silt loam soil.

	Days after treatment (DAT)									
Fraction	0	7	14	30	60	120	180	240	300	365
Parent	97.8	94.0	95.0	86.4	82.9	70.1	63.4	59.5	55.0	49.0
DCPMU[1]	-	1.7	1.9	4.7	8.2	13.6	16.9	17.7	17.5	22.2
DCPU[2]	-	0.3	0.4	0.8	0.6	0.5	0.6	0.7	0.7	0.7
CO_2		0.02	0.02	0.14	0.48	1.39	1.96	2.34	2.9	3.36
bound	0.2	5.0	4.7	5.7	7.8	9.5	11.4	11.6	14.2	14.9
Remainder[3]	0.22	0.9	1.5	4.8	3.0	5.0	4.6	6.1	6.2	7.1
Total Recovered	103.3	101.9	103.6	102.6	103.0	101.7	100.7	100.0	99.1	99.3

1) DCPMU = N'-(3,4-dichlorophenyl)-N-methyl urea; 2) DCPU = N'-(3,4-dichlorophenyl) urea; 3) Remainder of radioactivity on TLC plate.

The analysis of the extracted radioactivity was performed by TLC with some samples analysed by HPLC (0, 30, 120, 240 and 365 days) to identify other potential metabolites. Besides the parent, only two metabolites, DCPMU and DCPU were identified.

For the sterile soil, at the end of the incubation period extractable radioactivity accounted for 90.3% of the radioactivity applied with 6% remaining in the soils and no detectable evolution of CO_2. Diuron was recovered after 365 days as 81.1% of applied.

The half-life for the non-sterile soils was determined by first order kinetics as 372 days (r^2 = 0.976). The strong correlation suggests that the degradation is at least pseudo-first order. The half-life for sterile soil was given as 1920 days (r^2 = 0.950). The much longer half-life for sterile soil suggested that microbiological activity is important for degradation.

Study 2 – Danish guidelines

The degradation behaviour of ^{14}C-labelled diuron, uniformly labelled in the phenyl ring, was studied in three soils from Europe (a loamy sand (Nantuna), a sand (Langaveka); and a sandy loam (Mogenstrupvej)) with the sandy loam used under differing temperature and moisture regimes (Mackie and Hall, 1994). The study was conducted to Danish data requirements. The characteristics of the three soils are given in Table A1.3. (The Swedish soils from Nantuna and Langaveka were also used for the first lysimeter study.) The soils were dosed with the diuron at 3.52 mg/kg soil (dry) which corresponds to a field application rate of 2.5 kg ac/ha evenly penetrated to 5 cm deep.

Soil samples were incubated in the dark for 100 days at constant temperature at 20°C and 70% of maximum water holding capacity (MWHC), with the sandy loam also at 10°C or 35% MWHC as shown in Table A1.5. The soil was analysed at various times by TLC analysis and the final sample on termination at 100 days was also analysed by HPLC, which confirmed the TLC analysis. The degradation half-lives were derived using first order analysis and the strong correlation suggests that the degradation is first order.

Table A1.5. Degradation rates of diuron (first order analysis) under standard condition and different moisture and temperature regimes.

Soil and incubation condition	Half-life, days	DT90, days	r^2	DCPMU Max % of AR	Bound residues (% of AR)
Loamy sand, 70% MWHC, 20°C	20	65	0.986	28	36
Sand, 70% MWHC, 20°C	119	395	0.984	27	14
Sandy loam, 70% MWHC, 20°C	51	168	0.996	33	27

Sandy loam 70% MWHC, 10°C	143	475	0.997	23	12
Sandy loam 35% MWHC, 20°C	27	90	0.993	33	44

The mass balance of the experiments ranged from 91% to 100%. There was a small amount of CO_2 evolution on the loamy sand and sandy loam (35% MWHC) of 5 and 7% after 100 days respectively. The levels of volatiles were not reported for the other experiments, as these were not needed to establish a satisfactory mass balance. The TLC analysis identified 3 metabolites by comparison with authentic samples: DCPMU, DCPU and DCA. The two systems with the fastest degradation, loamy sand and sandy loam (dry), showed the metabolite DCPMU increasing to a maximum then decreasing with DCPU also increasing, to reach 25 and 11% of AR for loamy sand and sandy loam (dry) respectively, then decreasing. The other 3 systems, with longer half-lives, had low levels of DCPU (<5% of AR) after 100 days with DCPMU at a maximum on termination of the study (see Attachment A for chemical structures).

The results of the study showed diuron to be fairly to slightly degradable with half-lives under 'standard conditions' (20°C, 70% MWHC) of between 20-119 days. Reducing the temperature to 10°C increased the half-life to 143 days from 51 days, as would be expected, but interestingly reducing the moisture to 35% of MWHC reduced the half-life to just 27 days.

In a supplemental study (Bramble and Norwood, 1994), the bound residues from the final samples for all soils (amounts given in Table A.1.5) and all the sandy loam soil (35% MWHC) samples were further extracted under forcing conditions (1 N HCl with surfactant). This resulted in recovery of extra extractable radioactivity, amounting to 8.0-22.1% of AR for final samples and 1.3-22.1% of AR for the dry sandy loam. Analysis by HPLC showed that this comprised mainly diuron (1.1-5.98% of AR), DCPMU (1.2-21.6% of AR) and DCPU (0.2-10.82% of AR). Using the new data for diuron and combining with the original data for sandy loam (dry) the new half-life was 29 days compared to 27 days previously. DEWHA has recalculated the half-life for the sandy loam 'standard conditions' (20°C, 70% MWHC) adding in the extra residue for the forcing extraction and it reduced the fit (r^2 from 0.996 to 0.9578), but only slightly increased the half-life to 58 days from 51 days.

It is concluded that the half-lives of diuron in 3 European soils range from 20 to 119 days under 'standard conditions' (20°C, 70% MWHC) and slows down with colder conditions. There was an increase in the rate of degradation in the dryer conditions (35% MWHC).

Study 3 – EEC guidelines

The degradation behaviour of ^{14}C-labelled diuron, uniformly labelled in the phenyl ring, was studied in a German soil in accordance with EEC Guidelines (de Vries, 1996). The characteristics of the Speyer 2.1 soil are given in Table A1.3. The soil was pre-incubated for 22 days under aerobic conditions before being dosed with the ^{14}C-diuron at 8 mg/g dry soil corresponding to a field application rate of 8.0 kg ac/ha evenly distributed to 7.5 cm deep.

Soil samples were incubated in the dark with positive flow of CO_2 free air for 101 days at constant temperature at 20°C and at field capacity (pF2.5[1] approximately field moisture capacity). The soil was analysed at various times by TLC analysis. The degradation half-life was derived using the Timme model (Timme *et al*, 1986).

[1] unit formerly used in agricultural science to measure "soil suction" or soil moisture tension. Soil moisture tension is the pressure that must be applied to the moisture in the soil to bring it to hydraulic equilibrium with an external pool of water. This was measured in pF units as the logarithm of the pressure in centimetres of water. Currently measurements are usually made directly in kilopascals (kPa).

The mass balance of the experiments ranged from 90.7% to 99.8%. There was a small amount of CO_2 evolved till day 54 (2.1% of AR) after which the evolution increased and reached 31% by termination of the test. The TLC analysis identified 2 metabolites by comparison with authentic samples: DCPMU and DCPU. The metabolite DCPMU increased to a maximum of 19.1% of AR by day 54 then decreased. DCPU reached 1.6% of AR by day 84 and then decreased. The microbial biomass (determined from glucose metabolism) was 83 mg/100 g soil (dry weight) at the start and decreased slightly to be 67 mg/100 g soil dw after the experiment.

The results of the study showed diuron to be slightly degradable with half-life of 186 days (square root time, 1.5 order kinetic best fit). In a short supplementary study (Schäfer, 1998), this half-life was recalculated using a 2-step system with both first order reactions (from diuron to DCPMU then to DCPU). The resulting equations were solved numerically to give half-lives of 112 and 35 days for diuron and DCPMU respectively. The fit of this 2-compartment model explained 94% of the variance.

Metabolite aerobic soil metabolism data

DuPont have provided two additional aerobic soil metabolism studies considering the metabolites mCPDMU and DCPMU. The following assessment of these studies is provided.

Title	Rate of Degradation of IN-12894 (mCPDMU) in Two Aerobic Soils
Authors	Sarff, P
Date	2007a
APVMA Data ID	9017
Test Guideline	OECD Test Guideline 307; US EPA Guideline 162-1
Data Validity	1 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

The degradation kinetics of [^{14}C]-mCPDMU, a metabolite of diuron, was investigated in two soils under laboratory aerobic conditions.

The test systems consisted of 50 g dw soil, with the test concentration of 1.02 mg/kg. The test material was applied in acetonitrile by syringe to the soil surface. A total of 22 treatments consisting of duplicate samples for each set of conditions were maintained. Air was pulled through a 5 N KOH scrubber and water hydrator, into the series of test vessels, then air exiting was passed through a series of trapping solutions. An ethylene glycol trap and two KOH traps were used to collect $^{14}CO_2$ and other organic volatiles. The test was run at ~20^{0}C in darkness. The two test soils had the following characteristics:

Soil	Classification	%Sand	%Silt	%Clay	%OC	pH	% moisture*	CEC**
Sassafras	Sandy loam	77	15	8	1.2	5.9	12.3	5.3
Tama	Light Clay	29	40	31	1.9	6.4	31.9	17.4

* @ 1/3 bar; ** meq/100 g.

Sampling intervals, including volatile traps were days 0, 7, 14, 28, 46, 61, 90 and 120 post application. Radioactivity was determined by LSC. HPLC was the primary method to characterise radioactivity soil extracts.

Findings

The following table shows the mass balance findings (% AR) during the course of the study.

Table A1.6: Material Balance of Radioactivity for Sassafras and Tama Soils Treated with ^{14}C-mCPDMU

Soil		Days after treatment							
		0	7	14	28	46	61	90	120
Sassafras	Soil Extracts	97.3	92.1	92.9	81.5	75.2	76.4	74.2	64.1
	Bound residues	1.2	2	6.6	8.8	13	13.7	16.5	21.1
	CO_2	-	0.5	1.1	2.2	2.2	2.2	4.5	4.6
	Mass Balance	**98.5**	**94.6**	**100.6**	**92.5**	**90.4**	**92.4**	**95.2**	**89.8**
Tama	Soil Extracts	95.3	93.2	94	86.6	83.6	86.3	83.2	78.2
	Bound residues	3.2	2.4	4	4.5	8.5	6.7	10.2	11.8
	CO_2	-	0.2	0.5	1	1.4	1.4	2.1	2.1
	Mass Balance	**98.5**	**95.8**	**98.5**	**92.1**	**93.5**	**94.5**	**95.5**	**92.1**

Mass balances were generally good throughout the study. No volatiles were found other than $^{14}CO_2$ in either soil. In both soils, loss of radioactivity from soil extracts to either bound residues or $^{14}CO_2$ was relatively slow, with around 10 to 20% AR found as bound residues at the end of the study, and around 2 to 4.6% AR found as CO_2.

The following table shows the breakdown pattern of mCPDMU in the test system. No other individual compound exceeded 10% AR.

Table A1.7: Rate of Degradation of mCPDMU in Sassafras and Tama Soils under Aerobic Conditions

Days after treatment	% mCPDMU Sassafras	% mCPDMU Tama
0	93.6	93.7
7	90.7	87.9
14	91.8	91.4
28	79.7	85.7
46	71.6	82.3
61	75.4	85.2
90	71.8	82.4
120	61.5	78.2

Conclusion

Using first order kinetics, the study authors calculated a DT50 in the Sassafras soil to be 205 days (r^2 = 0.83) and in the Tama soil to be 546 days (r^2 = 0.77); both soil half-lives are well in excess of the study duration. DEWHA agrees with the half-life calculations. While the values need to be viewed with caution due to the extrapolation, this metabolite is clearly persistent.

Title	Aerobic Soil Degradation of 3,4-Dichlorophenyl methylurea (DCPMU)
Authors	Hennecke, D
Date	2005
APVMA Data ID	9005
Test Guideline	OECD Test Guideline 307;
Data Validity	2 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

The degradation kinetics of DCPMU, a metabolite of diuron, was investigated in three soils under laboratory aerobic conditions.

The test systems consisted of 50 g dw soil, with a nominal test concentration of 0.8 mg/kg. The test material was applied in acetonitrile by syringe to the soil surface. Since only disappearance of the test item was investigated, no trapping of volatiles was performed. The test was run at ~20^{0}C in darkness. The three test soils had the following characteristics:

Soil	%Sand	%Silt	%Clay	%OC	WHC*	pH	CEC**
Wurmwiese	45.36	40.96	13.68	1.5	553	5.81	76
Höfchen	6.84	75.01	18.15	2.41	685	6.72	164
Laacherhof	67.36	24.70	7.95	2.29	561	6.76	92

* Maximum water holding capacity, mL/kg; ** mmol/kg.

Duplicate samples were taken for analysis at intervals of 0, 1, 3, 7, 14, 28, 50, 80 and 120 days after treatment. In addition, duplicate sterilised samples were sampled after 28 and 120 days for each soil. HPLC was the primary method to characterise radioactivity in the soil extracts.

Findings

The purpose of the study was to only consider disappearance, so no mass balance was performed.

The following table shows the breakdown pattern of DCPMU in the test system.

Table A1.8: %DCPMU in Three Soils under Aerobic Conditions

Days after treatment	Wurmwiese	Höfchen	Laacherhof
0	77.1	71.1	80.1
1	66.6	71.3	73.1
3	66.9	68.7	69.8
7	55.7	52.3	57
14	52.3	52.2	45
28	45.6	45.2	43.1
50	38.9	44	35.4
80	36.5	37.5	41.7
120	34.9	33.1	35.7
28 d sterilised	72.6	72.9	75.3
120 d sterilised	41.0	45.0	44.8

Neither DCPU nor DCA could be detected at any sampling within this study. While the 28 day sterilised results show very little degradation (<5%) over the first 4 weeks compared to biologically active soils, by the end of the experiment, there was significant loss of parent material (26-36%) in the sterilised soils.

Conclusion

Based on the obtained data sets, degradation kinetics were calculated by the study authors using two different kinetic models, single first order (SFO) and first order multi-compartment (FOMC). The FOMC model provided the best fit of the data, and the following DT50 values were calculated:

Soil	DT50 (days)	r^2
Wurmwiese	73	0.98
Höfchen	89	0.96
Laacherhof	40	0.92

Literature

The degradation of 14 radiolabelled pesticides (diuron was ^{14}C-labelled in carbonyl position) was studied in Matapeake silt loam soil amended with either sewage sludge (60% primary/40% secondary) or dairy manure (Doyle, Kaufman and Burt, 1978). The manure and sludge were applied to the soil at rates of 0, 50 and 100 tonnes/ha, then the soil leached to remove excess soluble salts and incubated (30°C) for two weeks prior to application of the pesticides. The evolution of CO_2 was stimulated in the manure treatments (15-16% of AR) but slightly inhibited in sludge treatments (1.4% of AR) compared to controls (3.6% of AR). There was also a difference in the distribution of ^{14}C-degradation products. In the manure treatments both dealkylated products (DCPMU and DCPU) were seen, but for sludge and controls only parent and the monodealkylated degradate (DCPMU) were observed.

2.2 Aerobic aquatic metabolism

Study 1 – EC/SETAC guidelines

The aerobic aquatic metabolism of diuron (^{14}C-labelled phenyl ring) was conducted according to EC Directive 95/36 and SETAC-Europe Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides using two sediment-water systems (Sneikus, 2001). Water and sediment were collected from two locations in the Germany; River Erft, a river flowing into the Rhine where diuron and DCA have been detected in the past and the micro-organisms able to metabolise diuron, and Hönniger Weiher, an artificial pond formed by the damming of the Honniger Creek; the characteristics of the water and sediments are given in Table A1.9.

Table A1.9. Characteristics of the sediments and water used (German classifications and soil textures).

	Water pH	Sediment pH (CaCl2)	Sediment Texture	Sand (%)	Silt (%)	Clay (%)	% om
River Erft	7.5	7.0	Silty loam	11.9	63.4	24.7	9.8
Hönniger Weiher	6.5	5.9	Sandy loamy silt	24.4	62.3	13.3	7.6

Each system consisted of water (4.5 cm deep) and sediment (1.5 cm deep) and the ratio of water to sediment was about 3:1. Test systems were pre-incubated for around 14 days for equilibrium to be established during which the pH and oxygen concentration of the water and redox potential of the sediment were monitored. The labelled diuron was applied to the water surface at 4 kg ac/ha, the maximum German

rate to give each test system a concentration of approximately 7 mg/L in water, based on total amount of water in the test systems. The systems were incubated aerobically at 20°C in the dark for 120 days. Duplicate samples of each water/sediment type were taken for analysis at various times and analysed by LSC, and TLC with selected water and sediments further analysed by HPLC. Gas traps were used to trap volatile organics and CO_2. Dissolved CO_2 in the water was measured by acidification and trapping evolved gasses.

During the incubation the waters remained essentially aerobic (according to Tebbutt, 1992[2]) with dissolved oxygen ranging from 41-94% of saturation and redox of 220-266 mV. The Erft sediment was mainly aerobic with redox measurements of 188-218 mV but for 2 samples, day 7 and 14, the measurements were anaerobic (-162 to –212 mV; reducing conditions according to Tebbutt). For the Hönniger sediment these were essentially anaerobic for first 28 days with redox potential of –38 to –183 mV (reducing conditions), then aerobic for the day 91 and 120 samples (205-219 mV) with the intervening sample (day 55) having one replicate anaerobic (-94 mV) and the other more aerobic (+138 mV). The report notes the changes in the redox potential and comments that it may be caused by the lack of oxygen in the unmoved lower sediment layer, similar to that reported in the environment, with the sediment/water boundary being aerobic.

The applied radioactivity moved from the water into the sediment as indicated in Table A1.10 for Erft River and Table A1.11 for Hönniger Weiher. Almost all radioactivity in the water and radioactivity extractable from the sediment was diuron. There were relatively few metabolites formed that were detected and/or identified with sediment bound products the main degradate. DCPMU was identified in the sediments of both systems. Carbon dioxide was significant for the Erft river but not in the Hönniger system and the Erft system degraded diuron more rapidly than the Hönniger system. The dechlorinated metabolite m-CPDMU, 3-(3-chlorophenyl)-1,1-dimethyl urea) was the major metabolite found the in the Hönniger stystem, both in the aquatic phase and in sediment but was not detected in the Erft system. This could indicate two metobolic pathways for degradation of diuron.

Table A1.10. Recovered radioactivity for River Erft in water and sediment as a percentage of applied radioactivity identified metabolites. Average of duplicate samples

Time days	Total CO2	Water		Sediment			
		Diuron	Other*	diuron	bound	DCPMU	Other*
0	-	90.3	0.3	8.2	0.9	nd	0.3
7	0.17	43.2	0.3	50.9	4.21	nd	0.2
14	0.68	29.9	1.8	57.9	10.04	0.4	0.4
28	0.68	17.3	0.4	73.5	10.11	0.9	0.6
55	4.34	3.3	2.5	47.3	33.83	2.2	1.3
91	23.3	0.2	0.5	18.8	44.24	4.4	1.1
120	29.7	nd	0.6	10.2	45.92	3.5	1.9

* Other includes minor and unidentified metabolites, as well as radioactivity at TLC origin.

Table A1.11. Recovered radioactivity for Hönniger Weiher in water and sediment as a percentage of applied radioactivity identified metabolites. Results are the average of duplicate samples.

[2] Tebbutt (1992) defines aerobic (oxidising) conditions as >200 mV with anaerobic (reducing) conditions as <50 mV. Another reference (Wolfe, Mingelgrin and Miller, 1990) gives the range 200 to 400 mV as moderately oxidising and 200 to –50 mV as moderately reducing (moderately anaerobic) and also notes that the boundaries between various redox states are arbitrary.

Time days	Total CO2	Water			Sediment				
		diuron	m-CPDMU	Other*	diuron	bound	m-CPDMU	DCPMU	Other*
0	-	92.0	nd	0.1	9.7	1.19	nd	nd	nd
7	0.14	38.0	nd		57.5	5.04	nd	nd	nd
14	0.61	28.1	0.1	1.7	60.1	8.00	nd	0.3	1.8
28	1.33	23.0	1.5	1.4	57.7	9.87	5.0	1.1	0.4
55	1.56	14.5	6.7	0.7	50.7	14.66	8.5	1.3	1.4
91	1.56	13.5	0.6	0.6	64.0	14.7	1.4	2.1	nd
120	2.05	10.3	2.3	0.9	60.2	17.48	3.1	3.7	1.6

*Other includes minor and unidentified metabolites, as well as radioactivity at TLC origin.

DEWHA has calculated half-lives based on the equation DT50 = -ln(2)/*k*. The results are shown in Table A1.12.

Table A1.12. Half lives of dissipation of diuron in 2 sediment/water systems (Calculated by DEWHA).

System	DT50 days	r2
Erft River (water only)	10.8	0.99
Erft River (total system)	35	0.96
Hönniger Weiher (water only)	5.5; 67	1; 0.96
Hönniger Weiher (total system)	277	0.83

In the Erft River system, diuron moved from water to sediment with a half-life around 11 days. Sediment concentrations of diuron increased steadily until day 28 and then declined. Bound residues steadily increased throughout the study. It is possible a considerable amount of the bound residues remained as unchanged diuron or DCPMU as found with a more thorough extraction of soils described by Bramble and Norwood (1994) above. In terms of total residues, dissipation from the whole system was much slower and from day 28 until the end of the study, the half-life for total residues was 111 days (r^2 0.99).

In the Hönniger Weiher system, there was a relatively fast initial movement of diuron from water to sediment during the first seven days. However, from then, diuron was quite persistent in the water column. The first half-life of diuron was 5.5 days. From day 7 until the end of the study, the half-life in the water column was considerably longer at 67 days. In terms of total diuron residues in the whole system, dissipation was slow with a half-life of 277 days (r^2 0.83 ignoring the day 55 data where less diuron was detected, but an increased amount of m-CPDMU). However, the dissipation of these extractable diuron residues did seem somewhat biphasic and a first phase half-life (day 0 to day 28 data) of 83.5 days (r^2 0.98) was calculated with a second phase half-life of 533 days (r^2 = 0.82). Bound residues and $^{14}CO_2$ were at much lower levels than in the Erft River system. If bound residues are considered to be largely unaltered diuron or one of the main metabolites, the dissipation half-life for total residues from the whole system is well over 4 years (>1700 days).

DEWHA concludes that the report shows that diuron moves to the sediment but significant amounts remain in the aqueous phase. It is degraded via two possible pathways, one involves demethylation and is associated with aerobic conditions while the other is probably slower and proceeds via dechlorination of the phenyl ring. However, it is noted there is rapid degradation via dechlorination in the anaerobic aquatic metabolism study below.

Study 2 – US EPA guidelines

The aerobic aquatic metabolism of ^{14}C-diuron (labelled in the phenyl ring) was studied under aerobic conditions using a clay loam sediment in accordance with the EPA Guideline 162-4 (Hausmann and Kraut, 1992). The sediment and water used were collected from an irrigation cannel. The sediment was classified as a clay loam (sand 34.8%; silt 29.6%; clay 35.6%; pH 7.4; om 3.6%) and the pH of the water was 7.8-7.9.

The microbially viable sediment was flooded with the water at a 2:1 ratio of water to sediment. The test system was pre-incubated for 3 days to allow an equilibrium to be established during which the redox potential of the sediment indicated aerobic/anaerobic conditions (84 mV). The redox of the water or sediment was not measured again - a weakness of the study as it is not known if aerobic conditions were maintained. The labelled diuron was applied to the water surface at 1.67 mg ac/kg of total system (water + sediment), given as approximately equivalent to 12.3 kg ac/ha (11 lb/acre) and then incubated in a dark at 25°C for 30 days. Volatiles were trapped. Samples were collected for analysis throughout the study and analysed by HPLC with metabolites confirmed by TLC.

Recovery of applied radioactivity averaged 97% and ranged from 88 to 106% throughout the study. The majority of the applied radioactivity (73% of AR) was recovered from the sediment with just 22% in the water after 30 days. As before, diuron partitioned to the sediment (40% of AR after 30 days) but significant amounts remained in the water phase (8.3% of applied after 30 days).

Diuron degraded under the study conditions with a degradation half-life of 33 days for the whole system using first order kinetics (r^2 = 0.97). There were 2 main metabolites, m-CPDMU that reached 25% of AR after 30 days and DCPMU that reached 9.2% of AR after 22 days. Non-extractable radioactivity reached 7.2% after 30 days. Small amounts of carbon dioxide were evolved during the study, a maximum of 0.7% of AR after 30 days and no other volatiles were recovered.

The degradation pathway proposed is the same at for the previous aerobic aquatic metabolism study and involves two pathways, one via demethylation while the other proceeds via dechlorination of the phenyl ring. In a supplemental report (Hausmann, 1997a), it is noted by the author that the reductive dechlorination, which leads to the formation of m-CPDMU, is fast and explains the relatively short half-lives of diuron in the aquatic metabolism studies compared to that in the aerobic and anaerobic soil studies. (The supplemental report was a response to a request from the US EPA to explain the short half lives in the aerobic and anaerobic aquatic metabolisms studies compared to the results from the aerobic and anaerobic soil studies.) The presence of this metabolite suggests conditions were at least partly anaerobic.

Metabolite aerobic aquatic metabolism data

DuPont have provided one additional aerobic aquatic metabolism study considering the metabolite mCPDMU. The following assessment of this study is provided.

Title	Rate of Degradation of IN-12894 (mCPDMU) in Two Aerobic Aquatic Sediment Systems
Authors	Sarff, P
Date	2007b
APVMA Data ID	9016
Test Guideline	OECD Test Guideline 308; US EPA Guideline 162-4
Data Validity	2 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

The degradation kinetics of [^{14}C]-mCPDMU, a metabolite of diuron, was investigated in two water/sediment systems for up to 100 days under aerobic conditions.

Water and sediment were sieved (2-mm) with the test systems consisting of 40 g dw sediment and 160 mL water. The test material was added at 1.0 mg/L in acetonitrile. A total of 22 treatments (2 replicates per time point), 2 control replicates and 9 biomass sample replicates were maintained. Air was pulled through a 5 N KOH scrubber and water hydrator, into the series of test vessels, then air exiting was passed through a series of trapping solutions. An ethylene glycol trap and two KOH traps were used to collect $^{14}CO_2$ and other organic volatiles. The test was run at ~20^{0}C in darkness. The test sediments had the following characteristics:

Soil	Classification	%Sand	%Silt	%Clay	%OC	% moisture*	CEC**
Goose River	Sandy clay loam	63	16	21	1.2	30.1	15.9
Golden Lake	Sandy Loam	79	14	7	1.7	18.1	11.1

* @ 1/3 bar; ** meq/100g.

The Goose River water had an initial pH of 8.3 and a hardness of 638 mg/L $CaCO_3$, while the Golden Lake water had an initial pH of 8.4 and a hardness of 655 mg/L $CaCO_3$.

Sampling intervals, including volatile traps and measurement of pH and redox potential (water and sediment) and dissolved oxygen (water), were days 0, 7, 15, 29, 44, 61, 76 and 100 post application. Radioactivity was determined by LSC. HPLC was the primary method to characterise radioactivity in the water layers and sediment extracts.

Findings

OECD TG 308 states the aerobic test system, as described by the guideline, consists of an aerobic water layer (typical oxygen concentrations range from 7 to 10 mg/L), and a sediment layer, aerobic at the surface and anaerobic below the surface. In this study, the redox potential of the sediment was not reported. However, the redox potential of the water layer was provided, and mean replicate values were reported as follows:

The following table provides mean water redox potentials found in the test systems during the study:

Table A1.13: Mean Replicate Redox Potential of Test Water (mV) During the Study Period

		Days after treatment							
		0	7	15	29	44	61	76	100
Goose River	Test	100	-239	-188	-66	51	14.9	-171	-27
	Control	118	-233	-151	-158	-15	-37	-115	-241
Golden Lake	Test	161	-207	-31	-152	50	29	-144	-39
	Control	163	-152	-89	-148	-18	-42	-145	-245

The test guideline states that (for an anaerobic test system), the sediment and water are regarded as anaerobic once the redox potential is below -100 E_h (1 mV = 1 E_h). In this sense, it is important that the reference electrode is identified, and this is not found in the test report. It appears that the equipment used for measuring redox potential (Accumet Model AR50) could use either a calomel electrode, or a Ag/AgCl electrode. If these have been used to determine mV, then they need to be converted to E_h to give the reading of a standard hydrogen electrode (adding +197 to +241 mV depending on the reference electrode).

It is unclear whether such a transformation has been made in the reported data. If not, the conditions were clearly aerobic throughout the study. However, if this conversion was done, then the water redox potentials clearly indicate conditions were reducing through much of the study. Further, dissolved oxygen concentrations were typically below 5 mg/L in both test systems, further suggesting conditions were not truly aerobic during the study period.

In the Goose River system, mass balance measurements showed recovery of radioactivity ranging from 93.3% AR at 100 days after application to 97.3% AR at 61 days after application. Of this, 92.7% AR was found in the water at day 0, and this had been reduced to 23.6% AR after 100 days. Conversely, the amount of extractable radioactivity in the sediment increased from 3.8% AR at day 0 to 59.8% AR after 100 days. Bound residues accounted for 9.3% AR after 100 days, no organic volatiles were detected with the exception of 0.6% $^{14}CO_2$ after 100 days.

In the Golden Lake system, mass balance measurements showed recovery of radioactivity ranging from 93.0% AR at 76 days after application to 97.5% AR at 0 days after application. Of this, 92.0% AR was found in the water at day 0, and this had been reduced to 30.6% AR after 100 days. Conversely, the amount of extractable radioactivity in the sediment increased from 5.4% AR at day 0 to 36.3% AR after 100 days. Bound residues accounted for 25.4% AR after 100 days, no organic volatiles were detected with the exception of 1.7% $^{14}CO_2$ after 100 days.

The following table shows the breakdown pattern of mCPDMU in the two test systems. No other individual compound exceeded 10% AR, although the high levels of bound residues in the Golden Lake system was not able to be characterised.

Table A1.14: Rate of Degradation of mCPDMU in Two Aerobic Sediment/Water Systems

Days after treatment	% mCPDMU			
	Goose River		Golden Lake	
	Water	Total	Water	Total
0	91.5	95.3	90.0	95.4
7	55.8	94.1	72.3	92.3
15	55.3	102.8	70.8	99.9
29	38	88.3	52.4	87.6
44	32.8	89.1	51.0	85.4
61	32.7	90.9	51.8	86.0
76	29.2	88.4	39.9	73.3
100	22.1	79.6	29.2	61.9

It is not possible to estimate a half-life of mCPDMU in the sediment. In the Goose River system, mean sediment residues of this metabolite peaked at 59.3% AR 75 days after treatment and were still found at 57.7% AR after 100 days. In the Golden Lake system, mean sediment residues peaked at 34.4% after day 29 and were still found at 32.7% AR after 100 days. These values suggest the metabolite is persistent in sediment.

Conclusion

Using first order kinetics, the study authors calculated half-lives in water of 44 days (r^2 = 0.82) for the Goose River system, and 69 days (r^2 = 0.91) for the Golden Lake system. Whole system half lives were calculated as 415 and 183 days respectively. The shorter whole system half-life in the Golden Lake system is possibly due to the much higher levels of bound residues in the sediment.

Literature

Knauert *et al* (2008) describe outdoor mesocosm studies undertaken to evaluate effects of mixtures of similar acticng compounds on the photosynthetic activity of phytoplankton. Three PSII inhibitors, atrazine, isoproturon and diuron, and an equitoxic mixture of all three were applied for a constant exposure period of 5 weeks. In a subsequent post exposure period of five months, the dissipation of the herbicides was quantified and considered in relation to the photosynthetic activity of the phytoplankton community. Based on triplicate results, the dissipation of diuron during the post exposure period (that is, from day 34 until day 173, although really, this is from day 20 as that is when the last application of diuron occurred) is described as following first order kinetics. The half-life was calculated to be 43 days in the water column (r^2 = 0.97). At the end of the experiment, diuron concentrations in the water (actual results were expressed as “toxic units”, not as a concentration) appeared to still be around 10% of the initial levels. These results again show the potential persistence of diuron in a water body.

A literature report of the degradation of diuron under aerobic conditions using sediment and water from a natural pond (first in spring, then in summer) that had been pre-treated with diuron at 1.6 kg/year (number of years not given) was presented (Ellis and Camper, 1982). The media were prepared (2 media conditions were used - mineral salts and mineral salts plus additional carbon source [glycol 0.05% v/v]) before being dosed with diuron (10 mg/L), inoculated with sediment, pond water or sediment + pond water then incubated at 30°C for 10 weeks. These conditions do not conform to the current testing guidelines.

There was extensive degradation (>50%) of diuron from the first series (spring) in 4 experimental cultures (from 60), with 3,4-dichloroaniline as the major product and DCPMU and DCPU as minor products. In the remaining cultures demethylation occurred in 52 cultures and there was no degradation in 4 cultures. The summer samples showed less degradation (34% of incubation flasks showed no degradation) with none degrading diuron to dichloroaniline. The paper states that there was less biological activity in the summer samples compared to the spring samples (104 colony forming units cf 107). No half-lives were determined. This report clearly shows that diuron can be degraded in aerobic conditions using pre-conditioned sediments. DEWHA notes that there was no mass balance, the extraction technique used may not recover bound sediment (only single ethylacetate extraction) and the pre-conditioning does not conform to current guidelines.

2.3 Anaerobic soil metabolism

An anaerobic soil degradation study of ^{14}C-labelled diuron was performed according to US EPA Guideline N-162-1 (Yu, 1988).

A Keyport silt loam soil (details given in Table A1.3) was dosed with radiolabelled diuron, labelled as previously, at a nominal concentration of 8.27 mg/kg of soil (dry), then the soil moisture adjusted to 75% of field capacity. The dosing of diuron was to achieve a field rate of 11.4 kg ac/ha (10 lb/acre). The soil was determined to be microbially active at the start and throughout the incubation. The dosed soil was incubated under aerobic conditions (stream of air) in the dark at 25˚C for 30 days and then the conditions were changed to anaerobic by purging with nitrogen and incubation was continued for 60 days under a stream of nitrogen. There was no test conducted/reported to show that the soil was anaerobic. Volatiles were collected (ethylene glycol and KOH solutions). Samples were extracted and analysed by HPLC and TLC. After the methanol/water (9/1) and methanol extractions, the soil was further extracted with refluxing methanol for 24 hours (Soxhlet) then with acetone/water/phosphoric acid (85/13/2) to extract additional residues. Table A1.15 gives the results.

Table A1.15. Recoveries (%AR) to various fractions as total of applied from Keyport silt loam soil.

Fraction	Time of sample, Days after treatment (DAT)						
	0	15	30*	45	60	75	90

Diuron	92.4	95.6	87.0	92.2	94.8	89.7	90.7
DCPMU	7.6	4.4	13.0	7.8	5.2	10.3	9.3
bound	3.7	2.4	5.4	7.8	7.0	7.8	9.6
Total Recovered	99.9	107.8	107.2	101.0	102.0	96.5	108.8

* After 30 days conditions were changed to anaerobic by passing nitrogen through the system.

There were no volatiles trapped with the total of all trapped radioactivity being <0.1% AR. The amount of radioactivity extracted using the forcing conditions (soxhlet and phosphoric acid solvent) was relatively high throughout the study ranging from 26.7% of AR at day 0 to 40% after 30 days and remained approximately at this level during the anaerobic phase (35-42% of AR). The report notes the some of the diuron becomes tightly bound very rapidly and could only be recovered by forcing conditions. This was also noted in one of the aerobic studies (Mackie and Hall, 1994 above)

After the system was purged with nitrogen and presumably anaerobic conditions were established (no evidence was presented that anaerobic conditions were established), the metabolism of diuron appears to stop with the amount of diuron recovered remaining constant (within experimental error see Table A1.15). The half-life for the anaerobic phase was calculated as 1000 days with an r^2 of 0.32 (calculated by DEWHA), that is, not statistically significant. It was concluded that the study shows that under anaerobic conditions the metabolism of diuron is very slow. This is in contrast to the other anaerobic studies below.

2.4 Anaerobic aquatic metabolism

Study 1 – US EPA guidelines

The anaerobic aquatic metabolism of ^{14}C-diuron (labelled in the phenyl ring) was studied using a clay loam sediment in accordance with the EPA Guideline 161-3 (Hausmann, 1992). The sediment and water used were collected from an irrigation channel and were the same as used in the previous aerobic aquatic metabolism study (see 1.2.2: Study 2). The sediment was classified as a clay loam, details of which were given previously and the pH of the water ranged from 6.3-7.9 throughout the study.

The microbially viable sediment was flooded with the water at a ratio of water to sediment of about 2:1. The test system was incubated under nitrogen for either 5 days (test system 1) or 62 days (test system 2) to allow an equilibrium to be established before being dosed with diuron on day 0. The redox potential of the sediment, from –33 to -188 mV, indicated anaerobic conditions had been achieved (Tebbutt, 1992). The labelled diuron was applied to the water surface at 1.70 mg ac/kg of total system (water + sediment), given as approximately equivalent to 13.4 kg ac/ha (12 lb/acre), and then incubated in a dark under nitrogen at 25°C for 370 days. Volatiles were trapped. For test system 1, samples were collected after day 21 while samples from test system 2 were collected from 0 to day 21. Analysis was achieved by extraction followed by HPLC with metabolites confirmed by TLC.

Recovery of applied radioactivity averaged 98% and ranged from 91 to 106% throughout the study.

Diuron degraded under the study conditions with a degradation half-life of 1.2 days using first order kinetics (r^2 = 0.79, 4 data points). There was one main metabolite, m-CPDMU, that reached 81% of AR after 7 days, remained at that level until day 98 (82% of AR), and then declined to 15% of AR at the end of the study. Other metabolites were phenyl dimethyl urea (PDMU or fenuron - another herbicide), which reached 13% of AR after 288 days and then declined to 3.6% by day 370, and m-CPMU that reached 18% of AR after 370 days. Non-extractable radioactivity slowly increased to 20% of AR after 288 days, then rose rapidly to reach 64% after 370 days. These unextracted residues were further characterised with 50% of AR in the humin fraction, 9.2% of AR in the humic acid fraction and 8.2% of AR in the fulvic fraction.

The degradation pathway proposed is rapid dechlorination of the phenyl ring to give m-CPDMU then slowly followed by further dechlorination to give PDMU, or demethylation to m-CPMU. In a supplemental report (Hausmann, 1997b), it is noted by the author that the reductive dechlorination, which leads to the formation of m-CPDMU, is fast and explains the relatively short half-lives of diuron in this study. (The supplemental report was a response to a request from the US EPA to explain the short half lives in the aerobic and anaerobic aquatic metabolisms studies compared to the results from the aerobic and anaerobic soil studies.) It should be noted that in sediment monitoring data described in Section 8.5.2 of this report, unchanged parent diuron was found in sediments to a depth around 1 m indicating that anaerobic degradation may not always be fast.

Metabolite anaerobic aquatic metabolism data

DuPont have provided one additional anaerobic aquatic metabolism study considering the metabolite mCPDMU. The following assessment of this study is provided.

Title	Rate of Degradation of IN-12894 (mCPDMU) in an Anaerobic Aquatic Sediment System
Authors	Sarff, P
Date	2007c
APVMA Data ID	9018
Test Guideline	OECD Test Guideline 308; US EPA Guideline 162-3
Data Validity	2 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

The degradation kinetics of [^{14}C]-mCPDMU, a metabolite of diuron, was investigated in a water/sediment system for up to 100 days under anaerobic conditions.

Water and sediment were sieved (2-mm) with the test system consisting of 40 g dw sediment and 160 mL water. The test material was added at 1.0 mg/L in acetonitrile. A total of 22 treatments (2 replicates per time point), 2 control replicates and 9 biomass sample replicates were maintained. Nitrogen was flowed through a water hydrator. An ethylene glycol trap and two KOH traps were used to collect $^{14}CO_2$ and other organic volatiles. The test was run at ~20^{0}C in darkness. The sediment had the following characteristics:

Soil	Classification	%Sand	%Silt	%Clay	%OC	% moisture*	CEC**
Goose River	Sandy clay loam	63	16	21	1.2	30.1	15.9

* @ 1/3 bar; ** meq/100g.

The water had an initial pH of 8.3 and a hardness of 638 mg/L $CaCO_3$.

Sampling intervals, including volatile traps and measurement of pH and redox potential (water and sediment) and dissolved oxygen (water), were days 0, 7, 15, 29, 44, 61, 76 and 100 post application. Radioactivity was determined by LSC. HPLC was the primary method to characterise radioactivity in the water layers and sediment extracts.

Findings

OECD TG 308 states that for anaerobic test systems, the sediment and water are regarded as anaerobic

once the redox potential (E_h) is lower than -100 mV.

The following table provides mean water redox potentials found in the test systems during the study:

Table A1.16: Mean Replicate Redox Potential of Test Water (mV) During the Study Period

		Days after treatment							
		0	7	15	29	44	61	76	100
Goose River	Test	155.8	-25.8	-175.1	-176.0	-3.3	-15.1	-140.0	-51.5
	Control	151.1	1.8	-90.2	-207.7	-41.3	-56.2	-223.6	-71.2

The test guideline states that (for an anaerobic test system), the sediment and water are regarded as anaerobic once the redox potential is below -100 E_h (1 mV = 1 E_h). Again, it is important that the reference electrode is identified, and this is not found in the test report. It appears that the equipment used for measuring redox potential (Accumet Model AR50) could use either a calomel electrode, or a Ag/AgCl electrode. If these have been used to determine mV, then they need to be converted to E_h to give the reading of a standard hydrogen electrode (adding +197 to +241 mV depending on the reference electrode). It is unclear whether such a transformation has been made in the reported data. If not, the conditions in the water were clearly aerobic throughout the study. However, if this conversion was done, then the water redox potentials indicate conditions were reducing through much of some periods of the study. Dissolved oxygen concentrations in the water were below 1 mg/L in both test systems, at all time points except day 0 in the control, indicating reducing conditions in the water. Unfortunately, no redox potentials for the sediment during the study period are available.

Mass balance measurements showed recovery of radioactivity ranging from 95.1% AR at 76 days after application to 100.1% AR at 15 days after application. Of this, 92.1% AR was found in the water at day 0, and this had been reduced to 37.3% AR after 100 days. Conversely, the amount of extractable radioactivity in the sediment increased from 5% AR at day 0 to 56.7% AR after 100 days. Bound residues accounted for 3.8% AR after 100 days, no organic volatiles were detected with the exception of 0.1% $^{14}CO_2$ after 100 days.

The following table shows the breakdown pattern of mCPDMU in the test system. No other individual compound exceeded 10% AR.

Table A1.17: Rate of Degradation of mCPDMU in Goose River Sediment/Water System under Anaerobic Aquatic Conditions

Days after treatment	%mCPDMU water	%mCPDMU Sediment	Total mCPDMU
0	90	4.8	94.8
7	55.3	41	96.3
15	48.8	48.2	96.9
29	41	53.3	94.3
44	37.2	51.7	88.9
61	35.6	54.5	90.1
76	32.8	50.8	83.6
100	30	53.5	83.4

Conclusion

Using first order kinetics, the study authors calculated a DT50 in water of 57 days (r^2 = 0.71) and a total system DT50 of 436 days (r^2 = 0.783), which exceeded the study duration. It is apparent looking at the data for water concentrations that levels in water fall quicker in the initial stages of the study than later. DEWHA has recalculated the degradation kinetics based on the 0-15 days after treatment (3 data points only), and the 15-100 days after treatment data, and found the following water half-lives:

	r^2	Half-life (days)
Day 0-15	0.87	17.2
Day 15-100	0.89	100

Literature

The literature contains a report of the degradation of diuron under anaerobic conditions (atmosphere of nitrogen 95% and carbon dioxide 5%) using preconditioned sediment (Attaway *et al*, 1982). The sediment was from a natural pond that had been pre-treated with diuron at 1.36 kg/year (number of years not given) and was stated to be highly anaerobic (black colour with sulphide aroma). The media were prepared (7 media conditions were used based on variations of sediment extracts, mineral salts and carbon sources) before being dosed with diuron (40 mg/L), inoculated with the anaerobic sediment and incubated at 30°C for 80 days. These conditions do not conform to the current testing guidelines.

In all cultures diuron 'completely' degraded in 17-25 days as evidenced by the non-detection of diuron in the HPLC analysis of the extract (one ethyl acetate extraction). There was only one degradate observed, that of the mono-dechlorinated metabolite m-CPDMU, which appeared in approximately stoichiometric amounts. DEWHA notes that there was no mass balance, the extraction technique used may not recover bound sediment (there was only 78% recovery from spiked sediment) and the pre-conditioning does not conform to current guidelines.

3. MOBILITY

3.1 Volatility

Diuron has a vapour pressure of 1.1×10^{-3} mPa at 25°C and a calculated Henry's Law Constant of 7.0×10^{-6} Pa m^3/mole, which are both indicative of only very slight volatility.

As part of a wider experiment on the fate of diuron in a field lysimeter experiment, Guzzella *et al*, (2006) considered volatilisation of diuron from the soil surface. The field lysimeter component of the study is described further below. Briefly, the test plot (~30 m^2) was sprayed with 6.8 g diuron (~2.3 kg ac/ha). A meteorological station with a data acquisition system was placed inside the field and an air sampling system (polyurethane foam cartridge [PUF] connected with a tygon tubing system to a pump) was installed at the station in the centre of the plot. Air samples were collected for the first 13 days after herbicide application. The filters and PUF were extracted with acetone (three times) and analysed by HPLC. Detection limits for 1 m^3 air sample concentrated to 1 mL were 0.1 ng/m^3 for diuron, DCPMU, DCPU and DCA.

The sampling flux was a constant 2 L/min. While daily temperatures were not reported, the temperature on the soil surface (5 cm depth) was recorded at 34°C at the time of application and the air temperature was 28°C, so conditions at least at application would have been conducive to volatilisation. The analysis of the PUF filters showed that diuron was never detected confirming the low volatility of this compound.

3.2 Adsorption/desorption

Study 1 - diuron, m-CPDMU and fenuron (PDMU)

The adsorption/desorption of diuron, fenuron (PMDU, see p 26) and m-CPDMU in 5 soils was performed to meet US EPA Guideline 163-1 (Bramble, Behmke and Norwood, 1998). The ratio of soil to test solutions was 1:15 for diuron, 6:1 for m-CPDMU and 3:2 for fenuron with the equilibrium time of >12 hours, all determined in preliminary testing. The isotherm part of the study was conducted for the Chino, Barkley and Keyport soil only. In the preliminary studies the Myaka and Donna soils showed <10% adsorption and this was not sufficient for isotherm testing. The desorption study was conducted by adding fresh 0.01 $CaCl_2$ solution to each of the test soils after adsorption, again using 24 hours for equilibrium. There were two rounds of desorption, only the first is reported here. Table A1.17 gives the soil characteristics and Table A1.18 the results.

Table A1.18. Characteristics of test soils.

Origin	Soil Name	Soil Type	% OM	pH	% Sand	% Silt	% Clay	Koc1
Brademton, Florida	Myaka	Sand	0.5	6.7	91.2	4.0	4.8	578
Donna, Texas	Donna	Sandy clay loam	0.8	8.0	46.0	25.6	28.4	366
Madera California	Chino	Loam	1.4	8.2	43.2	46.0	10.8	1750
Newark, Delaware	Barclay	Silty clay loam	2.9	7.1	10.0	60.0	30.0	410
Chesapeake, Maryland	Keyport	Silt loam	7.7	4.1	20.0	66.0	14.0	607

1 Screening results only

Table A1.19. The adsorption coefficients for diuron, m-CPDMU and fenuron.

Soil Name	Kd, (µg/g)	Koc	1/n	Koc des	Kd, (µg/g)	Koc	1/n	Kd, (µg/g)	Koc	1/n
	Diuron				m-CPDMU			Fenuron		
Chino	14	1666	0.85	769	3.4	418	0.74	1.1	132	0.85
Barclay	7.9	468	0.85	230	2.3	139	0.69	0.66	39	0.70
Keyport	28	626	0.93	354	8.0	179	0.78	1.7	38	0.71

The Koc values from the screening test indicate that diuron is moderately adsorbed to the soils tested and is rated as being low to medium mobility (McCall classification) and the range indicates the organic matter is not the only determinant of adsorption – other factors such as physical-chemical properties of the soils and content and composition of clay mineral, could also be factors.

For the metabolite m-CPDMU the screening data Koc values (not given in Table A1.18) ranged from 40 to 323 and is rated as being low mobility to very high mobility (McCall classification). However, the isotherm data for the three soils tested (Chino, Barclay and Keyport) indicate that it is rated as low to high mobility (McCall classification). For fenuron, the screening results show Koc from 33 to 138 (high to very high mobility) and similar the isotherm data. In all cases the metabolites were more mobile than the parent compound diuron.

Study 2 - diuron

The adsorption/desorption of diuron was performed to meet US EPA Guideline 163-1 using 4 soils (Priester, 1990). The ratio of soil to test solutions was 1:1 (vol/soil dry wt) and the equilibrium time was 24 hours. The desorption study was conducted by adding fresh 0.01 $CaCl_2$ solution to highest concentration of the test soils after adsorption, again using 24 hours for equilibrium. There were 5 rounds of desorption and the desorption Koc was determined by fitting the Freundlich equation using all 5 desorption data points to generate the isotherm. Soil characteristics and results are summarised in Table A1.19.

Table A1.20. Characteristics of test soils and adsorption coefficients.

Origin	Soil Type	% OM	pH	% Sand/Silt/Clay	Kd, µg/g	Koc*	1/n	Kocdes*
Dover, Delaware	Sandy loam	1.1	6.6	60/33/7	2.9	452	0.85	661
Raleigh, North Carolina	Sandy loam	2.1	6.5	61/21/18	5.1	418	0.81	505
Rochelle, Illinios	Silt loam	4.3	5.4	2/81/17	14.0	574	0.87	278
Newark, Delaware	Silt loam	4.7	4.3	11/78/11	13.0	487	0.92	261

* Calculated by DEWHA from Kom using Koc = Kom X 1.74.

The Koc values indicate that diuron is moderately adsorbed to the soils tested and is rated as being low to medium mobility (McCall classification) and the narrow range indicates the organic matter is the major determinate of adsorption, in contrast to that from the previous study. The report gave the Kd and the results are presented as K_{ocdes} in Table A1.19. However, these need to be treated cautiously as they were generated from only one effective concentration. The desorption data shows that there was considerable loss of diuron from the Dover soil, 40% of the initially adsorbed diuron was lost after 5 cycles of desorption, compared to the other soils where 17, 7 and 8% of the adsorbed diuron was remobilised for Raleigh, Rochelle and Newark respectively. It is noted that the Dover soil has the lowest amount of clay of the four soils studied.

Study 3 - DCPMU

The adsorption/desorption of DCPMU, a major metabolite of diuron, in 4 soils was performed to meet US EPA Guideline 163-1 and OECD TG 106 (Brumhard *et al*, 1998). The ratio of soil to test solutions was 1:4 and the equilibrium time was 24 hours, both determined in preliminary testing. The desorption study was conducted by adding fresh 0.01 $CaCl_2$ solution to each of the test soils after adsorption, again using 24 hours for equilibrium. Table A1.20 gives the soils characteristics and Table A1.21 the results.

Table A1.21. Characteristics of test soils.

Origin	Soil Name	Soil Type	% OC	pH (Ca)	% Sand	% Silt	% Clay
Jockgrim Germany	BBA 2.1	Sand	0.7	5.3	89.4	10.5	0.1
Borstel, Germany	Borstel	Loamy sand	0.69	6.0	77.9	18.5	3.6
Burscheid, Germany	Höfchen	Silt loam	2.4	5.8	3.6	80.8	15.6
Landau, Germany	Tonboden	Clay	0.64	7.4	15.0	42.3	42.7

Table A1.22. The adsorption coefficients for DCPMU.

Soil Name	Kd, µg/g	Koc	r2	1/n	Kocdes
BBA 2.1	3.49	4989	1.000	0.7629	786
Borstel	9.37	1358	0.999	0.7561	2030
Höfchen	15.63	651	0.999	0.7565	929
Tonboden	4.76	744	1.000	0.7390	1205

The Koc values indicate that DCPMU is moderately adsorbed to the soils tested and is rated as being low to medium mobility (McCall classification). The isotherm data show a very good fit to the Freundlich equation and the exponents (1/n) show that the percentage of adsorbed DCPMU decreases with increasing concentration.

Study 4 - DCPU

The adsorption/desorption of DCPU (N-(3,4-dichlorophenyl) urea), a major metabolite of diuron, in 5 soils was performed to meet OECD TG 106 (Heintze, 2002). The ratio of soil to test solutions was 1:3 for the BBA 2.1 soil and 1:10 for the other soils and the equilibrium time was 48 hours, both determined in preliminary testing. The desorption study was conducted by adding fresh 0.01 $CaCl_2$ solution to each of the test soils after adsorption, again using 48 hours for equilibrium. Table A1.22 gives the soils characteristics and Table A1.23 the results.

Table A1.23. Characteristics of test soils.

Soil Name	Soil Type	% OC	pH (Ca)	% Sand	% Silt	% Clay
BBA 2.1	Sand	0.49%	5.7	89.8	8.9	1.3
BBA 2.2	Silty sand	1.48	6.0	74.8	21.0	4.2
BBA 2.3	Silty sand	0.76	7.0	64.5	27.8	7.8
Höfchen	Silt	2.11	6.7	8.2	81.5	10.3
BBA S6	Clay	1.89	6.9	21.7	35.4	42.9

Table A1.24. The adsorption coefficients for DCPU.

Soil Name	Kd, (µg/g)	Koc	r2	1/n	Kocdes
BBA 2.1	4.22	861	0.998	0.769	1035
BBA 2.2	11.38	769	0.999	0.789	995
BBA 2.3	8.95	1178	0.998	0.676	1542
Höfchen	11.12	527	0.999	0.757	659
BBA S6	12.02	636	0.998	0.787	792

The Koc values indicate that DCPU is moderately adsorbed to the soils tested and is rated as being low to medium mobility (McCall classification). The isotherm data show a very good fit to the Freundlich equation and the exponents (1/n) show that the percentage of adsorbed DCPU decreases with increasing concentration. The desorption isotherm showed a good fit to the Freundlich equation and the exponent (1/n) was similar to the adsorption figures.

The report indicates that there is high adsorption to soil, which is dependent on organic carbon in the soil but also on the silt or clay component due to the high adsorption in the BBA 2.3 soil with low organic carbon. The adsorption was considered to be reversible as the distribution coefficients calculated for adsorption and desorption were close in value.

3.3 Leaching potential

Soil Columns

No soil column leaching studies were presented.

Field Lysimeters

To evaluate the leachability of diuron under field conditions a field lysimeter study was undertaken in Sweden (Bergström *et al*, 1996).

Two sandy soils (Nantuna and Langaveka, details in Table A1.24) were used in the lysimeters that were treated with either 2 kg/ha or 4 kg/ha (1X and 2X rate; 4 lysimeters used) of radiolabelled diuron (labelled in the phenyl ring). Each lysimeter was planted with a single black currant bush in order to mimic normal

agricultural practices and to obtain a reasonable water balance. The lysimeters were approximately 1.1 metres in length and the leachates were collected every 2 weeks for 26 months. All lysimeters received irrigation, applied slowly at <4 mm/h to simulate natural rainfall and prevent ponding. The lysimeters received a total of 1737 mm of precipitation (including irrigation). After the study period the soil was sectioned into 8 increments (0-5, 5-10, 10-20, 20 to bottom of topsoil, then 50-70, 70-90, 90-105 cm). The leachates and soils sections were analysed for total radioactivity, diuron and metabolites.

TableA1.25. Soil characteristics in the soils used for lysimeters.

Soil		Soil Type	% OM	pH	% Sand	% Silt	% Clay
Langaveka,	topsoil	Loamy sand	0.9	5.8	85.1	11.5	1.6
	subsoil	Sand	0.4	5.8	91.6	6.0	1.8
Nantuna	topsoil	Loamy sand	1.1	7.4	80.5	8.2	9.1
	subsoil	Sand	1.0	-	95.4	4.6	0.0

At the normal rate of 2 kg ac/ha, there were 6 leachate samples where the leachate contained diuron above the limit of detection (0.05 µg/L; HPLC method) from the Langaveka soil lysimeter with 30 samples analysed; the maximum concentration of diuron was 0.73 mg/L. For the Nantuna lysimeter there was 1 sample above the detection limit at 0.06 µg/L from the 29 samples taken. At the higher rate of 4 kg ac/ha there were 17 positive samples from 34 samples taken from the Langaveka lysimeter with a maximum concentration of 12.55 µg/L of diuron and for the Nantuna lysimeter there was 16 positive samples, with a maximum of 1.25 µg/L from the 41 leachate samples. The highest concentration of diuron was associated with flow-events of short duration (and low volumes) during winter. When the highest flow occurred during spring, the concentration of diuron was below the detection limit. The total leaching of diuron was highest from Langaveka and represented just 0.012 and 0.027% of applied for 1X and 2X the rate respectively.

A similar leaching pattern occurred with DCPMU and DCPU, the only two metabolites detected, with the concentration of DCPMU comparable with diuron in the majority of leachate samples but DCPU was lower. The major radioactivity component recovered in the leachate was $^{14}CO_3^{=}$, which was taken as an indication that extensive metabolisation of diuron had occurred.

The soil analysis showed that the majority of the applied radioactivity remained in the topsoil (0-20 cm) with <1% of AR in the remaining soil (20-105 cm). Detectable concentrations of diuron remained in the topsoil. For Nantuna, the diuron was in the 0-5 cm layer and for Langaveka more had moved into the 5-10 cm layer. Also for Langaveka there was more diuron remaining in the soil profile than for Nantuna, reflecting the faster degradation in the latter soil. The laboratory half-lives were 20 and 119 days for Nantuna and Langaveka soils respectively at 20°C, 70 % MWHC (see aerobic soil metabolism, Mackie and Hall above).

It is concluded by DEWHA that the study shows limited leaching at the lower rate but also indicates that at higher rates the leaching is proportionately higher. The low temperatures in Sweden (average day time temperatures from the study was 5.6°C) would reduce the rate of degradation compared to Australian conditions and therefore the study may not reflect the expected leaching in some Australian conditions. However, the drier Australian conditions that occur inland would also reduce the microbial activity and hence the rate of degradation.

Guzzella *et al*, (2006) describe a more recent field lysimeter study. Ten lysimeters (28 cm internal diameter) were installed in a circle in the test plot. Five had a 40 cm depth and five had 20 cm depth. The lysimeters were pushed into the soil and the resulting soil enclosures transported back to the laboratory, where a Teflon draining bottom and glass funnel for collecting leachate was connected under the lysimeter. The soil

enclosure was reinstalled in the soil the following day and allowed to settle for 15 days. The soil was a silty loam with 35.5, 52 and 12.5% sand, silt and clay respectively in the 0-22 cm soil layer along with 4.5% OM and pH of 7.3. A meteorological station with a data acquisition system was placed inside the field.

Diuron (along with linuron at 560 g ac/ha) was applied to a test plot (~30 m^2) at a rate of 2.3 kg ac/ha. The experiment was undertaken for 245 days for 8 lysimeters (two were ceased after 52 days for use in a separate experiment). Twelve soil pore water samples (~ one for each week or after rain events) from each lysimeter were collected during the whole experiment. Soil was sampled by driving a 40 cm tube (5.6 cm internal diameter) inside the experimental area but outside the soil lysimeters. Core samples (in triplicate) were taken on days 1, 8, 16, 28, 90, 147 and 245 with analysis performed in 10 cm soil increments.

Application rates were verified through use of randomly distributed filter papers. Based on analysis of these papers, applied diuron ranged from 18 to 66% theoretical with a mean application rate of only 34.9% theoretical. No reason for this was provided in the paper.

The volume of water collected during 161 days for the ten lysimeters varied from 2 to 7 L. The first “rain” event (artificial) was 100 mm on day 16. In several of the lysimeters, the peak of herbicide concentrations was evident on this day, and in these lysimeters, no herbicide was detected after 97 days in leachate. In the remainder of the lysimeters (there was no distinction between those draining at 20 or 40 cm, both depths appeared to behave the same), the maximum concentration peaks were detected at day 20 with a rapid decrease, although some secondary peaks appeared between 40 and 90 days in concordance with other precipitation events. Reading the values from a graph, initial peak concentrations of diuron in leachate were 14 and 10 µg/L at days 16 and 20 respectively, with around 4.5 µg/L at day 38, 2 µg/L at day 41, and falling to day 97 where no further diuron was detected in leachate. The main metabolites were DCPMU and DCA, and their concentrations were always lower than 3 µg/L. Metabolites (appear to be DCA based on graphical representation in the paper) were found at levels approaching 0.5 µg/L around 140 days after application, but nothing is noted after this point. The total leached amount of diuron residues accounted for around 0.36% of the initially applied chemical.

In soil, the measured amount of diuron in the 0-10 cm soil layer on days 1, 8, 16, 28, 90, 147 and 245 was 562, 777, 716, 807, 250, 407 and 305 µg/kg respectively. No diuron was detected below the 10 cm soil layer in soil, despite unchanged diuron being found in leachate water at 20 and 40 cm depth. While not calculated in the report, the half-life of diuron based on these data is ~190 days (r^2 = 0.84 if the questionably low residues at day 90 are not included). The main metabolite was DCPMU, generally only in the top 10 cm but found distributed through the soil profile to 40 cm at the day 8 sampling event.

The authors suggest that the non-detection of diuron below 10 cm in soil, while found at 40 cm in soil pore water is possibly due to the different limits of detection of soil samples (1 µg/kg in soil compared to 0.05 µg/L in water).

4. FIELD DISSIPATION STUDIES

4.1 Australian field data

Study 1 - 4 agricultural sites in Australia

Recent studies funded by the Cooperative Research Centre (CRC) for Sugar have included field and laboratory studies at four field sites in the Bundaberg region to enhance understanding of on-site and off-site movement and persistence of pesticides commonly used in cane production systems (Simpson and Hargreaves, 2001). The results from this study are summarized in Table A1.25 below. The study was over a 3 year period and the weather was considered to be dry overall for this region. All sites were under commercial cultivation and were subject to normal farming practices. Sites were either bare soil or trash

covered, as is normal practice, in order to examine the effect of the trash cover. At the yellow chromosol site diuron was not used in the field study and therefore no half-life for diuron could be determined.

Table A1.26. Terrestrial degradation of diuron at 4 sites in Australia.

Site	Sand/silt/clay 0-10 cm	Soil type	pH	% OC	Koc 0-2.5 cm	DT50 days 0-50 cm
Yellow chromosol	84/9/6	Loamy sand	5.1	0.95	1326	-
Grey kandosol	91/6/3	Sand	7.2	0.8	3738	15[1]
Red ferrosol	16/21/63	Clay	6.0	1.23	2244	>250[1], >150[2] >, 250[3]
Redoxic hydrosol	82/9/8	Loamy sand	7.1	0.72	5240	6.5[1], 22[2]

1) Results from the 1997/98 summer. 2) From the 1998/99 summer. 3) From the 1999/2000 summer.

The results of this study show that the Koc values are in the range for the European and North American soils, although slightly higher but as these were determined in a non-standard method (standing for ~48 hours, then 30 minutes of shaking; soil:water ratio 1:50; single concentration of diuron [not given] and not Freundlich values), they are not truly comparable. Also, the DT50 values were calculated using a second order equation (y=ae(b/(x+c))) and the DT50 values are for the first half lives only; a number of sites had measurable levels of diuron that persisted to the end of the sampling period (120-250 days). It is noted that at the redoxic hydrosol site the DT50 between one year and the next varies considerably, from 6.5 days to 22 days. However, the application dates are different as is the depth of soil over which the dissipation time was calculated. The first dissipation time was from an application in February 1998 and for the 0-10 cm layer and the second was applied in December 1998 and is for the 0-50 cm soil layer (the 0-10 cm DT50 is 15.5 days).

The DT50 for the red ferrosol soil is very long and remained greater than 250 days over the 3 years of the study, in contrast to the other soils. A reason for this is not apparent. It does not appear to be due to stronger binding as the Koc is lower than other soils where there was rapid degradation.

The runoff of diuron and its leaching was also examined at these test sites. Runoff of diuron was monitored at sites 2, 3 and 4 and <0.2% of the annual application rate was detected in the runoff water. The maximum average concentration of diuron in runoff water was 120 µg/L that occurred at site 2 following a short but intense heavy rainfall event (26 mm in 7 minutes) 37 days after last application. In the next season's application another intense rainfall event (94 mm over 160 minutes, 26 days after the last application) also caused high levels of diuron in the runoff water at 113 µg/L. In the other runoff events at this site, the average levels of diuron were between 0.37-10.6 µg/L. The higher concentrations of diuron appear to correlate with high loads of suspended solids in the runoff water. Diuron was detected in a groundwater piezometer down slope at site 4 with maximum concentration of ~6.5 µg/L. The height of the ground water at this site responded to rainfall and was within 0.5 metres of the surface during the summer wet but fell to 3.5 metres during (winter) dry periods.

The trials where the cane fields were covered in trash, as is normal commercial practice showed that the trash intercepted the pesticides and reduced the amount reaching the soil below, as is expected. For atrazine and chlorpyrifos, the only pesticides where the concentration in the soil below the trash were measured, level of the pesticides were <15% of target (estimated graphically by DEWHA). When diuron was applied to the trash layer, diuron remained in the trash and was persistent, with 50% loss occurring in approximately 21 days (estimated graphically). The level of diuron in the covered soil was not measured.

The report concluded that this study highlighted the need for careful management of application timing and chemical selection, particularly in areas close to waterways and sensitive habitats.

Study 2 – Diuron dissipation under conventional production in a sugarcane farm

Field studies of diuron and its metabolites DCPMU, DCPU and DCA were conducted in a farm soil and in stream sediments in coastal Queensland (Burnett catchment), Australia (Stork *et al*, 2008). The farm soil in the top 15 cm contained 80, 17 and 4% sand, silt and clay respectively with a pH of 6.3 and 0.9% OC. The farm operated under a conventional regime of sugarcane production. Row widths in the crop were 1.6 m and a travelling water winch was used for irrigation. A spray application of diuron at 1.6 kg/ha was made to a 6.3 ha block nearing canopy closure of the crop on 18 December 2005 with ~25 mm irrigation applied immediately after spraying. Diuron had not been applied to the trial area for at least 2 years prior.

A 0.19 ha catchment within the sprayed area was used to quantify surface runoff (consisting of 5 cane rows of 300 m length with a gradient of 1.4%). Sampling was activated at preset time intervals when the flow rate exceeded 0.9 mm/h. Soil dissipation was carried out in three contiguous interrows adjacent to the runoff catchment area. Samples were collected from 0-45 cm in 15 cm increments and sampling was conducted at 2, 36, 57, 92, 129, 155 and 267 days after application. Stream sediment sampling was carried out over an approximate 5 km length of stream below a catchment that contained around 3500 ha of sugarcane farmland. The average width of the stream over this distance was around 6 m and the depth of sediment sampled was around 50 cm. Sampling was undertaken on 15 August 2006 and 6 September 2006 from 5 different locations spaced over the 5 km stream length. Limits of quantification in water for diuron, DCA and DCPMU was 1 µg/L (5 µg/L for DCPU), and for diuron, DCPU and DCPMU in soil/sediment was 5 µg/kg (1 µg/kg for DCA).

Runoff: Surface flows occurred during storm events on 7 January 2006 (20 DAA) and 8 November 2006 (325 DAA). At 20 DAA, rainfall totalled 46 mm during an approximate 1 h event and total flow amounted to 50 m^3/ha (around 5 mm runoff per hectare). The flow rate remained above the sample collection threshold for 55 minutes. Sequential sampling of the flow at approximate 1.5 minute intervals limited sample collection to the first 13 minutes of the 55 minute period. During this time, concentrations of diuron ranged between 64 and 73 µg/L and rose steeply to 280 µg/L in the last sampling. Concentrations of DCPU and DCPMU ranged from 23-39 µg/L and 70-94 µg/L, respectively, in the same period. Average concentrations during the 13 minute sampling period were 93 µg/L diuron, 30 µg/L DCPU and 83 µg/L DCPMU. The loading of all compounds during this time was equivalent to around 0.12% applied diuron. Given this amount was detected during the first 13 minutes of the 55 minute surface flow event (~25% of the period), the actual load of diuron lost could be in excess of 0.5% of the level applied during this one runoff event.

Soil dissipation: At 2 DAA diuron and DCPMU were detected in the 0-15 cm soil layer at 397 and 117 µg/kg respectively, and in the 0-30 cm layer at 33 and 43 µg/kg respectively. These residues amounted to a recovery of 91% of the applied amount. Diuron was restricted primarily to the 15 cm layer with levels generally 35 µg/kg or less (read from graph) in the 15-30 cm layer and 10 µg/kg or less (read from graph) in the 30-45 cm layer. Diuron dissipated steadily from the soil and the first order half-life was calculated to be 49 days (confirmed by DEWHA, $r^2 = 0.99$). DCPMU was found mainly in the 0-15 cm layer with low detections in the 15-30 cm layer (except for a higher reading of ~42 µg/kg in the 15-30 cm layer at 2 DAA). At the end of the sampling period (267 DAA), this metabolite was found in the 0-15 cm soil layer at a concentration of 6 µg/kg, equating to around 14 g/ha.

Sediment analysis: Diuron was detected in all sediment samples when measured at concentrations between 3 and 19 µg/kg while DCPMU was found (again in all samples) at concentrations of 4 to 31 µg/kg. Based on values read from a graph, the mean concentration of diuron (10 samples) was ~ 15.1 µg/kg while that for DCPMU was ~18.2 µg/kg.

4.2 International field data

Study 1 – 3 agricultural sites in USA

A terrestrial field dissipation study was conducted according to US EPA Guideline 164-1 (Bramble *et al*, 1998). The report presented is an interim report with the final report completed later (Tweedy, 1999).

Diuron (80% ac granular formulation) was applied to bare soil at three sites at a target rate of 13.44 kg ac/ha (12 lb/A; maximum US rate). There were 3 test locations: Bradenton, Florida; Greenville, Mississippi and Woodland, California, see Table A1.26 for soil characterisation at each site. From application monitoring samples placed on the treated plots, the applications averaged between 86 to 101% of target rate. There were 3 treatment plots plus a control plot at each site. The treatment plots were irrigated prior to the day 0 soil sample.

All sites received natural rainfall plus additional irrigation to ensure monthly totals were above the historical (from 1961 to 1990) monthly averages. The test sites in total received 1796, 1311 and 2119 mm of rainfall + irrigation for Bradenton, Greenville, and Woodland respectively.

Soil samples were taken before and 6 hours after application and then at 8-9 different times up to a maximum of 238, 301 and 269 days after application for Bradenton, Greenville, and Woodland respectively. Soil cores were taken to a depth of 90 cm. The samples were analysed for diuron and other metabolites but only DCPMU (see Attachment A) was detected. The limit of quantification was 20 µg/kg soil and results below this figure should be considered to be estimates only. Table A1.27 is a summary of soil residues found in upper most section of soil (0-15 cm), averaged from 3 plots at each site.

Table A1.27. Soil characteristics for 3 sites for field studies.

Site	Bradenton, FL			Greensville, MS			Woodland, CA		
Soil depth, cm	0-15	15-30	30-60	0-15	15-30	30-60	0-15	15-30	30-60
pH	6.0	5.9	6.1	5.7	6.1	6.3	7.0	7.2	7.5
Organic matter %	0.5	0.5	1.3	0.8	0.9	0.8	2.8	2.2	1.8
Sand %	98.0	98.0	94.0	24.0	22.0	26.0	4.0	6.0	12.0
Silt %	<2.0	<2.0	<2.0	62.0	60.0	56.0	68.0	66.0	60.0
Clay %	<2.0	<2.0	4.0	14.0	18.0	18.0	28.0	28.0	28.0
Texture	Sand			Silt loam			Silty clay loam		

Table A1.28. Residues of diuron and DCPMU in the 0-15 cm soil section. All results are averages from 3 plots and reported as µg/kg soil (dry weight).

	Bradenton								
Sample date, DAT	0.25	3	15	22	59	126	178	238	
Diuron	4330	4570	3840	3540	480	260	680	190	
DCPMU	54	146	511	296	146	110	61	188	
	Greenville								
Sample date, DAT	0.25	4	15	29	60	120	175	256	301
Diuron	4240	2700	3442	1593	807	758	660	679	501
DCPMU	25	55	259	312	299	315	231	237	151
	Woodland								
Sample date, DAT	0.25	3	15	30	60	120	191	269	
Diuron	5418	4551	3415	3141	2455	4724	2793	1451	
DCPMU	27	57	190	212	340	654	453	258	

The soil samples taken immediately after application showed a concentration in the 0-15 cm of between 4.2 to 5.4 mg/kg soil, the expected concentration is 6.89 mg/kg (soil density 1.3 g/cm^3) in the first 15 cm soil. There were occasional detections of diuron in the 15-30 cm soil section at low levels (0.04 to 0.001 mg/kg soil) with one at 0.141 mg/kg (day 0, Woodland) but as the 30-45 and 45-60 cm samples from the same plot also showed low levels of diuron (0.015 and 0.039 mg/kg respectively), this could indicate an artefact of some kind. There was only one other detection below 30 cm above the limit of quantification (LOQ = 0.020 mg/kg) at Bradenton (day 120) in one plot only at 0.023 mg/kg.

The metabolite DCPMU was mainly detected in the first 0-15 cm of the soil with only occasional detections lower down (15-30 cm). These were mainly trace levels (below the LOQ of 0.02 mg/kg) with the highest of 0.028 mg/kg in one plot at Woodland (day 120) and Greenville (day 256).

The results clearly indicate the diuron or its first metabolite are not readily leachable. While the initial degradation of diuron is fast in these soils, it slows down and the diuron remaining in the upper soil segment after 238-301 days was 3, 11 and 19% of the initially applied (time 0.25 days) for Bradenton, Greenville, and Woodland respectively.

The degradation of diuron in the soils was analysed as a two-compartment model (bi-exponential model) and the DT50 and DT90 were calculated as given in Table A1.28. Also included are the results of first order analysis, which show statistically acceptable results.

Table A1.29. The half-lives (days) and statistical factors for degradation of diuron in field studies.

Test site	DT50 days	DT90 days	r2	Transition time	First order (calculated by DEWHA)	
					DT50 days	r2
Bradenton	25	88	0.9115	126	53	0.7505
Greenville	20	439	0.8472	55	116	0.7102
Woodland	10	634	0.6926	16	204*	0.7151*

* Day 120 point removed from analysis as outlier; with point in analysis DT50 = 216 days with r^2 = 0.5384

In the final report for this study (Tweedy, 1999) three additional results were presented to approximately 540 DAT. These are given in Table A1.29. The additional results increased the calculated half-lives (cf first order analysis in Table A1.28) and these are also given in Table A1.29. The half–life of DCPMU at the 3 sites was also calculated as 182, 231, 112 days for Bradenton, Greenville and Woodland respectively with corresponding r^2 of 0.6144, 0.9258 and 0.9046.

Table A1.30. Residues of diuron and DCPMU in the 0-15 cm soil section for additional data and new DT50. All results are averages from 3 plots and reported as µg/kg soil (dry) and are rounded to the detection limit of 10 µg/kg.

	Bradenton			Greenville		Woodland			
Sample date, DAT	302	360	546	360	535	309	414	452	552
Diuron	90	50	40	540	160	1260	330	320	350
DCPMU	63	51	45	150	66	160	55	79	62
DT50 (days) and r2	73; 0.8245			141; 0.7978		135; 0.8689			

Study 2 – 2 agricultural sites in USA

A terrestrial field dissipation study was conducted according to US EPA Guidelines 160-5 and 164-1 (Stevenson, 1990b). Diuron (80% ac granular formulation) was applied to bare soil at two sites at a target rate of 13.44 kg ac/ha (12 lb/A). The test locations were Newark, Delaware and Madera, California; see Table A1.30 for soil characterisation at each site. There were 3 treatment plots plus a control plot at each site.

Over the 14 month test period, the Newark site received mainly natural rainfall amounting to 1659 mm (monthly average 118 mm, range 25.4 to 312 mm) plus some additional irrigation 2 months after application amounting to 26 mm. The California site received in total just 188 mm of rainfall (there was no rain during the first 5 months of the study). This site was irrigated for the first 3 months only but there is no indication of how much irrigation occurred, only that the site received 1 to 4 hours of irrigation per day when irrigated.

Table A1.31. Soil characteristics in the soils for field studies conducted in Delaware and California.

Soil	Soil Type		% OM	pH	% Sand	% Silt	% Clay
Newark,Delaware	0-30 cm 30-60 cm	Silty clay loam Silty clay loam	0.8 0.2	5.7 5.2	8.0 6.0	64.4 66.4	27.6 27.6
Madera, California	0-30 cm 30-60 cm	Sandy loam Loam	1.1 0.7	7.6 8.3	54.0 46.0	28.4 36.4	17.6 17.6

Soils samples were taken before and 6 hours after application and then at 14 times up to 538 and 415 days after application for Newark and Madera respectively. Initially soil cores were taken to a depth of 60 cm and at Newark from day 210 onward were sampled to 90 cm deep. The samples were analysed for diuron and DCPMU only based on the result from the aerobic metabolism study. The limit of quantification was 10 µg/kg soil. Table A1.31 is a summary of soil residues found in upper most section of soil (0-15 cm). At the sites either one, two or three plots were sampled at each sample, the results in Table A1.31 are averaged from two or three plots at each sites or from the plot sampled at that date.

Table A1.32. Mean Residues of diuron and DCPMU in the 0-15 cm soil sections for Newark and Madera. Results are from either single plots or averages from 2 or 3 plots and reported as mg/kg soil (dry).

	Newark													
DAT	0	7	14	30	61	90	124	149	181	210	243	299	359	418
Diuron	1.5	1.5	2.0	1.3	0.48	0.46	0.38	0.45	0.65	0.40	0.29	0.52	0.34	0.09
DCPMU	0.01	0.06	0.14	0.14	0.14	0.17	0.12	0.20	0.28	0.19	0.16	0.32	0.20	0.09
	Madera													
DAT	0	7	15	29	59	89	112	152	179	219	239	300	358	415
Diuron	2.3	1.5	2.15	2.2	1.3	1.2	0.91	1.0	0.72	0.90	0.55	0.27	0.16	0.16
DCPMU	bld	0.03	0.08	0.10	0.14	bld	0.16	0.14	0.12	0.34	0.16	0.12	0.08	0.07

The soil samples taken immediately after application at both sites showed a concentration in the 0-15 cm of between 1.5 and 2.3 mg/kg soil and the maximum concentrations were 2.0 and 2.2, the expected concentration is 6.89 mg/kg (soil density 1.3 g/cm^3) in the first 15 cm soil. Table A1.30 gives the concentration of diuron and DCPMU in the first 0-15 cm depth. There were occasional detections of diuron in the 15-30 cm soil section at Newark with one at 0.39 mg/kg (day 0) but as the 30-45 and 45-60 cm samples from the same plots also showed levels of diuron (0.16 and 0.19 mg/kg respectively), this could indicate contamination. There were detections at 30-45 and 45-60 cm deep of 0.06 and 0.07 mg/kg respectively on day 7 and at 0.02 mg/kg for both 30-45 and 45-60 cm on day 14.

At Madera there were also detections of diuron in the day 0 soil core in the 45-60 cm section (0.16 mg/kg, both plots). While it is very unusual for a chemical with diuron's mobility to be found at such depths so quickly, the results for the subsequent samples (days 7, 15, 29, 89 and 152) also show positive readings for

diuron of up to 0.70 mg/kg soil (30-45 cm, day 7). There would appear to be some indication that vertical movement of diuron has occurred.

The half-lives were calculated as 134 and 108 days for Newark and Madera respectively using first order analysis, comparable to the previous field study. For Newark, the fit was not the best (r^2 = 0.704 calculated by DEWHA) but it appears that the degradation slowed down during winter due to the cold conditions at Newark (the lowest monthly mean maximum/minimum temperature was just 5/-3.9°C during winter). At Madera the fit to first order kinetics was much better (r^2 = 0.937 calculated by DEWHA), presumably because the soil temperatures were slightly higher (lowest monthly mean maximum/minimum temperature was 10/-0.5°C) and lasted just 2 months (Dec and Jan) rather 3 months (Dec, Jan, Feb) as occurred at Newark. Note that overall temperatures at Madera were also higher and that monthly minimums were <5°C for 7 months at Newark.

The study has some problems in that the initial concentration in the soil of diuron is only some 30% of the target rate and it is unclear if this is due to variability in the application across the plots, a problem with preparation of the spray or with the spraying. Not all plots were sampled and analysed on each sample date, in several cases just one plot was analysed and with the high variability between plots this is unsatisfactory.

Study 3 – 6 agricultural sites in Germany

A terrestrial field study was conducted at 6 sites in Germany under field conditions without vegetation according to BBA Guideline IV-4.1 (Pogány, 1993).

Diuron as 80 WP was applied to bare soil at 8 kg ac/ha during German spring (April 24 to 11 May), and then the soils were sampled at approximately 30 day intervals for 300 DAT. The soils were sampled down to 30 cm and analysed in 10 cm sections by HPLC. The soils remained bare and were weeded by mechanical means. The half-lives in the soils were calculated using the Timme-Frehse (Timme *et al*, 1986) method of analysis and are for total diuron (0-30 cm). The best fit was 1st order. Table A1.32 gives the details of the soils and the calculated half-lives.

Table A1.33. Terrestrial degradation of diuron at 6 sites in Germany.

Site	Sand/silt/clay	pH	% OC	Soil type	DT50 days	r2 *
Birscheid, Höfchen	7.8/72.8/19.4	6.8	1.11	Silt loam	56	0.7777
Albig	12.7/51.4/35.9	7.6	1.16	Silty clay loam	231	0.8081
Massen	63.8/31.6/4.6	5.6	2.22	Sandy loam	533*	0.3389*
Kirchlauter	71.3/24.2/4.5	6.5	0.79	Sandy loam	177*	0.9011
Swisttal-Hohn	29/57.9/13.1	6.8	1.00	Silt loam	73	0.8904
Monheim, Laacherhof	57.2/29.8/13.0	6.7	1.27	Sandy loam	67	0.8693

* Results calculated by DEWHA.

The results show that diuron degraded with half-lives of between 67-231 days for most sites but at Massen the soil analysis showed high variability and very limited degradation; an explanation for this was not presented. While a half-life could be calculated, the fit is poor and the result unreliable. The main metabolite found was DCPMU and reached a maximum of between 0.363 (Laacherhof, 61 DAT) and 0.799 mg/kg (Kirchlauter 182 DAT) and then declined in all soils. There was no evidence of leaching, with diuron being found in the 10-20 cm soil sections only on 3 occasions (90 and 120 DAT at Kirchlauter and 90 DAT at Laacherhof). There were 3 additional detections on day 0 but these are likely to be due to contamination during sampling.

Study 4 – irrigation ditch in California

A field dissipation and transport study was conducted according to US EPA Guideline 164- 2 (Priester and Chesser, 1995). Diuron (80% ac granular formulation) was applied to either side of an irrigation ditch (slope and berms) at a target rate of 13.44 kg ac/ha (12 lb/A) using a CO_2 backpack sprayer. No application was made to the channel bed in the treatment area. The ditch was in Dixon, California and divided into 3 areas: upstream control area, treatment area and 3 downstream sampling (transport) areas. The treatment area was 7.6 X 64 m (0.0486 ha) and there was 16.7 m (55 feet) of untreated ditch between the control and treatment and 30.3 m (100 feet) between treatment and the first downstream sampling area. There was 13.7 m (45 feet) of untreated ditch between the three sampling areas.

The soil on the slope and berms (top of the bank forming the ditch) was a clay soil (sand/silt/clay: 17.6/33.6/48.8%; pH 8.0; om 2.7%) while the sediment in the irrigation channel was classified as a clay loam (sand/silt/clay: 20.1/43.2/36.8%; pH 8.2; om 1.7%). The water in the ditch had pH 7.1, dissolved organic carbon of 1.7 mg/L and had a dissolved oxygen concentration of 13 mg/L.

The weather at the site over the sampling period (May to January) of the study was drier than normal, with only 221 mm of total rainfall (8.72 inches) compared to the 10-year average of approximately 500 mm. There was no rain for approximately 2 weeks before application and the first significant rainfall occurred 24 days after application when 37 mm fell over 2 days. There was no further significant rain (> 25 mm) for ~230 days, apart from one on 183 DAT where 19.6 mm (0.77 inches) fell.

Soil from the treatment area was sampled for 178 days after application (DAT) and sediment was sampled from the control, treatment and transport channel areas for up to 256 days (2, 4, 6 10, 14, 30, 62, 91 120, 178 and 256 DAT). Soil and sediment samples were to 15 cm deep, with the final sediment sampled to 120 cm. Water in the channel was scheduled to be sampled on days 2, 4, 6, 10, 14, 30, 62, 91 120, 178 and 256 DAT but there was no water in the ditch on 62, 120, 178 and 256 DAT. Automatic samplers, located immediately downstream of the control and treatment areas were used to sample the water for 24 hours (1, 2, 4, 8, 16 and 24 hours) after water flowed in the ditch. These occurred on 10, 11, 36, 38, 54, 77 and 100 DAT but these dates do not correspond to any rainfall events at the site and therefore could be due to drainage from irrigation of surrounding fields. DEWHA notes that as there was no rain to fill the channel and cause runoff at the treatment site, there will be little likelihood of movement of diuron.

The results of the soil analysis (limit of quantification was 0.02 mg/kg) showed that diuron dissipated with a DT50 of 142 days calculated using a non-linear regression analysis (first order analysis gives 224 days with r^2 of just 0.3259). The time 0 analyses averaged 3.9 mg/kg soil (range 2.9-4.9 mg/kg) and after 178 days there was an average of 2.2 mg/kg soil (range 1.7 to 3.0 mg/kg). The sediment analysis (LOQ 0.05 mg/kg sediment) showed only positive results for 0, 2, 4 and, strangely, 256 DAT (average concentrations of 0.76, 0.059, 0.12 and 0.065 mg/kg respectively) and only in the treatment area. The sample on 256 DAT could be due to runoff from the surrounding treated soil as it was the first time sampling occurred on a day when it rained (19 mm). [The previous sample on 178 DAT occurred before rain on 183 DAT.] There were no other samples where diuron or it metabolites were detected above the LOQ. Similarly for the water samples, the only positive detections (LOQ 0.01 µg/L) were in the treatment area and for 2 and 4 DAT only (maximum of 0.013 µg/L). There were no other detections of diuron or its metabolites in any other water sample.

DEWHA concludes that the dry weather prevented any runoff occurring, which limited movement of diuron and it therefore remained on the dry soil. The degradation of diuron on dry soil is slow but the final sediment sample may indicate that when rainfall does occur erosion may allow diuron to enter drainage channels, either adsorbed or soil or dissolved in the water.

Study 5 - irrigation ditch in Arkansas

A field dissipation and transport study was conducted according to US EPA Guideline 164-2 (Hornshuh and Antle, 1996). Diuron (80% ac granular formulation) was applied to either side of an irrigation ditch at a target rate of 13.44 kg ac/ha (12 lb/A) using a CO_2 backpack sprayer. No application was made to the channel in the treatment area. The ditch was in Lonoke, Arkansas and divided into 3 areas: upstream control area, treatment area and 3 downstream sampling (transport) areas. The treatment area was 7.6 X 64 m (0.0486 ha) and there was 20.4 m (67 feet) of untreated ditch between the control and treatment and 20.3 m (80 feet) between treatment and the first downstream sampling area. There was 13.7 m (45 feet) of untreated ditch between the three sampling areas.

The soil on the slope and berms was a silt loam soil (sand/silt/clay: 15.2/73.3/11.5%; pH 5.5; om 1.4%) while the sediment in the irrigation channel was not analysed. The water in the ditch had pH 6.2, dissolved organic carbon of 5 mg/L and had a dissolved oxygen concentration of 4.5 mg/L.

The weather at the site over sampling period (November-May) of the study was typical, with ~860 mm of total rainfall (~34 inches) compared to the 10-year average of approximately 914 mm. The first significant rainfall occurred 4 days after application when 43.7 mm fell and 51.3 mm fell two days later (recorded at Adams Field, Little Rock Arkansas, estimated by DEWHA to be 30 km away). Over 2 to 6 DAT a total of 117 mm of rain fell. There were further significant rain events on 15 and 23 DAT of 30 and 65 mm respectively. The monthly totals ranged from 82 to 160 mm over the sampling period.

Soil from the treatment area was sampled for 179 days after application (DAT) and sediment was sampled from the control, treatment and transport channel areas for up to 256 days (2, 4, 6, 10, 14, 30, 62, 91, 120, 178 and 256 DAT). Soil and sediment samples were to 15 cm deep with the final sediment sample to at least 60 cm. Water in the channel was also sampled on days 2, 4, 6, 10, 14, 30, 62, 91, 120, 178 and 256. Automatic samplers, located immediately downstream of the control and treatment areas were used to sample the water for 24 hours (1, 2, 4, 8, 16 and 24 hours) after water flowed in the ditch. These samples commenced on 4, 5, 6, 7, 15, 22, 33, 93, 119 and 152 DAT. A number of these dates correspond to rainfall events as recorded at the weather station used.

The results of the soil analysis (limit of quantification was 0.02 mg/kg) are given in Table A1.33 for samples taken on the berm and slope of the ditch. Note that some are duplicate analyses (4, 9 and 61 DAT) while the rest are a single analysis. Diuron dissipated from the soil with a DT50 of 105 days calculated using a non-linear regression analysis (first order analysis gives 108 and 100 days with r^2 of 0.5166 and 0.5128 for berm and slope sites respectively). The time 0 analyses were 6.39 and 4.66 mg/kg for the berm and slope respectively. After 178 days the levels of diuron had decreased to 1.03 and 1.49 mg/kg soil respectively. The metabolite DCPMU was detected in these soil samples, initially from 0 and 4 DAT for the berm and slopes respectively, and then slowly increased to reach maximums of 0.45 (91 DAT) and 0.34 (179 DAT) mg/kg respectively.

Table A1.34. Concentration of diuron in the upper soil segment (0-15 cm) in mg/kg soil (dry). Results rounded to ±0.01 mg/kg.

		Day after Treatment, DAT											
Sample	Site	0	2	4	7	9	13	34	48	61	91	119	179
Soil	Berm	6.39	5.54	3.95	3.37	12.6	3.81	2.39	4.00	2.03	4.93	2.92	1.03
	Slope	4.66	4.44	2.11	2.34	3.45	5.12	2.58	3.88	2.04	2.15	0.79	1.49
Sediment	Treatment	1.26	0.31	0.65	0.49	0.96	0.46	0.49	0.48	0.37	0.51	0.75	1.61
	Plot a	blq	-	-	blq	0.08	0.07	0.14	0.11	0.15	0.15	0.08	0.26
	Plot b	blq	-	-	0.13	blq	0.12	0.10	0.17	0.15	0.10	0.09	0.21
	Plot c	blq	-	-	blq	blq	blq	blq	blq	blq	blq	0.06	0.11

blq = below limit of quantification = 0.05 mg/kg for sediment. – No sample

The sediment analysis (LOQ 0.05 mg/kg sediment) showed positive results in the treatment area at time zero and was considered by the authors to be due to spray drift. The sample on 179 DAT shows a high value that could be due to runoff from the surrounding treated soil as it was the first time sampling occurred after a heavy rainfall on 153 DAT when 70 mm (2.77 inches) of rain fell. The concentration of diuron in the sediment in the treatment area shows a reasonably consistent level of around 0.5 mg/kg for most of the samples. Only one metabolite was detected, that being DCPMU, and only in the sediment from the treatment area of the channel after 119 DAT. The maximum concentration of DCPMU was 0.13 mg/kg by 179 DAT. These results for sediment in the channels show a pattern that is consistent with the hypothesis that sediment was washing off the treated area and moving downstream.

The results from the scheduled water samples are given in Table A1.34. There were no metabolites detected in any water sample. The majority of positive detections (greater than the LOQ of 0.01 µg/L) were mainly 9 to 34 DAT in both the treatment and downstream areas. However, the 3 representative raw data sheets for water collected from downstream sampling areas a, b and c on 48 DAT all show levels of diuron only slightly below the limit of quantification but clearly above the detection limit. If this is a general situation, then the information tends to show that diuron is a low level contaminant of water systems. The raw data sheets for all the water samples should be presented to refute this hypothesis.

Table A1.35. Concentration of diuron in water (µg/L) from scheduled sampling. Results averaged from duplicate analysis (3 samples from treatment area, 1 sample from each downstream area).

	Day after Treatment, DAT									
	4	7	9	13	34	48	61	91	119	180
Treatment	blq	blq	29	-	blq	16	-	101	blq	
Plot a	-	blq	28	38	101	blq (9)2	blq	blq	blq	
Plot b	-	blq	30	28	11	blq (8)2	blq	blq	blq	blq
Plot c	-	blq	28	29	12	blq (9.8)	blq	blq	blq	blq

blq = below limit of quantification 10 µg/L. – No sample. 1) arbitrary figure, some replicates were blq with others >10 µg/L ; 2) Calculated by DEWHA from the raw data sheets.

Of the 10 events that the automatic water samplers sampled over 24 hours, the peak concentrations were associated with the first 2 events sampled that occurred in from 4 to 6 DAT. The peak concentration was 130 µg/L (event 2, 8 h sample) with high figures of 120-130 µg/L that lasted for 12 hours (samples taken 4, 8 and 16 hours). Subsequent samples during events 3 to 10 (6-152 DAT) had most concentrations of diuron below the LOQ but there were a number just above this level, ie event 5 (23 DAT), 16 h, 11 µg/L. The last positive sample occurred on 152 DAT (event 10, first sample) when one of 2 duplicate analyses gave a reading of 10 µg/L (this is likely to be first flush effect). As the scheduled water samples showed that the samples that are recorded as below the LOQ may only be slightly below the LOQ, the possibility that the data is showing a continuous low level of contamination cannot be ruled out.

It is concluded that while the study does show that diuron primarily remains in the soil at the site of application, runoff causes diuron to enter aquatic systems, either dissolved in water or soil bound from erosion, where it either is mobilised or degrades. The study gives some hints as to the likely fate of diuron but due to the relatively insensitive limit of quantification used, further conclusions are speculative. The study should have reported measured concentrations to the limit of detection, noting that the result below the LOQ may not be accurate.

Study 6 – highway rights-of-way in California

A study was conducted in California's northern Central Valley, to examine the loss of simazine and diuron in runoff from application along highway rights-of-way (Powell, Neal and Leyva, 1996). [This is based on the California Department of Pesticide Regulations web site.] In California these pre-emergence herbicides are

widely used during the rainy season from November to March. Simazine and diuron were applied together in a spray to a 2.4 metre wide strip next to the highway pavement, at the rate of 2.02 kg simazine/ha and 3.59 kg diuron/ha. Concentrations of simazine and diuron in highway runoff were measured during both simulated (13 mm in 1 hr; relatively light to moderate rainfall) and natural rainfall during several winter storms. Simulated rain was applied to plots on treated highway shoulders at three sites (no information on time between application and simulated rain). At one site, none of the artificial rainfall ran off the plot. At the other two sites, 5-12% and 17-46% of the applied water ran off.

Concentrations of diuron in runoff at these two sites ranged from 144-1175 and 348-1770 µg/L. Total mass of herbicide leaving the plots in runoff accounted for 0.2-3.2% and 2.5-5.4% of the applied diuron. Soil was sampled to a depth of 3 m at the site where no runoff occurred, and to 1 m at the other sites. No herbicide was found below 0.3 m depth at any of the 3 sites. Of the total 38 samples taken from the top 0.3 m of soil, 17 contained diuron (maximum concentration 874 µg/kg, just after rainfall simulation). Natural rain runoff (no measure of intensity or amounts were given) was sampled at a fourth site during several winter storms with concentrations of diuron ranging from 46-2849 µg/L. The largest amount removed in any sampled period was 8.4% of the diuron in one 28 h period.

DEWHA notes the high concentrations recorded in the runoff and that 8.4% of applied diuron ran off but comments that the application area (beside the highways) could be compacted and therefore there would be limited infiltration of diuron into the soil.

Literature

In an existing tree orchard on a loam soil (sand 13%; silt 75%; clay 12%; om 2.9%, pH 6.5) in Belgium, diuron was applied at 3 kg ac/ha in April (Rouchaud *et al*, 2000). There were 2 plots used, one never having received any application of diuron while the other had been treated annually for the previous 12 years. Analysis of diuron in the 0-10 cm surface soil layer gave first order degradation curves with half-lives of 81 days ($r = 0.9899$) for the plot receiving diuron for the first time and 37 days ($r^2 = 0.9984$) for the plot treated for the past 12 years. There appears to be an indication that soil micro-organisms can be conditioned to degrade diuron, resulting in quicker degradation rates.

Two grass-seed fields in Oregon (Willamette Valley) were monitored for diuron loss in surface runoff and tile drainage during the first wet season after planting (Rupp *et al*, 2006). One of the fields was 4.34 ha (Field 1) in size and the other smaller, 1.48 ha (Field 2). The soil in both fields was identified as a Woodburn silt loam (10-30% clay and 3-5% organic matter). The average slope of Field 1 was 1% and in the other field the slope was 3.6%.

For Field 1, diuron was applied at 2.2 kg ac/ha on 15 September 2001 and for Field 2 at 2.5 kg ac/ha on 18 October 2002. Samples were collected using an automatic sampler and surface samples were from collection points (flumes) at the bottom of the fields. Each sample represented an average 8 h period (10 samples collected at 48 minute interval; and pooled to a common sample) and was centrifuged before analysis. Sampling commenced for Field 1 with the first surface flow event some 45 days after application and finished in March. Sampling in Field 2 commenced on 15 November with the first surface flow event, 29 days after the application of diuron, and finished on 14 March.

The tile drains, one each in Fields 1 and 2, were also sampled but concentrations in the tile drains were as much as 1000 times lower than in the surface runoff during the first few weeks of runoff events, and they remained lower than surface water concentrations throughout the season. These will not be discussed further but DEWHA notes that it indicates that subsoil movement of diuron is limited.

Initial diuron concentrations in surface runoff were high (initial sample was 2160 µg/L, 45 days after application) and a maximum of 2830 µg/L (approximately 70 days after application) in Field 1 and for Field 2 the maximum was 180 µg/L, though they decreased by two orders of magnitude by the end of the season.

Total losses in surface runoff were between 1.3 and 3% of the amount applied, much higher than losses via the tile drains. The surface runoff production in Field 1 was ~3% of rainfall whereas that from Field 2 was 18% of rainfall.

The concentration of diuron in the runoff water fitted first order kinetics against time in both Field 1 (r^2 = 0.78, ~50 samples) and Field 2 (r^2 = 0.64, ~65 samples). There was a slightly better first order fit against cumulative rainfall for both Field 1 (r^2 = 0.81) and Field 2 (r^2 = 0.67). The authors consider that it may be best to describe the depletion of total diuron in runoff water as a function of cumulative rainfall during the wet season.

To determine whether herbicide runoff along highways threatens water quality, a field study was conducted at two sites in northern California for three rainy seasons (Huang, Pedersen, Fischer, White, and Young, 2004). Several herbicides, including diuron, were selected for study with significant variation in physical/chemical properties.

Diuron was applied to the road verge in a 1.2 or 1.8 metre wide strip along the highway shoulder at 3.5 kg ac/ha (13 Nov 2000) and next year at 485 g ac/ha (27 Nov. 2001). Concentrations of herbicides in runoff were monitored for up to 11 storms following herbicide application, and 24 samples were collected per storm, providing temporal detail. Flow-weighted event mean concentrations were calculated for each herbicide in each storm. The results for the first year (monitoring from 21 Nov to 27 Jan) showed that the maximum concentration of diuron was 10.78 µg/L, with a mean of 1.34 µg/L and total loading corresponded to 0.57% of the applied diuron. Diuron was only detected in the first 8 rainfall events. The next year the maximum concentration was 2.46 µg/L (DEWHA notes that the application rate was much lower) with a mean concentration of 0.82 µg/L and total loading represented 4.44% of applied. Diuron was only detected in the first 4 runoff events. A first-order model successfully described the declining herbicide concentrations in soil and in surface runoff for all sites. The authors noted that the fitted first-order coefficients were always higher for runoff than for soil, indicating that the herbicide that persists in the source zone becomes less available for runoff as the time since application increases. The authors concluded that the most critical factors in determining seasonal herbicide loss to surface water were the timing and intensity of the first storm following application, affecting total seasonal runoff by up to 2 orders of magnitude.

The authors also conducted an analysis of the 'first flush effect' by looking at the percentage of herbicide loading against the percentage of runoff for each runoff event they monitored. The authors state that a first flush effect was not apparent. Although herbicide concentrations at the beginning of an event were often higher than at the end, the higher concentrations were limited to a short period and stabilized for the duration of the event.

4.3 Modelling studies

A modelling study to assess the impact of management practices with diuron use in sugar cane on water concentrations in the Pioneer River has been provided.

Title	A Modelling Assessment of the Effect of Management Practices on Diuron Concentrations in the Pioneer River
Authors	Hoogeweg et al
Date	2009
APVMA Data ID	
Test Guideline	NA – modelling study
Data Validity	2*
Data Relied On	Yes - the data were considered to be critical and was relied on in this assessment.

Test System

The objective of the modelling study was to develop effective and practical best management practice (BMP) for diuron use in sugarcane in Queensland, supported by modelling of primary routes of entry, typical agronomic practices and management/mitigation practices, along with consideration of the environmental fate of diuron in water systems on a catchment scale. The Pioneer River watershed was selected as the subject for the modelling study. The watershed was modelled with the Riverine Water Quality (RIVWQ) model using extensive information on soils, topology, long-term hydrology and climatic data, land use and digital image data from publicly available sources. Runoff was estimated with the Pesticide Root Zone Model (PRZM) using different scenarios developed to account for soils, cropping practices and weather throughout the watershed. Runoff and drift loadings were applied to the receiving waters defined by RIVWQ so that concentrations of diuron could be calculated at many locations in the watershed.

Within the Pioneer River catchment, agricultural land uses are dominated by grassland (30.5%) and irrigated sugarcane (23%). Forestry uses account for around 41%.

Baseline modelling

The basic cropping scheme for modelling used a fixed period (12 months) before harvest. Following planting (day 1), emergence was assumed at 10 days, application at 11 to 60 days following planting and temporally distributed. Crop maturing occurs on day 245, harvest on day 365 and ratoon emergence occurring 10 days following harvest unless a fallow year.

Peak application was modelled to occur during November and December (50% of all application in the catchment). The soil half-life chosen for modelling was 74 days, which was a geometric mean of available soil half-lives. The water half-life was set at 33 days and the anaerobic sediment half-life set at 5 days based on study data. The Koc was set at 366 L/kg, which was the lowest value in the available Koc range from test data.

For baseline management practices, the application rate was set at 1.8 kg ac/ha. It was assumed that full market penetration was reached and all fields cropped in sugarcane are treated. Based on a typical year, 20% of all sugar cane areas were assumed to be fallow (assigned randomly in the model), and 65% of the sugarcane received irrigation (assigned randomly in the model).

Evaluation of BMP

To evaluate the impact of BMPs, a series of scenarios were developed which included the following changes to management practices:

- No sugarcane was grown on slopes >5%;
- Application rate was reduced (band spraying reducing per hectare rate to 0.9 kg ac/ha);
- No application of diuron in the wet season;
- Combined effect of reducing the application rate and dry season application;
- Improved cultivation using reduced tillage;
- Presence of a vegetative buffer strip;

- Presence of a sugarcane trash layer;
- Proximity of paddocks/farm to stream;
- Combined effect of reduced application rate, dry season application, trash layer presence and no application on slopes >5%.

Findings

Baseline modelling

The model estimated drift and runoff contributions in the Pioneer River catchments and estimated concentrations in the Dumbleton Weir and at the mouth of the Pioneer River during a 12-year simulation period from 1992 until 2003. The results showed drift being a very minor contributor, with runoff accounting for over 99% of the mass load in the catchment. Total run-off mass ranged from a minimum of 243 kg in 2002 to a maximum 1093 kg in 2000. The maximum annual estimated environmental concentrations for diuron in the Dumbleton Weir ranged from 0.73 µg/L (2002) to 5.02 µg/L (2000) while predicted annual maximum concentrations at the river mouth ranged from 0.36 µg/L (1995) to 3.70 µg/L (2000).

To gauge how the baseline modelling performed, these predicted results need to be compared to available measured results. In the 2002-03 season, a 1 in 2 year rain event (~230 mm rain over 2 days) resulted in a peak measured concentration in the Dumbleton Weir of 8.5 µg/L. This is around 11.5 times higher than the estimated peak in the model for 2002, but not too dissimilar to the peak modelled value of 5.02 µg/L in the Dumbleton Weir. Nonetheless, DuPont in their report provide argument that this value is an outlier.

At the river mouth, the maximum computed concentrations were <1 µg/L for 7 of the 12 years modelled, and between 1 to 1.5 µg/L for four years. The peak concentration was predicted to be 3.7 µg/L. There are no actual monitoring data from 2003 or earlier to directly compare with these modelled results at the mouth of the Pioneer River. Rohde *et al* (2006) provide 2005 monitoring data from within the Pioneer River, although this isn't actually at the river mouth. In this year, from 23 January to 27 January 2005, diuron was found at 3.3 µg/L reducing to 0.55 µg/L over this period, while in the drier months (sampling from 9 April to 11 April), diuron concentrations remained relatively steady between 0.16 and 0.48 µg/L.

Based on very limited directly comparable data, it would appear the model is slightly underestimating diuron concentrations, although it should be noted that concentrations at the river mouth could reasonably be expected to be lower than those further upstream due to increased contribution to runoff from other areas. This may be due to the chosen half-life of 74 days being too short for the region modelled, or any number of other factors. There will always be difficulties in comparing complex modelled results with a limited number of monitoring data. However, overall, the model appears to work sufficiently using the baseline data to be able to compare current management practices with impacts on runoff from changing these practices.

Best Management Practices

The following table shows the outcomes of the modelling in terms of annual maximum daily estimated concentrations of diuron at the mouth of the Pioneer River for the baseline scenario and the various changes in management practices:

Table A1.36: Computed Annual Maximum Daily Estimated Environmental Concentrations (µg/L) in the mouth of the Pioneer River, 1997-2003

Management practice	1997	1998	1999	2000	2001	2002	2003

Baseline - Pioneer River	0.81	1.25	1.08	3.7	0.83	0.61	0.43
Slope scenario	0.8	1.24	1.08	3.44	0.79	0.61	0.43
Reduced rate	0.4	0.62	0.54	1.85	0.42	0.3	0.22
Delayed application	0.17	0.84	0.27	0.23	0.37	0.01	0.08
Combined rate/application	0.084	0.42	0.135	0.114	0.186	0.005	0.038
Reduced tillage	0.46	0.84	0.79	2.7	0.56	0.45	0.22
Vegetative buffer strip	0.32	1.09	1.02	3.17	0.63	0.67	0.2
Use of trash layer	0.24	0.59	0.58	1.94	0.36	0.35	0.1
100 m setback	0.76	1.1	0.96	3.3	0.7	0.47	0.41
Combined practices	0.021	0.218	0.016	0.059	0.012	0.003	0.009

Table A1.37: Reductions (%) of Annual Maximum Daily Estimated Environmental Concentrations at the mouth of the Pioneer River, 1997-2003

	Reduction in Runoff (%) compared to baseline management practice							
Management practice	1997	1998	1999	2000	2001	2002	2003	Average
Slope scenario	1.23	0.80	0.00	7.03	4.82	0.00	0.00	2.0
Reduced rate	50.62	50.40	50.00	50.00	49.40	50.82	48.84	50.0
Delayed application	79.01	32.80	75.00	93.78	55.42	98.36	81.40	73.7
Combined rate/application	89.63	66.40	87.50	96.92	77.59	99.18	91.16	86.9
Reduced tillage	43.21	32.80	26.85	27.03	32.53	26.23	48.84	33.9
Vegetative buffer strip	60.49	12.80	5.56	14.32	24.10	-9.84	53.49	23.0
Use of trash layer	70.37	52.80	46.30	47.57	56.63	42.62	76.74	56.1
100 m setback	6.17	12.00	11.11	10.81	15.66	22.95	4.65	11.9
Combined practices	97.41	82.56	98.52	98.41	98.55	99.51	97.91	96.1

Based on these values from 1997-2003, it can be seen that delaying application to the drier months, or reducing the application rate, can both significantly reduce the amount of runoff. A combination of these two practices leads to an overall predicted average reduction in maximum levels of almost 87% using the reduced number of years above, or by 80.8% if the whole 12 year modelling cycle is used.

The use of trash layers (modelled by decreasing the curve number) is also a potentially powerful tool in reducing runoff, while results from reducing tillage, vegetative buffer strips or setback distances can all have an improved, although somewhat variable, result with respect to reducing runoff.

A combination of all the major management practices resulted in an overall mean reduction in runoff of around 96% (7 year data set above) or 94.1% when using the whole 12 year simulation period.

Conclusion

Comprehensive modelling in the Pioneer River Catchment has demonstrated the potential impact of changing diuron management practices in sugar cane to reducing water concentrations resulting from runoff. While certain management practices such as use of vegetative buffer strips, setback distances and use of trash layers appear to help reduce runoff, the results are somewhat variable and such practices would be more subjective in their implementation.

However, easily controlled practices such as a reduction in per hectare application rates and adjusting the timing of application away from wetter months would appear to have a significant positive effect on reducing runoff, with a combination of these two practices predicted to reduce maximum exposure concentrations on average by around 80%.

5. MEASURED FIELD CONCENTRATIONS

5.1 Australia

Water – Drainage channels/Streams/Rivers

Mackay-Whitsunday region (Queensland)

The Mackay Whitsunday region covers an area of approximately 9000 km^2 along the central Queensland coast. Major land uses in the region include sugarcane, beef grazing and urban/industrial, with considerable areas of national park/state forest. The Mackay Whitsunday Healthy Waterways Program is an initiative of the Mackay Whitsunday Natural Resource Management (MWNRM) Group to ensure that sound science underpins aquatic resource management and water quality target setting in the region.

As part of this program there has been on-going monitoring of creeks and rivers for a range of parameters for several years, including chemical contaminants. This has been a relatively dry period compared to previous years with average annual rainfall 50% below average and significant runoff occurring only during a few days of heavy rainfall each year.

Season 2002-3

During a 3-day rainfall event (13 to 15 February 2002) water samples were collected at four sites in the Pioneer River catchment (Simpson, 2002). This river catchment is extensively used for sugarcane production with 19% of the total catchment of 1570 km^2 under cane production, predominantly on the river flats. The remaining area is for cattle grazing.

There were minor runoff events on the 13th February that had the effect of flushing the river. The next day a more significant rainfall event occurred with substantial rain falling mainly in the land under cane production in the centre of the catchment. The normal rainfall distribution is for heavier falls on the rim of the catchment. The total rainfall over the two days averaged 233 mm over 16 rain gauges in the catchment, with a range of 127-356 mm. Examinations of the rainfall records over the previous 10 years indicate that this is a 1 in two year event. Average rainfall in the catchment for February is ~350 mm.

Samples were taken from 4 sites across the catchment. At the Dumbleton Weir gauging station (located at the bottom of the catchment; drainage area of 1485 km^2, ~95% of catchment), three samples were taken during 14 February 2002 and one the next morning; and Finch Hatton creek, a small largely unimpacted creek within the catchment, two samples were taken on 14 February 2002. At the other two sites only one sample was taken, Mia Mia Bridge on the Pioneer River (drainage area of 326 km^2) and at Cattle Creek (drainage area of 757 km^2), both in the middle sections of the catchment. The highest levels were found in the Dumbleton Weir (8.5, 2.5 and 1.1 µg/L at the first, second and third samples on 14 February; 0.90 µg/L the following morning) while no diuron was detected at Finch Hatton Creek. The samples at Mia Mia Bridge and Cattle Creek showed 0.40 and 1.0 µg/L respectively.

The pesticide loads at Dumbleton was determined using simple interpolation and integration over the flow event with extrapolation to get a point concentration at the very start and end of the hydrograph. Total diuron load was estimated at 470 kg.

Considering that last usage of diuron would have been earlier during canopy closure (December/January) and that some degradation in the field and adsorption may have occurred, the amount of diuron in the runoff is significant, possibly accounting for more than 1% of total applied diuron.

A further water sample taken at Dumbleton Weir in June 2002 showed the level of diuron was below the detection limit (0.3 µg/L).

Season 2003-4

In the next year's 'wet' 2003-4 samples were taken from Goosepond Creek and Sandy Creek, again during major flow events (Queensland NRM, 2007). The Pioneer River was not sampled.

The sampling in Goosepond Creek at Willets Road commenced at 17:45 on the 25/2/2003 and finished the next day at 11:35 with 4 samples being taken over this 18 hour period. The maximum concentration of

diuron was 5.3 µg/L and the mean was 2.8 µg/L. The sampling at Sandy creek at Homebush commenced at 00:00 on 2 March 2003 and finished at 00:00 on 6 March with 6 samples taken over this period. The maximum concentration of diuron was 1.6 µg/L and a mean of 1.05 µg/L.

Season 2004-5

In the 2004-5 wet season there was a more extensive sampling program in the Mackay-Whitsunday region where 21 river catchments were analysed and sampled for diuron (Rohde *et al*, 2006).

A total of 21 sites were selected to represent runoff from single land use sub catchments (forest, sugar cane, grazing and urban) and mixed land-use catchments. There were two events sampled in January 2005 – in early January, samples were collected from 7 sites, and 18 sites in late January. A minor event was also sampled in April. Marine sampling occurred only from the larger event in late January. Diuron analysis was performed using gas chromatography, liquid chromatography and mass spectrometry.

The sugar cane sub-catchments produced the highest diuron concentrations compared to other land use sub-catchments. The range of diuron concentrations in the various land use sub-catchments was <0.01 to 0.04. µg/L (urban, n = 10); 0.17-6.3 µg/L (sugar cane, n = 12); <0.01 (forest, n = 6); 0.01-0.11 µg/L (grazing, n = 9); and <0.01-6.5 µg/L (mixed land use, n = 49). In addition, three drains were sampled (1 sample each). Two cane drains had residues of 36 and 26 µg/L while one forest drain did not detect any diuron. Considering the whole data set (minus the concentrations in the drain samples), there were 86 samples with diuron detected in 64 samples, and of these, 16 samples were >1 µg/L. The 50th, 90th and 95th percentile water concentrations were 0.12, 2.5 and 3.8 µg/L respectively (calculated by DEWHA).

Lower Burdekin and Don River Catchments (Queensland)

Several waterways in the lower Burdekin were monitored for pesticide residues from 2005 to 2007 (Lewis *et al*, 2007) in both low flow and event flow conditions. Sampling sites ranged from the Haughton River in the north to Yellow Gin Creek (a control site) in the south, as well as the Don River near Bowen. Overall, 132 water samples were analysed for pesticide residues in the lower Burdekin and Don River catchments during this period including 43 ambient (low flow) samples and 89 event (high flow) samples. Ten herbicide residues were detected including diuron.

Under ambient flow conditions, diuron was detected in 29 of the 43 samples and where detected, water concentrations ranged from 0.01 to 8.2 µg/L. Eight samples showed concentrations >1 µg/L, and the 50th, 90th and 95th percentile water concentrations of the ambient flow data set were 0.04, 1.8 and 2.7 µg/L respectively (calculated by DEWHA).

Under event flow conditions, diuron was detected in 63 samples with concentrations ranging (where detected) of 0.01 to 3.8 µg/L. Ten samples showed concentrations >1 µg/L and the 50th, 90th and 95th percentile water concentrations of the event flow data set were 0.22, 1.09 and 1.4 µg/L respectively (calculated by DEWHA).

Tully and Murray Rivers Region (Queensland)

Findings relating to monitoring of surface water (2005/06) in these regions are described in Faithful *et al,* (2007). The Tully and Murray regions are located within the wet tropics of North Queensland and drain areas of rainforest and intensive agriculture. Water quality monitoring sites (total of 16 stations) have been situated at specific locations along watercourses within the two catchments where a high proportion of their upstream catchment is represented by one of the major land uses in the region, including natural forest, sugarcane, bananas, grazing, urban and plantation forest.

The timing of sampling episodes generally correlated with flow events. Surface samples (top 50 cm of the water column) from all sites were collected in a triple rinsed bucket. Subsamples were then collected from the bucket for analysis. For herbicides, analysis was performed using liquid chromatography (LC/MS). Water samples were extracted with dichloromethane prior to analysis.

The sugar cane sub-catchments produced the highest diuron concentrations compared to other land use sub-catchments. The range of diuron concentrations in the various land use sub-catchments was <0.01 to 0.66 µg/L (urban, n = 11); 0.04-8.7 µg/L (sugar cane, n = 24 with one further sample showing a concentration of 19 µg/L); <0.01-0.02 (forest, n = 20, only one positive sample); <0.01-1.2 µg/L (grazing, n = 16); and <0.01 (bananas, n = 8). Considering the whole data set, there were 80 samples with diuron detected in 44 samples, and of these, 9 samples were >1 µg/L. One sample showed very high residues of 19 µg/L. Of the remainder of the full data set, the 50th, 90th and 95th percentile water concentrations were 0.03, 0.98 and 1.67 µg/L respectively (calculated by DEWHA).

Hervey Bay, Queensland

Low concentrations of diuron, together with other herbicides, were detected in surface waters in inter-tidal seagrass meadows of *Zostera capricorni* in Hervey Bay, Queensland (McMahon *et al*, 2004).

Two major rivers flow into Hervey Bay, the Mary and Burrum Rivers. The Mary River catchment (9595 km^2) is 60% dry land grazing, 33% forestry and 8% agriculture with sugarcane covering 0.8% of the catchment (8000 ha of cane, 9.6 tonnes of diuron used, Hamilton and Haydon 1997). The Burrum River has a small catchment (3118 km^2) but has a slightly larger sugarcane area covering 2.7% of the catchment (8500 ha, 3.3 tonnes of diuron used, Hamilton and Haydon 1997). The sugarcane is generally spread out along the lower reaches of the Mary River and is some distance up-stream from the estuary of the Burrum River. Note that the area of sugarcane is based on 1994 data.

Surface waters (together with sediments – discussed below), were sampled in the seagrass meadows and the health of the seagrasses monitored as well. The two major rivers flowing into the Hervey Bay, the Mary and Burrum Rivers were also sampled. Sampling occurred in April and December 2002, both periods of low rainfall and low river flows and in February 2003 and 2004 during moderate flow events (monthly rain fall 325 mm).

The concentration of diuron in April and December in the surface water at the seagrass meadows ranged from <5 (detectable but below limit of quantification) to 25 ng/L. Sampling of the Mary River in April and December 2002 gave levels ranging from 25 to 80 ng/L and for the Burrum River the levels in December were from <5 to 60 ng/L (no samples taken in April in the Burrum River).

Sampling of the Mary River in February 2003 during the moderate flows (first flush flow for a year but the tail of run-off event sampled) gave concentrations ranging from 15 to 105 ng/L with the lowest values at the bottom of the tide and highest on the incoming tide and on the high tide. The authors suggest that this pattern of diuron concentrations could be due to diuron being sourced from a marina downstream of the sampling site. The samples from the Mary River taken in 2004 gave levels of diuron between 25-35 ng/L. Sampling seawater at the seagrass sites in February 2003 and 2004 gave low levels of diuron of not detectable to 50 ng/L.

The seagrass at the sampling sites appeared healthy and there was growth and development during the study period. Seagrass abundance was greater and plants larger in December than in April. Seagrass health was not determined during the two river flow events. The authors conclude that with the low background levels herbicides in the water, predominantly diuron, there was no detectable impact on seagrass.

1991 to 2005 – New South Wales Cotton Growing Regions

The NSW Department of Land and Water Conservation (NSW DLWC), Central and Northwest Regions Water Quality Program routinely monitored the major rivers in the central and northwest of NSW for pesticides from 1991 to 1999 (Cooper, 1994, 1995 and 1996; Muschal, 1997 and 1998). This area of NSW is mainly associated with irrigated cotton and therefore the sampling of these rivers was focused on the cotton growing season (October to March/April). Table A1.37 summarises these results.

Samples were routinely taken weekly during December-January (8 samples), fortnightly for 2 months on both sides (October-November and February- March) and monthly for the rest of the year. The analyses used for diuron (and other herbicides) involved a solid phase extraction of the water samples and samples were either centrifuged or filtered to remove any sediment. Therefore the results in these reports are for the soluble (dissolved) diuron.

Table A1.38. Detections of diuron from the NSW DLWC Central and Northwest Regions Water Quality Program by river basins and year. Results as maximum concentration detected µg/L (estimated from graphs and are approximate values)

	1991/92	1992/93	1993/94	1994/95	1995/96	1996/97	1997/98
Borders Rivers	5	3	2.5	0.4	1	2	0.9
Gwydir River	5	4.2	1	5	23	5.4	10
Namoi River	0.65	0.9	0.2	<0.05	0.2	0.2	2
Macquarie Rivers	0.2	0.3	<0.05	<0.05	<0.05	-	-
Darling R		<0.05	<0.05	<0.05	<0.05	0.1	-
No. of positive samples (all rivers) and no. of samples[1]	63/230, 27.4%	33/230, 14.3%	35/255, 13.7%	28/209, 13.4%	14/280, 5%	27/300, 9%	56/300, 18.7%

1) Total number of analyses per annum for pesticides including upstream areas.

Diuron was detected in all river basins near irrigated cotton and not necessarily associated with runoff events. The highest figure, in the Gwydir River is from a runoff event and shows that very high levels can occur. Most detections were during the irrigation season (December-March) and in the irrigation areas. Sampling upstream of the irrigation areas showed only occasional detection and at low levels compared to the irrigation areas.

There was a heavy rainfall event in January 1997 that lasted for 3 days with 65-208 mm of rain across the Gwydir River catchments. Samples were taken in the Gwydir River during the rainfall gave a maximum concentration of diuron of around 23 µg/L in the first sample taken as the rivers started to respond to the heavy rain. Levels then declined to 6 µg/L as the water level in the rivers rose. Over the storm event the total load of diuron was estimated at 26.5 kg. After the rain finished, the rivers rose 2 days later to peak levels from flooding in the upper catchments. There were no detectable levels of diuron in the bulk of this water.

Sediments in these rivers were sampled in 1995-96 and 1997/98. Diuron is not reported has having been detected although it is unclear if it was below detection limited or just not reported.

Some more recent summary data for the Gwydir and Namoi rivers is given in Table A1.38 below (Mawhinney, 2005). While the results clearly show reduction in the concentration of diuron after 1999/00, it should be noted that this is also when there was dry conditions with below average rainfall for several years and thus less runoff of diuron. Also the frequency of sampling was reduced to monthly after 2000/01 and thus the chance of detecting peak values is reduced. It is also when Roundup Ready cotton was introduced into the market and use of residual herbicides such as diuron declined, as shown by a market audit survey conducted by Cotton Consultants Australia (presented by Cotton Australia, 2006). The number of positive samples in the total data for the river catchments from 2001/02 would appear to support this survey result.

Table A1.39. Detections of diuron from the NSW DLWC Central and Northwest Regions Water Quality Program by river basins/catchments and year. Results as maximum concentration detected in µg/L.

	1998/99	1999/00	2000/01	2001/022	2002/032	2003/042	2004/052
Border Rivers	4.9	13.4	1.3	2.8	0.3	0.3	1.0
Gwydir catchment	7.2	8.4	4.0	2.6	15.1	19.5	3.2
Namoi catchment	0.8	0.6	1.9	0.9	0.2	0.1	0.1
No. of positive samples (all rivers) and no of samples1	79/400, 19.7%	75/413, 18.2%	57/438, 13.0%	28/290, 9.7%	27/348, 7.8%	29/344, 8.4%	30/326, 9.2%

1) Total number of analyses per annum for pesticides including upstream areas. 2) Monthly samples only

For comparative purposes, DEWHA has undertaken a more detailed assessment of the data from 1991-2005 including consideration of monitoring from 1991-1998; monitoring from 1999-2005; monitoring in rivers only, 1999-2005; monitoring in creeks/brooks only, 1999-2005 (these data were provided by Cotton Australia in their submission to an earlier version of the Diuron review). The following table summarises these statistics.

Table A1.40: Summary of Monitoring Data for Diuron in the Riverine Systems of the Namoi, Gwydir and Border River Valleys, 1991-2005.

	n	% detection	Max	90th %1	50th %1
Whole data, 1991-1998	2259	12	82.1	5.9	0.4
Whole data, 1999-2005	2248	12	19.5	1.93	0.3
Rivers, 1999-2005	1346	8.4	8.4	1.3	0.3
Creeks, 1999-2005	902	17.2	19.5	2.6	0.3

1) from the range of positive detections

The data generally show that levels detected have decreased significantly since 1999 and onwards, with the 90th percentile of the 1999-2005 data of 1.93 µg/L being substantially below the 5.9 µg/L from 1991-1998 (based on positive detections only).

Further analysis of the 1999-2005 data showed that in rivers, frequency of detections were much lower than creeks (8.4% compared to 17.2% respectively), and levels found were generally lower. With the creek data, one creek in particular (Thalaba Creek at Merrywinebone) was found to have consistently higher levels of diuron than other creeks. Removal of this creek from the data set resulted in creek detections of 13% of observations with a 90th percentile of 1.7 µg/L.

1990-1995 – South Western NSW

Monitoring in the southwestern irrigation areas of NSW over a 5 year period (1990-1995) showed at times significant levels of diuron (Bowmer *et al,* 1998). The area is a major agricultural area comparing 2 irrigation schemes, the Murrumbidgee Irrigation Area (MIA) with 560,700 ha under irrigation and the Murray Valley region with 715,700 ha under irrigation. Diuron is used for weed control in horticulture particularly citrus and in irrigation channels during winter.

Sampling of the main drains (1991-93) in the MIA showed that in 41% of all samples taken diuron was detected in water (detection limit 0.1 µg/L) with the maximum of 9.5 µg/L. The supply water had no detectable level of diuron. During the 1994-95 irrigation season, from September to May, surface water was sampled monthly in the MIA (18 sites, 4 supply sites, 1 swamp, 2 lake sites, 1 creek and 10 drains). Diuron

was detected at least once per month and the maximum concentration was 5.4 µg/L that occurred in October. The maximum number of detections was 12 of the 18 sites in one month.

Tile (sub-surface) drains at 49 horticulture farms in the MIA were sampled in 1992 (January, May and August). Approximately 40% of farms had detectable levels (>0.05 µg/L) of diuron and generally the same farms were positive whenever sampled. Maximum concentrations were 28 µg/L.

The first surface runoff from a citrus farm after application at 4.5 kg ac/ha had concentrations of diuron of between 1.2 to 20 µg/L with an average of 10.9 µg/L. Grab samples for Mirrool Creek just above Barren Box Swamp (this creek drains the Mirrool and Yanco irrigation areas and flows into Barren Box Swamp) in 1991 showed diuron was present most of the time but at low levels (0.06-0.17 µg/L for 1991). In 1994 daily automatic monitoring from 5 October to 30 November of Mirrool Creek gave levels of between 0.05 and <1 µg/L. Daily automatic monitoring of Little Mirrool Creek at the junction with Mirrool Creek from 5 October to 30 November 1994 gave mean levels of 1.19 µg/L with range 0.1 and 7.5 µg/L. All samples from both creeks had diuron present above the detection limit (0.05 µg/L).

1997-2001 – South Western NSW

During the four years from July 1997 to June 2001, Murrumbidgee Irrigation Limited (MIL) reported to NSW Department of Environment and Conservation (NSW DEC) the results of water monitoring of drainage water at 15 sites (NSW DEC, 2005). The sampling was for diuron together with 13 other chemicals as required by the Environment Protection License. These were presented to DEWHA by NSW DEC as a statistical summary and a graph.

Table A1.41. Summary of chemical test results from Murrumbidgee Irrigation Limited July 1997 to June 2001. All concentrations are in µg/L

No. of Samples	Minimum	Maximum	Percentile			
			75th	90th	95th	99th
548	<0.1	22.7	0.4	0.9	2.26	12.6

As Table A1.40 clearly shows, diuron is detected in drainage water in the MIA at relatively high levels, significantly higher than those detected in the previous study conducted just 5 years earlier (1990-1995, see above). The data showed almost each year that there are several detection of >20 µg/L, which are high and of concern. However, it is unclear where these detections were taking place, how the samples were taken (monthly or weekly grab samples, automatic samples etc) and how these levels relate to levels in natural waterways.

2004-2006 – South Western NSW

DEWHA has reviewed the license compliance reports from MIL currently available for the last three reporting years (Murrumbidgee Irrigation 2005; 2006; 2007), and undertaken some more detailed analysis of the monthly data from these periods for the 14 different surface water areas sampled. Drought conditions have meant limited flows, so many samples were not taken (in times of “no flow”). Also, as the data are taken monthly, detections are unlikely to represent peak concentrations where found. Based on the data, the highest levels found (for example, where maximum levels are >2 µg/L) occur in the cooler months (April through August). Analysis of these months shows diuron found (0.1 µg/L or higher) in 60.6% of samples (n = 137), and where detected, the 90th percentile was 2.1 µg/L. The maximum level detected was 13.2 µg/L. 11% of samples were >1 µg/L. In the warmer months (taken as September through March), diuron was found (0.1 µg/L or higher) in 36.2% of samples (n = 185), and where detected, the 90th percentile was 0.54 µg/L. The maximum level detected was 1.1 µg/L. 1.1% of samples were >1 µg/L.

It is worth noting in regards to these data, maximum levels reported are unlikely to represent peak concentrations, and it is not possible to determine the likely period of time elevated levels can occur in surface waters. To illustrate this, Hyne and Aistrope (2006) report results of field measurements determined the cellulose membrane passive samples deployed over a 7 to 22-d period from mid-October to mid-November 2004, at two sites also sampled by MIL receiving runoff from citrus and rice fields. The average daily diuron concentrations at both sites were all between approximately 1.5 to 4.5 µg/L, reflecting the more typical diuron water concentrations at these sites for that period, rather than the low concentrations measured in the grab samples collected each monthly by MIL (values all <1 µg/L for the corresponding sites). This shows that exposure in surface waters could be at elevated levels for extended periods of time, but such periods are unlikely to be reflected in long term monitoring due to time between sampling.

Water – Marine waters

There was a visible flood plume off shore from Mackay from the Pioneer River that was sampled on 27 and 28 January 2005 with results reported in Rohde *et al* (2006). Samples were taken in the plume and followed the plume northward with the southerly current for approximately 80 km and up to 25 km off shore. There was also a plume from the Proserpine/O'Connell River that was also sampled. The plume was visible to satellites from the 23 January to 9 February. Table A1.41 gives these results and an estimate of the distance from the mouth of the relevant river.

Table A1.42. Concentration of diuron in off shore sites.

Site name	Date	Salinity (PSU)	Estimated distance from river month, km	Diuron µg/L
PSC1	27-01-05	30	23	0.07
PSC2	27-01-05	31	13	0.08
PSC4	27-01-05	7	3	0.44
PSC5	28-01-05	27	5	NDR
PSC6	28-01-05	18	22	0.24
PSC7	28-01-05	27	43	0.13
PSP1	27-01-05	29	3	0.33
PSP3	27-01-05	29	13	0.31
PSP8	28-01-05	34	36	0.06
PSP9	28-01-05	35	31	NDR
PSP12	28-01-05	33	5	0.05

PSC = the Proserpine/O'Connell River plume. PSP = Pioneer River plume. NDR = No diuron detected, detection limit given as 0.1 µg/L

The report graphed the salinity of the plume against the concentration of diuron from the O'Connell River, which showed a negative correlation (r^2 = 0.9899, determined by DEWHA), and concludes that dilution with seawater was the only mechanism reducing the concentration of diuron in the plume. All the data fit to this line reasonably well except for two points, PSP 1 and PSP3. As this shows that the only factor that reduced the concentration of diuron was dilution, it implies that there was no degradation within the plume.

Further plume samples are reported in Lewis *et al* (2007) from a flood plume produced from the Haughton River and Barratta Creek (Queensland) in 2007. Diuron was detected in 12 of 14 samples at concentrations of <0.01 to 0.08 µg/L. It is possible the extent of the plume was underestimated as a sample collected from an area thought to be outside the plume (Cape Cleveland) contained residues of diuron of 0.02 µg/L. The possibility of water influx from another source (for example, the Burdekin River) was considered unlikely and the report notes that pesticide monitoring within the Burdekin River plume in 2007 did not detect any pesticide residues.

Passive samplers were deployed at inshore creek and river mouth sites in the Wet Tropics of the GBR at the end of the dry (November 2004) and during the wet (January 2005; Shaw and Müller, 2005). The dry samples follow on from 2 relatively dry years where only one major flood event was recorded in the Wet Tropics (January 2003). The January samples were before the first big floods for the wet but there were small visible plumes extending a few hundred meters from the river mouths. The reef sites were Double Island, Fitzroy Island, High Island, Normanby Island, South Barnard Island and Dunk Island and the rivers were the Russell/Mulgrave and Johnstone Rivers. The reef sites were between 8.6 to 30 km from the nearest rivers and the river sites were 500 m offshore. The samplers were deployed for approximately 8 days in November and 11 days in January.

Of the ten herbicides included in the analysis of the passive samplers, diuron was commonly detected with levels of 0.2-0.7 ng/L in November and 0.5-1.6 ng/L in January, all expressed as integrated average samples over the deployment period. As no in-field calibrations were used, a conservative figure of 0.8 L/day was used, which could underestimate the true water concentrations. The authors note that the samplers provide a time weighted average of water concentrations and therefore do not pick up transitory peak concentrations. DEWHA also notes that the samplers were not used when high concentrations of diuron could be expected after runoff and are measuring the background levels some 2 years after the last period of significant runoff.

Souter (2009) provides electronic information on pesticide monitoring of the inshore Great Barrier Reef by the Reef Quality Marine Monitoring Program. Pollutants at trace concentrations in water are detected, monitored and quantified using time integrated passive sampling techniques. These techniques are based on the diffusion of chemicals from the water into a sampling phase that has a relatively high capacity for the chemicals of interest and provide a quantitative measure of the concentration of analytes in the samplers. Average water concentrations in the environment during the time of deployment are derived from the concentrations sequestered in the sampler from a deployment using calibrations conducted in the laboratory.

Based on information provided in ARCGIS format, DEWHA has calculated the approximate distances between the 13 inshore reef sites and the closest point to the Australian mainland. In addition, the average wet season concentrations between 2005 to 2008 (ng/L) are provided. These values are shown in the following table:

Table A1.43: Approximate distances (km) between sampling points and the mainland, and average wet season diuron concentrations (ng/L) from 2005 to 2008.

Sampling site	Approximate nearest distance (km) to mainland	Average wet season diuron concentration (ng/L), 2005-2008
Lizard Island	30	0.734
Pixies Garden	35	0.171
Low Isles	15	5.41
Fitzroy Island	4-5	5.07
High Island	4.5	5.41
Normandy Island	10.5	4.57
Dunk Island	4	4.12
Orpheus Island	15.5	2.2
Magnetic Island	6.5	2.31
Cape Cleveland	-	4.57
Inner Whitsunday	2.5	1.01
Outer Whitsunday	12.5	4.25
North Keppel Island	13	0.448

Kapernick *et al*., (2007) describe results from routine passive sampling from 10 of these inshore reef sites where sampling continued throughout the wet and dry seasons of 2006-07. The following results are summarised for diuron:

Table A1.44: Estimated concentrations in inshore reef waters (ng/L) predicted from passive samplers

	Dry Season			Wet Season		
Site	Max	Min	Number	Max	Min	Number
Pixies Pinnacle	<1	<1	1	0.59	0.51	2
Low Isles	1	0.08	4	5.2	0.44	6
Fitzroy Island	1.8	0.22	4	5.1	<1	5
High Island	0.54	<1	2	14	3.9	2
Normandy Island	0.84	<1	2	5.3	0.28	5
Orpheus Island	0.07	<1	2	0.67	<1	3
Magnetic Island	0.29	0.25	3	3.3	<1	3
Inner Whitsunday			0	9.4	0.89	5
Outer Whitsunday			0	17	<1	6
North Keppel Island	1.3	<1	4	2.6	<1	3

These data suggest inshore reef concentrations are higher in the wet season. For diuron, the highest estimated concentration was approaching 20 ng/L (0.02 µg/L), but were generally <10 ng/L (0.01 µg/L) in the wet season. In the dry season, levels were generally <1 ng/L (<0.001 µg/L).

Sediment

Sugarcane areas - estuaries

Following an episode of severe dieback of mangroves in the Pioneer River estuary (Mackay in Queensland), principally in 1998, diuron was detected in sediment at four sampled sites in a study by Duke *et al* (2001), where there was severe dieback of mangroves. The dieback of mangroves in the Mackay region was first noted early in the 1990s but dramatically increased during the wet years in 1997-99. The dieback was confined to mainly one species, *Avicennia marina* (the common mangrove). The concentrations were 4, 0.8 and 3 µg/kg dw in samples taken from areas affected by mangrove dieback and 0.2 µg/kg dw in one sample taken in an area of relatively normal mangroves in Bucasia/Eimeo Creeks. If it is assumed that the diuron detected has originated from sugarcane farms in the vicinity, these results indicate that transport of diuron has occurred from farms into drains and thence into the estuary.

Duke *et al* (2003) published a report of further work, conducted in 2002, investigating mangrove dieback in the Mackay district – it occurs with mainly one species only *Avicennia marina* (the common mangrove tree). Diuron was found in all sediment samples at 0.1-8.2 µg/kg dw with a detection limit stated to be 0.1 µg/kg dw. Diuron was detected in core water samples taken at the same site (taken from hole dug into sediment at root depth) at a maximum of 12.9 ng/L (range 3.3-12.9 ng/L) and water column samples (taken at the high tide on the same day as sediment samples) with of 5.2 ng/L (upstream) and of 1.1 ng/L downstream in the Pioneer River. For the two sites that were sampled in 2000 and again in 2002 (Barnes Creek, sites M1 and M2, see Table A1.42), the concentrations of diuron were similar in both years, possibly indicating that the level of diuron was being 'recharged' in the sediment, or was not degrading in these sediments.

Table A1.45. Measured concentrations of diuron in sediment (µg/kg dw). Samples taken from creeks/estuaries in sugarcane growing areas of Queensland as reported by Duke et al, 2001 and 2003.

Mackay area				South and north of Cairns			
Site	Code	2000	2002	Site	Code	2000	2002
		-	1.7	Johnstone	MP1	-	1

				R			
		-	6.0		MP2	-	0.4
	MCM1	-	1.2		MP3	-	0.7
Barnes Ck	M1	4	5.1		MP4	-	2.6
(Pioneer R)	M2	0.8	1.0		MP5	-	2.6
	M4	3	-		MP6	-	5
	BH1	-	7.9		MP7	-	5.2
	BS1	-	8.2				
Bakers Ck	BCH1	-	2.4	Daintree R	1	-	0.1
	BCS2	-	4.3		2	-	1.1
	BCM1	-	4.3		3	-	0.64
	BCS1	-	6.2				
Eimeo/Bucasia	M7	0.2	-				

Cape York to Moreton Bay, Queensland

The concentrations of diuron in sediment and seagrass from 16 inter-tidal sites (<1 m deep; 3 samples per site pooled), located from Cape York to Moreton Bay at important dugong habitats, together with 24 sub-tidal sites (<5 m deep, in duplicate 3 random grab samples, 500-1000 m apart) located near major estuaries have been determined (Haynes *et al*, 2000). In the inter-tidal samples, there were 3 detections in sediment (0.5, 1.7 and 0.6 µg/kg dw for Cairns, Cardwell and Moreton Bay respectively) and 4 in the seagrasses (0.6, 1.1, 0.8 and 1.7 µg/kg dw for Cairns, Cardwell, Pallarenda and Moreton Bay respectively). The limit of detection was set at 0.5 µg/kg dw for both matrices. It is noted that the positive detections in the sediment also coincide with detections in the seagrasses at the same site and at comparable levels. For the sub-tidal sites, diuron was detected at 9 of the 24 sub-tidal sites at concentrations ranging from 0.2 to 10.1 µg/kg dw (see Table A1.43). The positive detections were mainly near rivers draining the sugar growing areas.

Table A1.46. Levels of diuron found in sub-tidal sediments in rivers, area under sugarcane in nearby river catchments and amount of diuron used in catchment.

River1	DR	BR	RR	JR	TR	C	HR	L
Concentration µg/kg dw	0.22	0.35	1.1	10.0	1.42	0.8	2.0	1.63
Area under sugarcane4, km2	48	76	232	394	247	585	691	6916
Diuron used in catchment4 kg	2378	835	4700	17353	2768	12505	16600	166006

1) Abbreviations used: DR Daintree River; BR Barron Rivers; RR Russell River; JR Johnson River; TR Tully River; C Cardwell; HR Herbert River and L Lucinda. 2) Result from one replicate, other replicate was below detection limit(<0.1 µg/kg dw). 3) Not replicated. 4) From GBRMPA, 2001. 5) For Cardwell data from Murray River used. 6) Lucinda is close to the mouth of the Herbert River.

The results of a study that focused on pesticide contamination of sediments in irrigation channels and drains in various areas of Queensland have been published (Müller *et al*, 2000). Sampling occurred along the banks or the wet/dry bed in the channel and drain. Each sample was a composite of 8 sub-samples taken at 10 metre intervals. Diuron was detected in 75 of a total of 103 samples (72% of all samples reporting limit 0.4 µg/kg dw), with the most frequent detections and highest concentrations of diuron generally occurring in drains from cotton crops (Table A1.44). The highest levels of diuron from the sugarcane areas reached 120 µg/kg sediment.

The authors noted that transport of pesticides from cotton growing areas to the marine environment is unlikely due to distance from the coast and because drains in the relatively arid cotton growing areas are only infrequently flushed. They concluded that diuron (and other herbicides) that were present at relatively high concentrations in drain/channel sediment in the sugarcane growing areas were the only contaminants of

those investigated that may reach the marine environment in significant quantities (insecticides were present at relatively low concentrations in the sugarcane areas).

Movement of contaminants from drains in Queensland sugarcane areas to the marine environment would be assisted by the fact that sugarcane is cultivated in areas with at least 1000 mm annual rainfall, in areas where there are regular flood events, and where the distance to the sea is relatively short. Müller et al (2000) therefore argued that the risk of exposure of seagrass to diuron and other sugarcane herbicides needed to be assessed, particularly under light limiting conditions that might exacerbate their activity as photosynthesis inhibitors (eg in association with flood events).

Table A1.47. Results for diuron from a study examining pesticide residues in Queensland irrigation channels and drains.

Region	Irrigation system & crop sampled	No of + samples /number of samples taken	Concentration mean and range µg/kg dw
Emerald	mainly drains, cotton	25/26	17 (<1-54)
St George	mainly drains, cotton	7/12	6.3 (<0.4-14)
Dawson Valley	mainly drains, cotton	15/15	80 (8.8-340)
Mareeba-Dimbulah	mainly drains, sugarcane	5/10	9.1 (<0.36-37)
Burdekin	mainly drains, sugarcane	20/21	25 (<1-120)
Callide Valley	channels, sugarcane	1/4	0.56 (<0.4-0.56)
Bundaberg	channels, sugarcane	1/4	2 (<1-2)
Lockyer Valley	channels	0/3	<0.4
Warrill Valley	channels	0/3	<0.4
Lower Mary	channels	1/2	7.9
Eton	channels	0/3	<0.4

Hervey Bay, Queensland

Low concentrations of diuron, together with other herbicides, were detected in sediments in inter-tidal seagrass meadows of *Zostera capricorni* in Hervey Bay, Queensland (McMahon *et al*, 2004).

Sediments were sampled in the seagrass meadows and the health of the seagrasses monitored as well. The two major rivers following into the Hervey Bay, the Mary and Burrum Rivers were also sampled. Sampling occurred in April and December 2002, both periods of low rainfall and low river flows and in February 2003 and 2004 during moderate flow events (monthly rain fall 325 mm).

The concentration of diuron in April and December in the sediments was found from below detection levels to 0.2 ng/kg dw.

5.2 Overseas

USA

The United States Geological Survey (USGS) conducted a large water quality program in 1992-96 in 20 of that nation's hydrologic basins and collected about 8200 samples from surface and ground water (USGS, 1998). The samples were analysed for 76 pesticides including diuron. Table A1.45 gives the results for diuron only and are as broken down by the USGS into selective groups based on major activities with the catchments. The agricultural indicator sites have relatively small catchments (27 to 6000 km^2, with most less than 1000 km^2) and included a variety of different crop types and agricultural practices, some of which will not use diuron and others may only use diuron intermittently. The urban indicator sites have small catchments (25 to 108 km^2) in which the primary uses of pesticides are non-agricultural. The integrator sites

are on large streams and rivers that drain relatively large catchments (1800 to 92000 km^2) with heterogeneous land use, diverse soil types and topography, and usually a variety of pesticide uses.

Note that a select group of data points were used to represent more typical conditions and includes fixed frequency sampling along with some samples collected during high or low flow conditions. Samples collected during storm events or floods were not used.

Table A1.48. The results for diuron from the USGS survey for both surface and ground water in the USA.

	Site	No. Samples	Percent positives	10%	50% (mean) µg/L	95% µg/L	Max, µg/L
Surface water	Agricultural	942	7.96%	<MDL	<MDL	0.23	14
	Urban	315	13.02%	<MDL	<MDL	0.28	8.4
	Integrator	222	9.46%	<MDL	<MDL	0.21	1.2
Ground waters	Agricultural	897	2.34%	<MDL	<MDL	<MDL	2.0
	Urban	289	2.77%	<MDL	<MDL	<MDL	0.46
	Integrator	850	0.95%	<MDL	<MDL	<MDL	0.34

MDL = maximum detection limits and was set at 0.05 µg/L.

The results from the USGS survey of water supplies in the USA clearly show that diuron is mainly found in the surface water with lower levels in groundwater. This seems to indicate that diuron is not a significant leacher but it does enter surface waters. The low level of positive detections is a reflection of the limited use of diuron compared to other older herbicides (atrazine, simazine).

UK

The Environment Agency (UK) conducts routine monitoring of pesticides in freshwater and their results for diuron in 1996 and 1997 has been summarized (Pesticides Safety Directorate, 2002). The summary table in this report is reproduced below.

Table A1.49. Level of diuron in freshwater in the UK by regions for 1996 and 1997, from Pesticides Safety Directorate, 2002.

Region	No. of samples		MRV1 ng/L		Percent above MRV		Average concentration ng/L		Maximum concentration ng/L	
	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997
Anglian	417	200	24	14.5	40	40-80	52.8	54.8	1300	5010
Midlands	766	996	12.7	25.7	100-500	40-80	73.4	52.5	7610	1360
North East	190	261	10.5	20.3	30	30	57.3	124	2520	3400
Southern	205	411	20	15.6	20-40	25-50	586	44.6	51280	4310
South west	252	266	0.4	1.9	40	40-80	0.36	3.9	90	530
Thames	639	493	38.5	40.8	40	40	124	157	5710	3280
Welsh	1117	1132	3.9	7.4	20-100	20	7.8	7.1	987	841

1) MRV = minimum reporting value

As can be seen in Table A1.46, the level of diuron reported in UK freshwater varies considerably with the range of values reaching 51280 ng/L. The higher values reflect a large urban area where diuron is used for weed control in right-of-way situations. Diuron is not registered for use in UK agricultural crops.

The concentration of diuron in marine areas due to its use as a biocide was monitored monthly during the boating season (April-October 1998) at 3 sites in the UK (Pesticides Safety Directorate, 2002). These are single monthly samples and therefore may not represent the overall level of contamination. The sites were: Southampton Water (6 marinas and 13 estuary sites), Sutton Harbour Plymouth (3 marinas and 3 estuary sites) and the River Crouch (1 marina and 5 estuary sites). These results are summarised in Table A1.47.

Table A1.50. Measured concentrations in marine waters at 3 coastal areas of the UK during the 1998 boating season.

Sampling type	Average concentration, ng/L (and range of monthly averages)	Range of all samples, ng/L
Southampton Water		
Estuary water (13 sites)	41.5 (range 1-102)	<1-438
Marina (open; 4 sites)	170 (90-238)	<1-613
Marina (locked; 1 site)	1439	112-6742
Marina (inlet; 1 site)	124	4-405
Sutton Harbour Plymouth		
Estuary water (3 sites)	29.3 (8-72)	1-291
Marina (locked) (3 sites)	77 (30-108)	4-334
River Crouch		
Estuary water (5 sites)	25.4 (11-44)	5-226
Marina (inlet; 1 site)	88	36-305

As is clear in Table A1.47, the level of diuron is higher in marinas than the surrounding estuaries; an interpretation is that the marinas are the source of the contamination from anti-fouling paints (including leaching, cleaning, repainting, sanding), which then diffuses to the local estuary on the tidal flux. The highest level (6742 ng/L) was from Hythe Marina (Southampton) in April. This is a locked marina containing approximately 275 boats and it was noted that there was limited opening of the gates during winter and therefore minimal flushing. The levels of diuron at Hythe fell after April to approximately 400 ng/L by June and to 112 ng/L in August (peak of the boating season in the UK). At the other closed marinas (Plymouth) the peak concentration also occurred in April but at lower values (214-613 ng/L). At these marinas there was more usage during winter (fishing vessels) and the gates were kept open during high tide allowing for some flushing. The peak season concentrations were just 19-113 ng/L, similar to estuary levels.

It is concluded that the UK results show that use of diuron in urban areas can lead to high levels in nearby river systems. The marine results show that when used in marine paints, there can be high levels of diuron in marinas, especially if the exchange rate with less polluted water is low.

APPENDIX E - ENVIRONMENTAL EFFECTS

The following data have been obtained from the US EPA Pesticide Ecotoxicity Database, current as of March 2002 (US EPA, 2004) and/or provided by the applicants. The same data has been used by the US EPA in their Re-registration Eligibility Document (RED) for diuron, which is publicly available (US EPA 2003). These studies have been reviewed by the US EPA and rated by them as either "Core" (ie fulfilling current guideline requirements, though possibly with minor inconsistencies from standard recommended procedures - acceptable for use in a risk assessment) or "Supplemental" (scientifically sound, but performed under conditions that deviated substantially from recommended protocols - may be useful in a risk assessment). The regulatory studies reviewed by the DEWHA are rated as reliable (high level of confidence in the study and according to the relevant Guideline although there could be minor problems that do not affect the results), acceptable (scientifically sound and meets most of the requirements of the relevant Guideline but with a significant problem or lack of critical information) or for information only (not suitable for regulatory use).

Significant additional laboratory test data have been supplied by DuPont since the initial review of diuron published as the PRF. The evaluations of these studies are included in this appendix using current DEWHA formatting for such evaluations.

1. AVIAN

The applicants initially provided no data. However, several studies have now been provided and reviewed by DEWHA. In addition, other results available from the Pesticide EcoToxicity Database and the US EPA RED (US EPA 2003) are reported below. In acute studies, toxicity of diuron to bobwhite quail, the most sensitive species tested, is rated as slightly toxic in both the acute oral and dietary tests. It is rated as practically non-toxic to the other 3 species tested. Mallard duck was the most sensitive species for chronic testing with a NOEC of 10 ppm. These results are summarised in Table A2.1 and Table A2.2.

Table A2.1. Summary of reviewed avian toxicity studies with diuron

Species	LD50	NOEC	Reference
Technical – acute oral toxicity			
Bobwhite quail	1104 mg ac/kg bw	260 mg ac/kg bw	Leuschner, 2001
Technical - dietary			
Bobwhite quail	1730 mg/kg diet	-	Heath et al, 1972
Japanese quail	>5000 mg/kg diet	-	Heath et al, 1972
Ring-necked pheasant	>5000 mg/kg diet	-	Heath et al, 1972
Mallard duck	>5000 mg/kg diet	-	Heath et al, 1972
Technical - reproduction			
Bobwhite quail	NOEC = 100 mg/kg diet	LOEC = 300 mg/kg diet	Leuschner, 2002
Mallard duck	NOEC = 10 mg/kg diet	LOEC = 33 mg/kg diet	Temple et al, 2007

Table A2.2. Summary of avian toxicity studies with diuron from the Pesticide EcoToxicity Database, US EPA (2004) and available from the US EPA RED (US EPA 2003).

US EPA Guideline	Comments	Toxicity	Year reported1	US EPA category2
Bobwhite quail (Colinus virginianus)				
71-1a – acute oral exposure	Active constituent (92.8%) – 17 week old birds, 21 day study duration	LD50 = 940 (712-1183) mg/kg NOEL = <292 mg/kg	1985	Core
Mallard duck (Anas platyrhynchos)				

71-1a – acute oral exposure	Active constituent (95%) – 3 months old birds, 14 day study duration	LD50 = >2000 mg/kg NOEL = NR	1970	Core

1) From the US EPA Pesticide EcoToxicity Database; 2) Category listed on the US EPA Pesticide EcoToxicity Database. NR = not recorded

5.3 Acute

The Following study has been provided:

Title	Acute toxicity study of diuron technical by oral administration by gavage to birds (bobwhite quail).
Authors	Leuschner P
Date	2001
APVMA Data ID	9009
Test Guideline	OPPTS 850.2100 and Draft-OECD guidelines (1998)
Data Validity	1 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

Acute oral toxicity of diuron technical (99.3% pure white powder) to Bobwhite quail, *Colinus virginianus* was tested. The test followed a standard guideline and was conducted to GLP. No major deviations from the test guideline were noted.

Five test concentrations and a control (0.8% aqueous hydroxypropyl-methyl cellulose gel) were used. Based on results supplied by Bayer AG, at which a LD50 of 100 mg/kg bw was estimated, dose levels in the definitive test were 260, 432, 720, 1200 and 2000 mg/kg bw. The test was started with the highest dose and continued in descending order. Birds were approximately 16 weeks old at the start of the study. Tests were performed in with 5 birds/pen, and a total of 10 birds per test concentration and control were used. The initial body weight per bird ranged from 170 to 208 g. Test solutions were administered in a single dose of 5 mL/kg bw orally by gavage. The vehicle used was 0.8% aqueous hydroxypropyl-methyl cellulose gel. Temperature was held between 15 to 27^{o}C and relative humidity was 45 to 70%. An 8 h:16 h light:dark photoperiod was maintained.

During the test, mortality was observed twice on day 1, and once each working day. Body weight was observed on days 0, 5, 8 and 15 whereas food consumption was observed on days 1-5, 6-8 and 9-14. Intoxication and abnormal behaviour was observed for the first 60-120 minutes after dosing, 3 times the day after dosing and once each working day after. In the 2 week follow up period, observations were made daily until all symptoms subsided and then each working day thereafter. The 14 day LD50 was estimated using probit analysis. The 95% confidence interval could not be calculated due to the steep gradient of the dose-mortality curve and widely spaced dose levels.

Findings

The following results are summarised:

Table A2.3: Summary of mortality and body weight at each time interval and concentration

Concentration	Mortality	Mean body weight (g)

(mg/kg)	Within 6 h	Within 24 h	Within 7 d	Within 14 d	Start	Test day 5	Test day 8	Test day 15
Control	0	0	0	0	191.1	203.7	203.3	208.4
260	0	0	0	0	197.2	192.0	196.6	210.2
432	0	0	0	0	185.3	162.8	173.6	193.0
720	0	0	0	0	187.0	139.6	146.2	182.5
1200	0	3	4	7	190.8	137.4	115.5	160.7
2000	0	6	9	10	187.7	122.7	103.3	- a

[a] Mean body weight could not be determined due to mortality

No mortalities were observed in the control group during the 14 day exposure period. 100% mortality was observed in the 2000 mg/kg bw test group after 14 days. No sub-lethal effects were observed in the control and 260 mg/kg bw test group but were observed in the other treatment groups. Slight inhibition in body weight gain was observed for the 432 mg/kg bw test group. Lethargy, ruffled feathers and moderate inhibition of weight gain was observed for the 720 mg/kg bw group. Lethargy, ruffled feathers, moderate inhibition of weight gain, slightly reduced activity, slight dyspnoea and abdominal position was observed in most of the birds in the 1200 mg/kg bw test group. All birds in the 2000 mg/kg bw test group displayed all effects described above including severe inhibition of body weight gain.

No test substance related changes were noted at necropsy.

Conclusion

The authors calculated a 14 day LD50 of 1104 mg ac/kg bw, a no effect dose level of 260 mg/kg bw, a lowest lethal dose of 1200 mg/kg bw and a dose level with first intolerant reactions of 432 mg/kg bw.

5.4 Short-Term

The following study has been provided:

Title	Comparative Dietary Toxicities of Pesticides to Birds
Authors	Heath et al.
Date	1972
APVMA Data ID	9032
Test Guideline	Pre-dates established guidelines
Data Validity	2* (Non-GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

This report presents measurement of the LD50 values of 89 pesticides administered for 5 days in the diets

of young birds of four species, bobwhite quail (*Colinus virginianus*), Japanese quail (*Coturnix coturnix japonica*), ring-necked pheasant (*Phasianus colchicus*), and mallard duck (*Anas platyrhynchos*). The test system was broadly similar to current avian dietary test guidelines with chemicals generally administered in six dietary concentrations, selected after a range finding study. Test diets were prepared with chemicals dissolved in corn oil and mixed thoroughtly

Usually, 10 birds were assigned per pen. Dosage was never initiated before birds were 9 days old. The tests were undertaken for 8 days, including exposure to the test diet for 5 days and a 3 day observation period after this with non-treated diets. It is unclear whether test treatments were replicated. Included with each set of chemicals was a dieldrin "standard" of six concentrations and three to six pens of control birds fed untreated diets.

Deaths in each pen were recorded daily. All LC50s and associated statistics were derived by probit analysis.

Findings

For diuron, the LC50 was >5000 mg/kg diet to Japanese quail, pheasant and mallard duck. For Japanese quail, at the 5000 mg/kg diet, 14% mortality was observed, while 30% mortality was found at this level for mallard duck. For the pheasant, 33% mortality was found at 4200 mg/kg diet with 5000 mg/kg diet being noted as repellent to this species.

An LC50 of 1730 mg/kg diet was calculated for bobwhite quail (95% CI 1482-2035 mg/kg diet). No other observations are provided.

Conclusion

In testing dietary toxicity of diuron to four bird species, bobwhite quail was the most sensitive with an LC50 of 1730 mg/kg diet. The other species tested, Japanese quail, pheasant and mallard duck, had LC50s in excess of the highest test concentration, 5000 mg/kg diet.

5.5 Reproduction

The following two studies have been provided:

Title	Study on Reproduction in Birds (Bobwhite Quail) with Diuron by Oral Administration Via the Diet
Authors	Leuschner, P
Date	2002
APVMA Data ID	9013
Test Guideline	OECD TG 206; OPPTS 850.2300
Data Validity	1 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

This study was performed to provide information on establishing dietary levels in chronic reproduction studies. Technical diuron (99.3% pure) was administered in the diet of Bobwhite quail (*Colinus virginianus*) at nominal concentrations of 0, 100, 300 and 900 ppm. Due to high mortality in the 900 ppm test group, the dietary concentration was reduced to 700 ppm from week 6 onwards. Diets were analysed to confirm the test concentration at weeks 0.5, 6 (high dose only) and during weeks 10/11.

The experimental design consisted of 4 groups of 32 birds (16 pens of 1 male and 1 female) per treatment. Following 3 weeks adaptation, the test was conducted for 23 weeks, being an 8 week induction period (short day conditions), 3 weeks until start of egg-laying (long day conditions) and 12 weeks of egg collection and hatching (long day conditions).

Daily checks were performed on behaviour, external appearance and signs of toxicity of the adult birds and hatchlings. Body weight of the adult birds were measured at the start of exposure to the test material, prior to the onset of egg-laying, and at test termination. The body weight of young birds was determined at 14 days of age. Food consumption of adults was determined in one-week intervals throughout the study. For young birds, food consumption was measured in the first and second week after hatching.

All test parameters were evaluated using standard statistical techniques.

Findings

At the highest test concentration, 4 adult males and 6 adult females died prematurely during test days 12 to 37 prompting a decrease in the test diet concentration to 700 ppm. After that, no further adult mortality was observed. Body weight and body weight gain were not influenced at 100 ppm for both males and females, or at 300 ppm for males. At 300 ppm, the body weight of females was slightly decreased in test week 10 and at this time, body weight gain in females was also marginally reduced. In the highest exposure group, the body weight gain of males was slightly reduced compared to controls. The females revealed statistically significantly reduced body weight data in test week 10 and in test week 23. Body weight gain was slightly reduced at these times.

Table A2.4: Some Reproductive Performance from the Bobwhite Quail Reproduction Study.

Experimental Group (mg/kg diuron in the diet)				
Reproductive Parameter	Control	100	300	900/700
Eggs laid	740	759	643	425*
Viable eggs (mean/pen)	728 (60.7)	749 (62.4)	635 (52.9)	471 (46.3*)
Cracked eggs (mean/pen)	12 (1)	10 (0.8)	8 (0.7)	8 (0.9)
Eggs set (mean/pen)	704 (58.7)	725 (60.4)	611 (50.9)	399 (44.3*)
Viable 18-d embryos (mean/pen)	624 (52.0)	675 (56.3)	564 (47.0)	349 (38.8*)
Hatchlings (mean/pen)	572 (47.7)	622 (51.8)	508 (42.3)	316 (35.1**)
14-d survivors (mean/pen)	517 (43.1)	571 (47.6)	453 (37.8)	284 (31.6**)

* - $p \leq 0.05$; ** - $p \leq 0.01$

At 100 and 300 ppm diuron, the reproduction of the quails was not influenced by the test compound. At the high concentration, the egg production per hen was markedly reduced by 24%. Accordingly, the number of viable eggs per hen, the number of eggs set per hen and the numbers of viable embryos per hen were reduced. The number of hatchlings per pen and the 14 day survivors per pen were statistically significantly reduced by 26% and 27% respectively.

Body weight of the 14 day old birds and food consumption was not influenced at any of the tested dose levels.

Conclusion

Based on this study, the one-generation NOEC to bobwhite quail is 100 ppm diuron in the diet, due to slight effects on female adult body weights observed at 300 ppm.

Title	Diuron (DPX-14740) technical: A reproduction study with the mallard
Authors	Temple et al.
Date	2007
APVMA Data ID	9024
Test Guideline	OECD TG 206; OPPTS 850.2300.
Data Validity	1 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

The study was undertaken to evaluate the effects upon the adult mallard (*Anas platyrhynchos*) of dietary exposure to diuron over a 20 week period. Effects on adult health, body weight and feed consumption were evaluated. In addition, the effects of adult exposure to diuron on the number of reproductive parameters was evaluated.

Technical diuron (98.4% pure) was administered in the diet at 0, 10, 33, 100 and 160 ppm. The diet was tested for homogeneity and analysed to verify the test concentration.

The experimental design consisted of 5 groups of 16 birds (16 pens of 1 male and 1 female) per treatment. Following 2 weeks adaptation, the test was conducted for 26 weeks, being an 9 week pre-photostimulation period (short day conditions), 11 weeks egg-laying (long day conditions) and 6 weeks post adult-termination for final incubation, hatching and 14 d offspring rearing period (long day conditions).

During the study, all adult birds were observed daily for signs of toxicity or abnormal behaviour. Additionally, all offspring were observed daily from hatching until 14 days of age. Adult body weights were measured at weeks 0, 2, 4, 6, 8 and at termination. Feed consumption was evaluated. Reproductive parameters measured included eggs laid, fertility, embryo viability, hatchability, offspring survival and egg shell thickness. Results were analysed using standard statistical methods.

Findings

There were no treatment-related mortalities or overt signs of toxicity at any of the concentrations tested. There were no apparent treatment related effects on adult body weight at 10 ppm. While not statistically significant, there was a slight reduction in mean weight gain among hens in the 33 and 100 ppm groups. At 160 ppm, there was a loss in body weight from test initiation to week 2 for both males and females, and there were significant reductions in the mean body weights of males at weeks 2, 4 and 6, and among hens in the 160 ppm treatment group at adult termination. There were no apparent treatment related effects on feed consumption at 10, 33 and 100 ppm. At 160 ppm, there were slight, but statistically significant, increases in feed consumption during weeks 5, 6, 8 and 9, probably due to increased wastage.

Table A2.5: Some Reproductive Performance from the Mallard Duck Reproduction Study.

	Experimental Group (mg/kg diuron in the diet)				
Reproductive Parameter	Control	10	33	100	160
Total eggs laid	763	662	549	503*	253*
Viable embryos/Eggs set (%)	88	90	77	79	85
Live 3-week Embryos/viable embryos (%)	99	99	99	100	97
Hatchlings/Live 3-week embryos (%)	87	77	79	84	82
14 day old survivors/hatchlings (%)	100	99	99	99	99
Hatchlings/eggs set (%)	75	68	59	66	66
14 day old survivors/eggs set (%)	75	67	58	66	65

* - $p \leq 0.05$; ** - $p \leq 0.01$

There were no apparent treatment related effects upon reproductive performance at 10 ppm. At 33 ppm, there were reductions in the numbers of hatchlings and 14 day old survivors as percentages of the maximum number of eggs set that were statistically significant (not reported in above table). These reductions were reflective of a reduction in egg production and a reduction in viable embryos of eggs set at 33 ppm. At 100 ppm, there were statistically significant reductions in the numbers of eggs laid and in the numbers of hatchlings and 14 day old survivors as a percentage of maximum set (not reported in above table). At 160 ppm, there were marked reductions in egg production and in the numbers of hatchlings and 14 day old survivors as a percentage of the maximum set (not reported in above table).

There were no apparent treatment related effects upon egg shell thickness at 10 or 33 ppm. At 100 and 160 ppm there were slight reduction in egg shell thickness, but these were not considered statistically significant. When compared to the control group, there were no statistically significant differences in the body weights of hatchlings or 14 day old survivors from any treatment group.

Conclusion

Based on reproductive effects observed at 33, 100 and 160 ppm the NOEC for mallard exposed to diuron in the diet from this study was 10 ppm.

This appears to be primarily the results of statistical analysis of parameters such as hatchlings and 14 day old survivors as a percent of the maximum number of eggs set within one of the control replicates. DEWHA considers the main adverse effect from this experiment was the reduction in egg laying, and in terms of total eggs laid, a definite dose/response appears to occur. A reduction compared to control replicates of 13%, 28%, 34% and 67% of total eggs laid is found at 10, 33, 100 and 160 ppm respectively. Even at 10 ppm, this inhibition in egg laying exceeds 10% of control values.

2. AQUATIC TOXICITY

2.1 Fish - Acute

Table 10 in the Overview Report summarises the acute fish toxicity data.

Active Constituent

The following test was originally submitted by an applicant.

The acute toxic of diuron to rainbow trout was determined according to OECD Guideline No. 203 (Zoltán, 2001a).

Eight juvenile fish per test concentration were used in a nominal dosing regime of 0 (control), 5.0, 6.5, 8.5, 11.0, 14.3, 18.6, 24.1, 31.4, 40.8 and 53.0 mg/L. All solutions were prepared using sand-filtered Danube supply water. Water quality measurements of the dissolved oxygen, pH and temperature were satisfactory.

There were no mortalities at 5 to 11 mg/L, 13, 25 and 63% mortality at 14.3, 18.6 and 24.1 mg/L respectively, and 100% mortality at the 3 highest concentrations after 96 hours. Symptoms noted were reduced swimming activity and increased pigmentation. There were no symptoms noted at the 3 lowest test concentrations (5 to 8.5 mg/L) or in controls. The 96-h LC50 using nominal concentrations was determined as 22.2 (CI 10.6-46.3) mg/L by probits and the NOEC 8.5 mg/L. Diuron is rated as effectively slightly toxicity to rainbow trout according to the US EPA classification. Due to the lack of analysis of the test solutions, the results of this test are considered acceptable only.

One older study has also been submitted:

Title	Acute Toxicity of H-16,035 to the Sheepshead minnow, *(Cyprinodon variegatus)*
Authors	Drottar, K
Date	1986
APVMA Data ID	9000
Test Guideline	FIFRA Guideline 72-3
Data Validity	2 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

Acute toxicity of diuron (99% pure tan powder, H-16,035) to juvenile Sheepshead minnow *Cyprinodon variegatus* was tested in a static, saltwater system. The test followed a standard FIFRA guideline (pre-dating the current US EPA guideline) and was conducted to GLP.

Deviations from the current US EPA test guidelines include:

Test concentrations were not measured. The guidelines state that the concentration of the test substance should be measured, as a minimum, at the beginning and end of the study.

It is unclear if the test solutions were aerated.

The current test guidelines require the dissolved oxygen (DO) in each concentration to be greater than 60% saturation. However, the two highest exposure concentrations fell below this mark at the 96 h period (with DO saturation of 49% and 56% for 10.0 and 6.0 mg ac/L respectively).

Fish used in this test came from two sources (Aquatic research organisms in New Hampshire and SP Engineering, Inc. Massachusetts). The current EPA guidelines state that fish must originate from the same source and population.

No replicates were used in this test, however, current guidelines state that two replicates per test concentration are preferred.

No other major deviations from the current US EPA test guideline were noted.

Five test concentrations, a seawater control and a solvent control (500 µL/L of DMF) were used. Based on the results of a range finding study, at which 50% mortality was observed between 1 and 10 mg ac/L, nominal concentrations in the definitive test were 1.3, 2.16, 3.6, 6.0 and 10.0 mg ac/L. Tests were performed in 43.9 L glass test containers with 35 L test solution. Ten fish per concentration were used and test concentrations were not replicated. Test solutions were held between 21^{o}C and 22^{o}C (mean 21.5^{o}C). A 16 h:8 h light:dark photoperiod was maintained.

Dissolved oxygen and pH were measured daily. Mortality was recorded at 24, 48, 72 and 96 h. The 96-hour LC50 and the 95% confidence limits were estimated using nonlinear interpolation.

Findings

At the start of the test, the seawater had total hardness of 1509 mg/L $CaCO_3$. Dissolved oxygen was 7.4 mg/L at the start of the test and ranged from 3.7 – 5.6 mg/L at the end of the study while pH ranged from 8.3-8.4 at the start and 8.1 – 8.2 at the end of the study while the test salinity was 20 ppt.

The following results are summarised:

Table A2.6: Summary of the number of mortalities at each time interval and concentration

Nominal Concentrations (mg/L)	***Cumulative mortality (%)***			
	24 h	***48 h***	***72 h***	***96 h***
Seawater Control	***0***	***0***	***0***	***0***
Solvent Control	***0***	***0***	***0***	***0***
1.3	***0***	***0***	***0***	***0***
2.16	***0***	***0***	***0***	***0***
3.6	***0***	***0***	***0***	***0***
6.0	***0***	***0***	***0***	***30***
10.0	***0***	***0***	***40***	***100***

No mortalities were observed in the water control or the solvent control group during the 96 h exposure period. After 96 hours, there was 100% mortality for the 10 mg/L exposure group. While no sub-lethal effects were observed in either of the control groups, one was found in the treatment groups. After 48 h, all fish in the top two exposure groups showed signs of equilibrium loss.

Conclusion

The study authors conclude a 96 h LC50 of 6.7 mg ac/L (nominal) with 95% confidence limits of 3.6 to 10 mg ac/L. The NOEC level was estimated to be 3.6 mg ac/L.

Literature

Nebeker and Schuytema (1998) report a study on the effects of diuron to two life stages of fathead minnow (*Pimephales promelas*). Testing followed ASTM (1997) guidelines. In the first test, juvenile fish were 1.5 months old at test initiation and were exposed for 10 days at 24^{o}C. Mean measured diuron concentrations in the test were 0, 3.4, 6.5, 12.2, 20.0 and 27.1 mg/L. For each concentration there were three replicate 400 mL beakers containing 300 mL test solution with four randomly assigned fish per beaker. Half the solution was replaced on day 5. Test parameters were survival, weight and length at 10 days. No mortality was found at any concentration except the highest where 50% mortality was observed (the 10 d LC50 was given as 27.1 mg/L with no confidence intervals). However, based on growth parameters, the LOEC was 3.4 mg/L (lowest rate tested) and the NOEC was <3.4 mg/L with exposed fish being significantly smaller than control fish (~50% reduction in weight at the lowest test concentration).

The second test tested effects of diuron on embryo/larval stage in a 7 day test. At test initiation, 5 eggs (2.5 days old) were placed in each beaker (three replicates per test concentration; 150 mL solution in 250 mL beakers in a 25^{o}C water bath). Initial measured concentrations of diuron were 0, 1.0, 2.0, 4.2, 8.3, 15.1 and 31.2 mg/L. The test solution was not renewed. Test parameters were number of eggs hatched, survival and growth in weight and length. All eggs hatched at all treatment rates except the highest test concentration where no eggs hatched. However, at 15.1 mg/L, 7 day survival was only 0.7/replicate compared to complete survival in the control group and all other treatment groups (94% survival at 2 mg/L). At 8.3 and 15.1 mg/L there were statistically significant effects on mean total length, but no effects on mean wet weight were observed. The 7 day (~2.5 days unhatched embryos and ~4.5 days as swimming larvae) EC50 was calculated to be 11.7 mg/L (95% CI 10.1-13.5 mg/L). The 7 day LOEC and NOEC were 8.3 and 4.2 mg/L respectively.

Pesticide EcoToxicity Database

According to the available data from studies in the Pesticide Ecotoxicity database and US EPA RED (US EPA 2003), diuron can generally be classified as slightly to highly toxic to fish. The most sensitive result is a 96 h LC50 of 0.71 mg/L for cutthroat trout and the range is from 0.67 to 240 mg ac/L (results converted to active consistent from the purity of test material, see Table A2.7). The wide range is surprising and the figure of 300 mg/L (80% ac) is very high compared to others in the table and therefore may be an error in the database or an outlier. Excluding this result the range is 0.67-23.5 mg ac/L, corresponding to a rating of slightly to highly toxic.

Table A2.7. Summary of aquatic toxicity studies with diuron – fish, acute and chronic exposure.

US EPA Guideline	***Comments***	***LC50 mg/L test substance (95% CL)***	***Year reported1***	***US EPA category2***
Bluegill sunfish (Lepomis macrochirus)				
72-1, 96 h	***Active constituent (28%); static***	***84.0 (68.3-103.3)***	***1975***	***Core***
	Active constituent (95%); static	***3.2 (2.53-4.05)***	***1976***	***Core***
	Active constituent (95%); static	***2.8 (2.3-3.3)***	***1986***	***Core***
	Active constituent (80%); static	***>300 (NR)***	***1991***	***Core***
Rainbow trout (Oncorhynchus mykiss)				
72-1, 96 h	***Active constituent (28%); static***	***23.8 (20-28.3)***	***1975***	***Core***
	Active constituent (95%); static	***1.95 (1.5-2.54)***	***1976***	***Core***
	Active constituent (80% WP); static	***16 (11-23)***	***1980***	***Supplementary***

	Active constituent (80%); static	***19.6 (NR)***	***1991***	***Core***
Fathead minnow (Pimephales promelas)				
72-1	***Active constituent (98.6%); static***	***14.2 (13.4-15.0)***	***1975***	***Supplementary***
Cutthroat trout (Oncorhynchus clarki)				
72-1, 96 h	***Active constituent (95%) static***	***1.4 (1.1-1.9)***	***1980***	***Core***
		0.71 (0.53-0.96)	***1986***	***Core***
Coho salmon (Oncorhynchus kisutch)				
72-1 96 h	***Active constituent (95%) static***	***2.4 (NR)***	***1986***	***Supplementary***
Lake trout (Salvelinus namaycush)				
72-1, 96 h	***Active constituent (95%) static***	***2.7 (2.4-3.0)***	***1980***	***Core***
		1.2 (0.9-1.6)	***1986***	***Core***
Striped mullet (Mugil cephalus)				
72-1, 48 h	***Active constituent (95%) static***	***6.3 (NR)***	***1986***	***Supplementary***

1) Only the year when study was done as reported in Pesticide EcoToxicity Database; 2) Category listed on the US EPA Ecological Effects Branch Pesticide EcoToxicity Database. NR = Not reported

Hepatotoxicity of Diuron to Australian Marine fish

The toxicity of diuron to pink snapper (*Pagrus aratus*) was measured by its effect on plasma concentrations of sorbitol dehydrogenase (SDH) (Gagnon, 2002). Normally SDH concentration is negligible in the bloodstream but its presence indicates that hepatocellular (liver) damage has occurred.

The juvenile snapper were exposed to 3 concentrations of diuron (1.0, 5.0 and 10 mg/L) for 7 days. During the exposure (and acclimation) period 50% of the water was replaced daily and the diuron concentration adjusted daily. The fish were fed during the exposure period.

No mortalities occurred and fish weight, length and liver somatic index were similar in all groups. The SHD activity was increased at 10 mg/L compared to control ($p < 0.0380$) and there was an increase at 5 mg/L that was not significantly different (Tukey's Test).

DEWHA notes that these results would appear to indicate that while diuron is only rated as moderately toxic to fish based on the acute toxicity test, diuron is causing hepatocellular toxicity at considerably lower levels. At this stage, chronic effects are largely unknown but such effects are considered possible. There are additional concerns over long term exposure of diuron given that several important fish species, including pink snapper, inhabit estuaries early in their life cycles and could be exposed to levels of diuron similar to those used in this study.

Formulation

Two additional acute fish toxicity studies have been provided testing diuron formulations.

Rainbow Trout

Title	***Static, Acute, 96-hour LC50 of DPX-14740-165 (KARMEX DF) to Rainbow Trout (Oncorhynchus mykiss)***

Authors	***Baer, K***
Date	***1991a***
APVMA Data ID	***8996***
Test Guideline	***US EPA Guideline 72-1***
Data Validity	***2 (GLP)***
Data Relied On	***Yes - the data was considered to be critical and was relied on in this assessment.***

Test System

Acute toxicity of diuron (80% in formulation DPX-14740-165) to fingerling, rainbow trout *(Oncorhynchus mykiss)* was tested in a static system. The test followed a standard US EPA guideline and was conducted to GLP. The test guideline requires a minimum of 7 fish per replicate with a preference for 10 fish per replicate. However, in this test, the number per replicate was 5. No other major deviations from the test guideline were noted.

Six test concentrations and a water control were used. Based on the results of a range finding study, at which 80% mortality was observed at 100 mg/L formulation, nominal, total formulation concentrations in the definitive test were 16, 26, 43, 72, 120 and 200 mg/L. These correspond to nominal concentrations of 12.8, 20.8, 34.4, 57.6, 96.0 and 160.0 mg ac/L. The concentrations were determined analytically. Tests were performed in 19 L glass aquaria with 15 L test solution. Two replicates of each concentration with 5 fish per replicate were used. Test solutions were held between 11.1^{o}C and 12.2^{o}C (mean 11.7^{o}C) and were unaerated. A 16 h:8 h light:dark photoperiod was maintained.

Dissolved oxygen and pH were measured daily. Mortality was recorded at 24, 48, 72 and 96 h.

The 96-hour LC50 and the 95% confidence interval were estimated using probit analysis.

Findings

At the start of the test, the dilution water had total hardness of 74 mg/L $CaCO_3$. Dissolved oxygen ranged from 9.5-9.6 mg/L at the start of the test and was 8.8-9.8 mg/L at the end of the study, while pH ranged from 7.3-7.4 at the start of the test and was 8.0-8.1 at the end of the study.

Measured test concentrations (once aquaria had settled) showed that, while concentrations remained relatively steady over the test period, the amount of diuron in the water was much lower than nominal concentrations. Average measured levels of diuron for the nominal 12.8, 20.8, 34.4, 57.6, 96.0 and 160.0 mg ac/L were 9.4, 12.5, 13.5, 14.5, 15.0 and 21 mg ac/L.

The following results are summarised:

Table A2.8: Summary of the number of mortalities at each time interval and concentration

	Cumulative mortality (%)				
Measured concentrations (mg/L)	***24 – 48 hours (Both A and B)b***	***72 hours***		***96 hours***	
		A	***B***	***A***	***B***
Water Control	***0***	***0***	***0***	***0***	***0***
9.4	***0***	***0***	***0***	***0***	***0***
12.5	***0***	***0***	***0***	***0***	***0***
13.5	***0***	***20***	***0***	***20***	***0***
14.5	***0***	***0***	***0***	***0***	***0***
15.0	***0***	***0***	***20***	***20***	***20***
21	***0***	***0***	***0***	***20***	***100***

[b]A and B refer to replicates containing five fish at the beginning of each test

No mortalities were observed in the control group during the 96 h exposure period. Two mortalities occurred in the exposure groups at the 72 hour observation point. After 96 hours, there was 100% mortality in one replicate of the 200 mg/L exposure group. While no sub-lethal effects were observed in the control group, several were found in the treatment groups. After 72 hours, all fish were recorded at the surface in all test concentrations with dark colouration. All fish in the top five exposure groups showed signs of gasping for air, lying on the bottom and partial loss of equilibrium. At the 96 h observation time, all fish in all exposure groups displayed one or more of these sub-lethal effects. Other sub-lethal effects included partial curved and curved spine, lethargy and erratic swimming.

Conclusion

The study authors conclude a 96 h LC50 of 190 mg formulation/L with a 95% confidence interval of 130 to 590 mg formulation/L. Based on measured diuron levels in water, DEWHA has calculated the LC50 to be 22.2 mg ac/L (TOXCALC). However, based on sub-lethal effects, the study NOEC would appear to be <9.4 mg ac/L.

Bluegill Sunfish

Title	***Static, Acute, 96-hour LC50 of DPX-14740-165 (KARMEX DF) to Bluegill Sunfish (Lepomis macrochirus).***
Authors	***Baer, K***
Date	***1991b***
APVMA Data ID	***8995***
Test Guideline	***US EPA Guideline 72-1***
Data Validity	***2 (GLP)***
Data Relied On	***Yes - the data was considered to be critical and was relied on in this assessment.***

Test System

Acute toxicity of diuron (80% in formulation DPX-14740-165) to bluegill sunfish (*Lepomis macrochirus*) was

tested in a static system. The test followed a standard US EPA guideline and was conducted to GLP. The test guideline requires a minimum of 7 fish per replicate with a preference for 10 fish per replicate. However, in this test, the number per replicate was 5. No other major deviations from the test guideline were noted.

Six test concentrations and a water control were used. Based on the results of a rangefinding study, at which no mortality was observed up to 100 mg/L formulation, nominal, total formulation concentrations in the definitive test were 23, 39, 65, 108, 180 and 300 mg/L. These correspond to nominal concentrations of 18.4, 31.2, 52, 86.4, 144 and 240 mg ac/L. The concentrations were determined analytically. Tests were performed in 19 L glass aquaria with 15 L test solution. Two replicates of each concentration with 5 fish per replicate were used. Test solutions were held between 21.4^{o}C and 21.5^{o}C (mean 21.5^{o}C) and were unaerated. A 16 h:8 h light:dark photoperiod was maintained.

Dissolved oxygen and pH were measured daily. Mortality was recorded at 24, 48, 72 and 96 h. Statistical analysis of the results (LC50 determination) was not undertaken due to a lack of mortality.

Findings

At the start of the test, the dilution water had total hardness of 74 mg/L $CaCO_3$. Dissolved oxygen ranged from 8.7-8.8 mg/L at the start of the test and was 7.2-8.0 mg/L at the end of the study, while pH ranged from 7.4-7.5 at the start of the test and was 7.8-7.9 at the end of the study.

Measured test concentrations (once aquaria had settled) showed that, while concentrations remained relatively steady over the test period, the amount of diuron in the water was much lower than nominal concentrations. Average measured levels of diuron for the nominal 18.4, 31.2, 52, 86.4, 144 and 240 mg ac/L were 14.5, 17.5, 19.5, 21.0, 20.5 and 25 mg ac/L.

No mortalities were observed in the control group or any treatment group during the 96 h exposure period. While no sub-lethal effects were observed in the control group, several were found in the treatment groups. After 24 hours, all fish were recorded at the surface in all test concentrations with one fish showing a partial loss of equilibrium in the 180 mg/L test group. Other sub-lethal effects included lethargy, erratic swimming or gasping for air. At the 96 h observation time, in the top four exposure groups, all fish exhibited one or more of these sub-lethal effects.

Conclusion

The study authors conclude a 96 h LC50 >300 mg formulation/L, the highest rate tested. Based on measured diuron levels in water, DEWHA considers the 96 h LC50 to be >25 mg ac/L (no mortality at this level). However, based on sub-lethal effects, the study NOEC would appear to be around 17.5 mg/L.

Metabolites

One study has been provided testing acute toxicity of the mCPDMU metabolite to fish.

Rainbow Trout

Title	***Acute Toxicity Testing of the Diuron Metabolite mCPDMU in Rainbow Trout (Oncorhynchus mykiss) (Teleostei, Salmonidae)***
Authors	***Heintze A,***
Date	***2002a***
APVMA Data ID	***9003***
Test Guideline	***OECD 203: "Fish, Acute Toxicity Test"***

Data Validity	***1 (GLP)***
Data Relied On	***Yes - the data was considered to be critical and was relied on in this assessment.***

Test System

Acute toxicity of the diuron metabolite mCPDMU (99.5% pure, white powder) rainbow trout *(Oncorhynchus mykiss)* was tested in a static system. The test followed a standard OECD guideline and was conducted to GLP. No major deviations from the current test guideline were noted.

Six test concentrations, a dilution water control (dechlorinated drinking water and deionised water) and a solvent control (acetone with dilution water) were used. Based on the results of a range finding study, at which 20% mortality was observed at 100 mg ac/L, nominal concentrations in the definitive test were 10.0, 15.9, 25.1, 39.8, 63.1 and 100 mg/L. Tests were performed in 25 L test aquaria with 24 L test solution. Ten fish per test concentration or control were used without replicates. Test solutions were held between 15.1^{o}C and 16.1^{o}C and were continuously aerated. A 16 h:8 h light:dark photoperiod was maintained.

Dissolved oxygen, pH, metabolite concentration and temperature were measured daily. Behavioural changes and mortality were observed at 3, 6, 24, 48, 72 and 96 h. The 96-hour LC50 and the 95% confidence interval were estimated using statistical analysis.

Findings

At the start of the test, the dilution water had total hardness of 232 mg/L $CaCO_3$. Dissolved oxygen ranged from 96-99% saturation at the start of the test and was 99-100% at the end of the study, while pH ranged from 8.28-8.43 at the start of the test and was 8.56-8.63 at the end of the study.

Measured test concentrations showed that, while concentrations remained relatively steady over the test period, the amount of diuron metabolite in the water was much lower for the 100 mg ac/L nominal concentration. Average measured levels of mCPDMU at for the nominal 10, 15.9, 25.1, 39.8, 63.1 and 100 mg ac/L were 10.1, 15.5, 24.5, 36.6, 61.4 and 72.9 mg ac/L.

The following results are summarised:

Table A2.9: Summary of the number of mortalities at each time interval and concentration

Nominal Concentrations of mCPDMU (mg/L)	***Mortality (%)***					
	3 h	***6 h***	***24 h***	***48 h***	***72 h***	***96 h***
Water Control	***0***	***0***	***0***	***0***	***0***	***0***
Solvent Control	***0***	***0***	***0***	***0***	***0***	***0***
10.0	***0***	***0***	***0***	***0***	***0***	***0***
15.9	***0***	***0***	***0***	***0***	***0***	***0***
25.1	***0***	***0***	***0***	***0***	***20***	***30***
39.8	***0***	***0***	***10***	***70***	***80***	***90***
63.1	***0***	***0***	***80***	***90***	***100***	***100***
100	***0***	***0***	***0***	***50***	***70***	***80***

No mortalities were observed in the control groups during the 96 h exposure period. After 96 hours, there was 100% mortality in the 63.1 mg/L exposure group. While no sub-lethal effects were observed in the

control group, several were found in the treatment groups. After 72 hours, difficulty in maintaining equilibrium was observed in the 15.9 mg/L exposure group. Upside down fish with gill movement as the only sign of life, as well as difficulty maintaining equilibrium, was observed in the 25.1 mg/L exposure group after 48 h and the 39.8 mg/L exposure group after 24 h. Reduced activity, orientation to the top or bottom of test vessels and the previously described sub lethal effects were observed in the 63.1 and 100 mg/L group after ≥3 h. Solid metabolite was observed in the test vessels for the duration of the test.

Conclusion

Based on nominal concentrations, the study authors conclude a 96 h LC50 of 28.7 mg ac/L with 95% confidence limits of 22.1 to 39.8 mg ac/L. The observed 96 h NOEC was concluded to be 10.0 mg ac/L, nominal.

2.2 Fish - Chronic

Initially, only one study was submitted by an applicant.

Rainbow trout, 14 day semi-static

The sublethal toxic effects of diuron (technical, 97.8% ac) to juvenile rainbow trout (4.5 cm length) were investigated under semi-static conditions (renewed every 48 hours) for a period of 14 days according to OECD Test Guideline 204 (Zoltán, 2001b). Ten trout per treatment were exposed to test nominal concentrations of 5.8, 11.2, 22.5, 45, 90 and 180 mg/L. Water quality measurements of the dissolved oxygen, pH and temperature were satisfactory.

Mortalities commenced by day 1 in the highest concentrations and continued thereafter. By the end of the study there was 10, 20 and 100 % mortality at 6.5, 8.5 and 11.0 (and greater) mg/L respectively. Toxic symptoms were observed in the 6.5 and 8.5 mg/L with symptoms such as reduced swimming, increased pigmentation, first reduction then cessation of food intake. By the end of the test the 5.0 mg/L exposure group were showing reduced food intake, one of the first symptoms noted in the higher exposure groups. The average body weight and length in the three lowest test concentrations did not appear to be significantly different to the control group, although there were no statistical comparisons presented.

The NOEC was given as 5.0 mg/L for rainbow trout with LC50 (4 days) as 19.8 mg/L and LC50 (14 day) as 14.2 mg/L. DEWHA has recalculated the results using probits as LC50 (96 h) = 18.4 (CI 16.4-20.6) mg/L and LC50 (14 days) as 8.8 (CI 7.9-9.8) mg/L.

Since then, one further study has been submitted:

Title	***Early life stage toxicity of DPX01470-166 (diuron) to the sheepshead minnow Cyprinidon variegatus***
Authors	***Ward T and Boeri R,***
Date	***1992a***
APVMA Data ID	***9027***
Test Guideline	***US EPA Pesticide Assessment Guideline subdivision E, 72-4***
Data Validity	***1 (GLP)***
Data Relied On	***Yes - the data was considered to be critical and was relied on in this assessment.***

Test System

Early life stage toxicity of diuron (96.8% pure yellowish powder Haskell number 18,921) to Sheepshead

minnow *Cyprinidon variegatus* (embryos, larvae and juveniles) was tested in a flow through system. The test followed a standard US EPA guideline and was conducted to GLP. The current US EPA test guidelines require the total hardness to be measured at the beginning, throughout and at the end of the test. The total hardness was not reported in this study. No other major deviations from the test guideline were noted.

Five test concentrations, a dilution water control (filtered natural seawater) and a solvent control (DMF) were used. Based on information supplied by EnviroSystems Inc, at which the 96 h LC50 for sheepshead minnow was observed at 6.7 mg/L, nominal concentrations in the definitive test were 0.48, 0.90, 1.5, 3.0 and 6.0 mg/L. Correcting for purity, these correspond to nominal concentrations of 0.46, 0.87, 1.45, 2.9 and 5.8 mg ac/L. The respective mean measured concentrations were 0.44, 1.0, 1.7, 3.6 and 7.1 mg ac/L. The measured concentrations were determined analytically and were used for all calculations.

Embryo tests were performed in cylindrical glass cages with 8 cm diameter closed at one end with a Nitex screen. Two replicates of each concentration with 40 embryos per replicate were used. Two cages containing 20 embryos each were suspended in each replicate test vessel and were oscillated at two cycles per minute. After hatching, the fish were reduced to 20 per replicate and were released into the test vessels. The test vessels were 23 L glass aquaria with 15 L of test solution. A 16 h:8 h light:dark photoperiod was maintained. Aeration was employed after 2 days.

Before and after hatching, an intermittent flow of test substance entered each test vessel at a rate of 4.9 media exchanges per 24 h. Test solutions were held between 29.0 and 31.0 ^{o}C.

Dissolved oxygen, pH, salinity, temperature and mortality were measured daily. Test water samples from days 0, 7, 14, 21, 28, 35 and 38 were analysed.

Findings

Dissolved oxygen remained above 75% saturation throughout the test and ranged from 5.7-8.0 mg/L. pH ranged from 7.4 to 8.3 and salinity ranged from 19 to 20 ppt throughout the test.

Measured test concentrations showed that concentrations remained relatively steady over the test period and the amount of diuron in the water remained comparable to the nominal concentrations.

The following results are summarised:

Table A2.10: Summary of the number of survivors at each time interval and concentration

Mean Measured concentration (mg/L)	***Mean percent survival at Hatch (day 6)***	***Mean percent survival (days post hatch)***			
		11	***18***	***25***	***32***
Seawater Control	***75.0***	***100.0***	***100.0***	***97.5***	***97.5***
Solvent Control	***77.5***	***97.5***	***97.5***	***97.5***	***97.5***
0.44	***81.2***	***97.5***	***97.5***	***97.5***	***97.5***
1.0	***78.8***	***100.0***	***100.0***	***100.0***	***100.0***
1.7	***81.2***	***100.0***	***100.0***	***100.0***	***100.0***
3.6	***76.2***	***52.5***	***40.0***	***12.5***	***7.5***
7.1	***72.5***	***0.0***	***0.0***	***0.0***	***0.0***

Table A2.11: Mean total length and weight findings.

Mean Measured concentration (mg/L)	***Total Length (mm) Mean ± std. dev***	***Weight (g) Mean ± std. dev***
Seawater Control	***22.0 ± 1.4***	***182.0 ± 21.6***
Solvent Control	***23.0 ± 1.2***	***228.3 ± 33.2***
0.44	***23.5 ± 1.5***	***203.6 ± 19.6***
1.0	***24.0 ± 1.1***	***207.9 ± 31.8***
1.7	***23.5 ± 1.3***	***188.7 ± 23.1***
3.6	***7.7a ± 0.4***	***10.4a ± 4.2***
7.1	***N/Ab***	***N/Ab***

[a] not an average (only one value recorded)

[b] values not available due to mortality

[a, b] The values for the 3.6 and 7.1 mg/L test concentrations were not included in the statistical analysis since survival at these concentrations was observed to be different to the control

The hatching time was identical for all test concentrations (6 days). A minimum 75% of embryos hatched (day 6) in the control groups. The survival of control fish post hatch (days 11-32) was a minimum 97.5%. After 11 days, there was 100% mortality in the highest test concentration 7.1 mg ac/L. While no sub-lethal effects were observed in the control group, one was found in the treatment groups. Lethargy was observed in all surviving fish in the 7.1 mg/L test group on days 7 and 8 and in the 3.6 mg/L test group from day 13. No fish were observed to be edematous.

Conclusion

The study authors conclude a LOEC of 3.6 mg ac/L, a NOEC of 1.7 mg ac/L and a MATC of 2.5 mg ac/L.

Pesticide EcoToxicity Database

One further chronic fish toxicity result is reported in the Pesticide Ecotoxicity database and US EPA RED (US EPA 2003)

Table A2.12. Summary of aquatic toxicity studies with diuron – fish, chronic/reproductive exposure from US EPA Pesticide EcoToxicity Database and available from the US EPA RED (US EPA 2003).

US EPA Guideline	***Comments***	***Toxicity***	***Year reported1***	***US EPA category2***
Fathead minnow (Pimephales promelas)				
72-4a early life stage study (60 days total)	***Active constituent (98.6%) – flow through conditions***	***LOEC = 61.8 µg/L NOEC = 26.4 µg/L***	***1975***	***Core***

1) From US EPA Pesticide EcoToxicity Database; 2) Category listed on the US EPA Pesticide EcoToxicity Database

3. AQUATIC INVERTEBRATES

3.1 Acute Exposure

Active Constituent

Initially, only one study was submitted by an applicant.

Daphnia magna, technical

The acute toxicity of diuron to Daphnia magna was determined following OECD Test Guideline 202 (Zoltán, 2001c).

Neonate daphnia (<24 h old, 5 per replicate, 4 replicates) were exposed to nominal concentrations of diuron (technical 97% ac) of 8.0, 11.0, 15.0, 21.0 and 30 mg/L for 48 hours. Measurements of the physical properties of the test solutions were satisfactory.

After 48 hours, 20, 45, 40, 90 and 100% of the daphnia were immobilised in the 8.0, 11.0, 15.0, 21.0 and 30 mg/L concentrations respectively. The LC50 was calculated (using probit analysis) as 12.8 (CI 10.5-14.7) mg/L and the NOEC = 2.2 mg/L (determined from the range finding test). Again there was no analysis of the test solutions and therefore the results are considered acceptable only.

Since then, three additional studies for saltwater species have been submitted:

Mysid Shrimp

Title	***Static Acute Toxicity of Haskell Sample Number 16,035 to the Mysid, Mysidopsis bahia.***
Authors	***Boeri, R***
Date	***1987***
APVMA Data ID	***8999***
Test Guideline	***FIFRA Guideline 72-3***
Data Validity	***2 (GLP)***
Data Relied On	***Yes - the data was considered to be critical and was relied on with restrictions in this assessment.***

Test System

Acute toxicity of diuron (99% pure tan powder, Haskell Sample Number 16,035) to the marine crustacean *Mysidopsis bahia* was tested in a static, saltwater system. The test followed a standard FIFRA guideline and was conducted to GLP.

Deviations from the current US EPA test guidelines include:

A 16 h:8 h light:dark photoperiod was maintained instead of a 14 h:10 h light:dark photoperiod

The temperature specified by the US EPA is 25 ± 2^{o}C, however, the temperature maintained was 22^{o}C.

A range finding test to determine the life stage of the mysid and the concentrations of the test substance for use in the definitive test should be performed. It is unclear if a range finding test was done.

Concentrations were not measured at the start or end of the study.

The total hardness (mg/L $CaCO_3$) of the dilution water, the identity and concentration of the solvent used was not reported.

No other major deviations from the current US EPA test guideline were noted.

Six test concentrations, a dilution water control and a solvent control were used. Nominal concentrations in the definitive test were 0.6, 1.0, 1.6, 2.6, 4.3 and 7.1 mg ac/L. Tests were performed in 2 L glass culture bowls with 1 L test solution. Two replicates of each concentration with 10 mysids per replicate were used. Test solutions were held at 22^{o}C and were unaerated. A 16 h:8 h light:dark photoperiod was maintained.

Dissolved oxygen, pH, salinity and temperature were measured daily. Mortality was recorded at 24, 48, 72 and 96 h. The 48- and 96-hour LC50 and the 95% confidence interval were estimated using probit analysis and moving average respectively.

Findings

Salinity was 20% at the start of the test and 21% at the end of the test. Dissolved oxygen was 8.0 ppm at the start of the test and ranged from 6.0-6.2 ppm at the end of the test. pH was 7.9 at the beginning and 7.7 at the end of the test.

The following results are summarised:

Table A2.13: Summary of the number of survivors at each time interval and concentration

Nominal concentrations (mg ac/L)	*Total Number of Survivors (sum of two replicates)*				
	0 h	*24 h*	*48 h*	*72 h*	*96 h*
Dilution Water Control	*20*	*20*	*20*	*20*	*20*
Solvent Control	*20*	*20*	*20*	*20*	*19*
0.6	*20*	*20*	*20*	*20*	*19*
1.0	*20*	*20*	*19*	*18*	*18*
1.6	*20*	*20*	*13*	*5*	*0*
2.6	*20*	*13*	*0*	*0*	*0*
4.3	*20*	*0*	*0*	*0*	*0*
7.1	*20*	*0*	*0*	*0*	*0*

No mortalities were observed in the water control group and one mortality was observed in the solvent control group during the 96 h exposure period. After 96 hours, there was 100% mortality for the studies containing 1.6 mg ac/L or above. While no sub-lethal effects were observed in either of the control groups, one was observed in the treatment groups. After 48 h, mysids in the 1.6 mg ac/L test group displayed a loss of reflex until mortality. No other sub-lethal effects were observed.

Conclusion

The study authors conclude a 96 h LC50 of 1.1 mg ac/L with a 95% confidence interval of 0.9 to 1.3 mg ac/L. The 48 h LC50 was concluded to be 1.7 mg ac/L with a 95% confidence interval of 1.5 to 1.9 mg ac/L. The NOEC level was estimated to be 1.0 mg ac/L.

Eastern Oyster

Title	***Acute toxicity of H-16,035 on shell growth of the eastern oyster (Crassostrea virginica)***
Authors	***Johnson, I***
Date	***1986***
APVMA Data ID	***9006***
Test Guideline	***Guideline 72-3***
Data Validity	***2 (GLP)***
Data Relied On	***Yes - the data was considered to be critical and was relied on in this assessment.***

Test System

Acute toxicity of diuron (99% pure) to Eastern oysters Crassostrea virginica was tested in a flow-through, saltwater system. The test followed a standard guideline and was conducted to GLP. No major deviations from the US EPA test guideline were noted.

Five test concentrations, a seawater control and a solvent control (97.7 µL DMF/L seawater) were used. Based on the results of a range finding study, at which the EC50 value was observed between 1.0 and 10 mg/L, nominal concentrations in the definitive test were 1.3, 2.16, 3.6, 6.0 and 10.0 mg ac/L. Tests were performed in 16.3 L glass aquaria with 8.2 L test solution at a depth of 7.6 cm. A continuous flow of natural, unfiltered seawater entered each aquarium at a rate of 20.5 L/h through a calibrated sandpipe. The stock solutions entered the aquaria at a rate of 2.00 mL/h. Twenty oysters per concentration and control were used and test concentrations were not replicated. Test solutions were held between 20oC and 22oC (mean 21oC). A 16 h:8 h light:dark photoperiod was maintained.

Water samples were taken daily and their diuron concentrations analysed. Mortality was recorded at 24, 48, 72 and 96 h. The mean shell deposition was reported for the 96 h period. The 96-hour LC50 and the

95% confidence limits were estimated using probit analysis.

Findings

Dissolved oxygen remained ≥ 4.5 mg/L (≥ 63 % saturation) throughout the test, pH ranged from 7.6 to 7.8 and the test salinity was 36 ppt.

Measured test concentrations showed that, concentrations fluctuated over the test period. Average measured levels of diuron for the nominal 1.3, 2.16, 3.6, 6.0 and 10.0 mg ac/L were 1.34, 1.08, 1.08, 1.14, and 2.52 mg ac/L. The decrease in percent of nominal concentration with increasing concentration indicates that diuron was at the limit of solubility at the solvent concentration used in the study (also supported by observation of undissolved chemical in the diluter mixing chambers). Despite this, a definite dose/response was observed. This is somewhat counter intuitive, but is explained by the study authors that the physical presence, not measured concentrations of diuron was the cause of the observed effects. As a result nominal concentrations were used to calculate effect levels.

The following results are summarised:

Table A2.14: Summary of the number of mortalities, shell deposition and percentage change at each time interval and concentration

Nominal, Concentrations (mg ac/L)	***Cumulative mortality (%)***				***Mean shell deposition 96 h (mm)***	***Percentage change***
	24 h	***48 h***	***72 h***	***96 h***		
Seawater Control	***0***	***0***	***0***	***0***	***1.04 ± 1.11***	***-1***
Solvent Control	***0***	***0***	***0***	***0***	***1.05 ± 1.08***	***-***
1.3	***0***	***0***	***0***	***10***	***0.80 ± 0.97***	***-23.8***
2.2	***0***	***0***	***0***	***30***	***0.71 ± 0.83***	***-32.4***
3.6	***0***	***0***	***0***	***70***	***0.65 ± 0.77***	***-38.1***
6.0	***0***	***0***	***0***	***75***	***0.18 ± 0.40***	***-82.9***
10.0	***0***	***0***	***0***	***85***	***0.00 ± 0.00***	***-100***

No mortalities were observed in the seawater control or the solvent control during the 96 h exposure period. After 96 hours, there was 85% mortality for the 10 mg/L exposure group. No sub-lethal effects were reported in either of the control groups or the treatment groups. No differences in shell growth were observed due to solvent. Undissolved chemical was observed in the diluter mixing chambers.

Conclusion

The authors calculated a 96 h EC50 of 3.2 mg ac/L nominal with 95% confidence limits of 1.5 to 6.6 mg ac/L and a 96 h LC50 of 3.2 mg/L with 95% confidence limits of 2.5 to 4.2 mg ac/L. DEWHA considers the study NOEC to be <1.3 mg ac/L.

Title	***Acute flow-through mollusc shell deposition test with DPX-14740 (diuron)***
Authors	***Ward T and Boeri R***
Date	***1991***
APVMA Data ID	***9026***
Test Guideline	***US EPA Pesticide Assessment Guideline Subdivision E, 72-3***
Data Validity	***1 (GLP)***
Data Relied On	***Yes - the data was considered to be critical and was relied on in this assessment.***

Test System

Acute toxicity of diuron (96.8% pure white powder, Haskell number 18,921) to juvenile Eastern oysters *Crassostrea virginica* was tested in a flow-through, saltwater system. The test followed a standard US EPA guideline and was conducted to GLP. No major deviations from the US EPA test guideline were noted.

Five test concentrations, a seawater control and a solvent control (dimethylformamide) were used. Based on data supplied by Du Pont Agricultural Products, nominal concentrations in the definitive test were 2.25, 3.75, 6.0, 9.0 and 15.0 mg ac/L. Correcting for 96.8% purity, the respective concentrations were 2.17, 3.63, 5.8, 8.7 and 14.5 mg ac/L. The EC50 was calculated using the mean measured concentrations. Tests were performed in 20 L glass aquaria with 15 L test solution and were unaerated. Test media intermittently entered each aquarium at an average rate of 0.6 L/oyster/h which resulted in an average of 18 volume exchanges per day. Twenty oysters per concentration and control were used and test concentrations were not replicated. Test solutions were held between 22.4^{o}C and 23.7^{o}C. A 16 h:8 h light:dark photoperiod was maintained.

Water samples were taken at 0 and 96 h and their diuron concentrations were analytically determined. Dissolved oxygen, pH, salinity and temperature were measured daily. Mortality and observations were recorded at 24, 48, 72 and 96 h. The mean shell deposition was reported for the 96 h period. The 96-hour EC50 and the 95% confidence limits were estimated using probit analysis.

Prior to the test described above, a definitive test with a seawater control, solvent control and nominal concentrations of 0.375, 0.625, 0.975, 1.475 and 2.5 mg ac/L was attempted. This test had to be repeated using the test system described above since the shell deposition for oysters exposed to 2.5 mg ac/L for 96 h was 88% of the amount deposited by the control oysters.

Findings

Dissolved oxygen ranged from 5.7 to 7.4 mg/L, pH ranged from 7.7 to 7.9 and the test salinity was 30 ppt throughout the test.

Measured test concentrations showed that concentrations remained relatively steady over the test period and the amount of diuron in the water was consistent with the nominal concentrations. Average measured levels of diuron for the nominal 2.25, 3.75, 6.0, 9.0 and 15.0 mg ac/L were 2.4, 3.6, 5.6, 8.8 and 14 mg ac/L.

The following results are summarised:

Table A2.15: Summary of the shell deposition and percent of seawater control at each concentration

Measured Concentration of Diuron (mg ac/L)	***Mean shell growth at longest finger (mm)***	***Percent of seawater control shell depositon***
Seawater Control ***Solvent Control*** ***2.4*** ***3.6***	***3.7*** ***3.6*** ***3.2*** ***2.9***	***100*** ***97.3*** ***86.5*** ***78.4***

5.6	***1.4***	***37.8***
8.8	***0.5***	***13.5***
14	***0.0***	***0.0***

No mortalities were observed in the seawater control, solvent control or the test concentrations during the 96 h exposure period. While no sub-lethal effects were observed in the control groups, faeces production was observed as being reduced for 14 mg ac/L. No other sub-lethal effects were observed. Insoluble white particles were observed on the bottom of all non-control test vessels throughout the study.

Conclusion

The study authors conclude a 96 h EC50 of 4.8 mg ac/L with 95% confidence limits of 4.4 to 5.2 mg ac/L. The 96 h NOEC was concluded to be 2.4 mg ac/L, although it is noted that there was still a 13.5% reduction in shell deposition at this level compared to seawater control oysters, and 11% compared to solvent control oysters.

Literature

Nebeker and Schuytema (1998) describe a series of experiments considering effects of diuron on freshwater cladocerans, amphipods, midges, worms and snails. Effects described are considered as chronic in the paper and in the *Daphnia pulex* study, reproduction end-points were assessed. However, exposure periods were not long (7 to 10 days) and test parameters mainly related to survival and growth end-points. DEWHA will treat these tests as acute toxicity end points. The studies followed acceptable guidelines (ATSM, 1997) and the results are considered acceptable. Concentrations were measured and statistical analyses performed used standard techniques. All exposures were through the water phase, and all organisms were maintained in test solutions with no addition of sediment to the test vessels.

<u>*Daphnia pulex*:</u> The test used five 5-day old animals in 250 mL test beakers (150 mL test solution) with 7 days exposure and no renewal. Animals were fed during the study. Test parameters were adult survival and number of young produced. Mean measured diuron concentrations were 0, 0.4, 0.9, 1.9, 4.0, 7.7 and 17.8 mg/L. No mortality was recorded up to 1.9 mg/L. At 4.0, 7.7 and 17.8 mg/L, mortality of 6, 60 and 100% was recorded after 7 days. No young were produced at 7.7 or 17.8 mg/L, but there was no statistical difference between numbers of young produced at any other test concentration compared with controls. The 96 h and 7 d LC50s are reported as 17.9 (95% CI 14.2-22.6) and 7.1 (95% CI 5.8-8.8) mg/L respectively. The 7 day LOEC and NOEC values were 7.7 and 4.0 mg/L respectively.

<u>Amphipod*, Hyalella azteca*:</u> For this 10 day test, young animals (<9 days old) were used with 5 animals per beaker and 3 replicates per test concentration with a test temperature of 22^{o}C. Half the test solution was renewed on day 5. Mean measured test concentrations were 0, 4.2, 7.9, 15.7, 22.9 and 28.5 mg/L. Test parameters were survival and growth (length and weight). There was no survival at the highest test concentration. Survival at 15.7 and 22.9 mg/L was 14 and 86% respectively with no mortality found at lower test concentrations. There was no statistically significant difference between surviving amphipods and control organisms in terms of weight and length at any test level. Based on survival, the 96 h LC50 was 19.4 mg/L (95% CI 14.2-22.6) and the 10 d LC50 was 18.4 mg/L (95% CI 16.5-20.5). The 10 d LOEC and NOEC values were 15.7 and 7.9 mg/L respectively.

<u>Midge *Chironomus tentans*:</u> The 10-day midge test used 10 animals per beaker (three replicates per concentration) with 2 day old first instar larvae that had begun to build burrows. Prior to test initiation, 75 mL of an algal culture was poured into the beakers and allowed to settle out to form food and burrow material on the bottom of the beaker. The water was then poured off and 200 mL test solution added to each beaker. They were held in a water bath at 24^{o}C. Test solutions were renewed (half beaker volume) on day 7. Test parameters were survival and larval weight at the end of the test. Mean measured test concentrations were

0, 1.9, 3.4, 7.1 and 12.2 mg/L. There was no survival at the two highest test concentrations compared with 90%, 67% and 53% survival at 0, 1.9 and 3.4 mg/L respectively. At 3.4 mg/L, there was a difference in wet weight (mean 0.2 mg) compared to control animals (mean 0.5 mg), although this was not considered statistically significant. Animals at 1.9 mg/L were the same as those in the control. The 10 d LC50 was calculated to be 3.3 mg/L (95% CI 2.4-4.5). The LOEC and NOEC values based on the most sensitive survival end-point were 1.9 and 3.4 mg/L respectively.

Annelid worm *Lumbriculus variegatus*: The 10 day test with this species was started with 10 worms in each of three replicate 250 mL beakers per concentration with each beaker containing 75 mL test solution in a 23^{o}C water bath. Small, short adult worms were used to provide for growth potential. Half the test solution was replaced on day 5. Test parameters were survival and wet weight at the end of the study. Mean measured concentrations were 0, 0.4, 1.8, 3.5, 7.1, 13.0, 22.8 and 29.1 mg/L. Some worms reproduced by splitting in two (fragmentation) and at the end of the study, there were 31 worms in the control group with a range of 30 worms (highest test concentration) to 37 worms (7.1 mg/L) in the exposure groups. No effects were therefore found on survival. There was, however, an effect on worm weight. Mean weight in the control group was 8.8 mg. At test concentrations of 3.5 mg/L (mean wet weight of 6.7 mg) and up, a statistically significant reduction in worm weight was observed with worms in the highest test group having a mean weight of 3.2 mg. The report did not calculate an EC50. DEWHA has calculated the value (TOXCALC V5.0; maximum likelihood - probit) to be 19.3 mg/L, but no confidence intervals were calculated as individual replicate data were not available. The study reports a LOEC and NOEC based on weight to be 3.5 and 1.8 mg/L respectively.

Snail *Physa gyrina*: The 10 day test with this species was started with 15 day old, 1-1.5 mm diameter snails in three replicate beakers (10 snails per beaker) in 150 mL test solution. Snails grazed on an algae/bacteria film that settled out of the beakers prior to test initiation. Two thirds of the test solution was replaced on day 6. Test parameters were survival and wet weight. Mean measured concentrations were 0, 1.8, 3.5, 7.6, 13.4, 22.8 and 29.1 mg/L. Survival of 90% was found in the control group compared to 87% in the highest test concentration to 100% at 22.8 mg/L. Again, there were significant effects on snail weight with a mean of 5.3 mg per snail in the control group compared to 3.7, 3.7, 3.3, 2.7, 1.2 and 0.4 mg per snail in the 1.8, 3.5, 7.6, 13.4, 22.8 and 29.1 mg/L groups respectively. Only the two highest test concentrations were deemed to be statistically significantly different to the control giving a LOEC and NOEC of 22.8 and 13.4 mg/L respectively. The report did not calculate an EC50. DEWHA has calculated the value (TOXCALC V5.0; maximum likelihood - probit) to be 8.2 mg/L, but no confidence intervals were calculated as individual replicate data were not available. This value is lower than the reported study NOEC, and the calculated EC05 (used to statistically approximate a NOEC) based on TOXCAL was around 1 mg/L.

Pesticide EcoToxicity Database

Additional unreviewed results are reported in the Pesticide Ecotoxicity database and US EPA RED (US EPA 2003) as follows:

Table A2.15. Summary of aquatic toxicity studies with diuron – aquatic invertebrates, acute and chronic exposure.

US EPA Guideline	***Comments***	***Toxicity (95% confidence limits)***	***Year reported1***	***US EPA category2***
Water flea (Daphnia magna)				
72-2b	***Active constituent (80%); Static***	***48 h EC50 = 8.4 (6.3-13.0) mg/L; NOEC = NR***	***1991***	***Core***
72-4b	***Active constituent (98.2%) early life stage; Static***	***28 d LOEC = 0.2 mg/LNOEC = not determined (assumed to be <0.2 mg/L)***	***1979***	***Supplemental***
Water flea (Daphnia pulex)				

72-2a	***Active constituent (80%) – 1st instar; Static***	***48 h EC50 = 1.4 (1.0-1.9) mg/L; NOEC = NR***	***1980***	***Core***
Daphnid (Simocephalus sp)				
72-2a – acute exposure	***Active constituent (95%); Static***	***48 h EC50 = 2.0 (1.4-2.8) mg/L; NOEC = NR***	***1980***	***Core***
Scud (Gammarus)				
72-2a	***Active constituent (95%) – embryo/larvae, static***	***96 h LC50 = 0.16 (0.13-0.19) mg/L; NOEC = NR***	***1980***	***Core***
Brown shrimp (Penaeus aztecus)				
72-3	***Active constituent (95%) Flow-through***	***48 h LC50 = 1.0 mg/L; NOEC = NR***	***1986***	***Supplemental***

1) From US EPA Pesticide EcoToxicity Database; 2) Category as listed on the US EPA Ecological Effects Branch Pesticide EcoToxicity Database. NR = Not reported

Formulation

The following study has been submitted testing acute toxicity of a diuron formulation to *Daphnia*.

Daphnids

Title	***Static, Acute, 48-hour EC50 of DPX-14740-165 (KARMEX DF) to Daphnia magna***
Authors	***Baer, K***
Date	***1991c***
APVMA Data ID	***8997***
Test Guideline	***US EPA Guideline 72-2***
Data Validity	***2 (GLP)***
Data Relied On	***Yes - the data was considered to be critical and was relied on in this assessment.***

Test System

Acute toxicity of diuron (80% in formulation DPX-14740-165) to *Daphnia magna* neonates was tested in a static system. The test followed a standard US EPA guideline and was conducted to GLP. No other major deviations from the test guideline were noted.

Nine test concentrations and a water control were used. Based on the results of a range finding study, at which 40% mortality was observed for 100 mg/L and 100% mortality was observed for 500 mg/L, nominal, total formulation concentrations in the definitive test were 5.0, 8.4, 14, 23, 39, 65, 108, 180 and 300 mg/L. These correspond to nominal concentrations of 4.0, 6.7, 11.2, 18.4, 31.2, 52.0, 86.4, 144.0 and 240.0 mg ac/L. The concentrations were determined analytically. Tests were performed in 250 mL pyrex beakers with 200 mL test solution. Four replicates of each concentration with 5 daphnids per replicate were used. Test solutions were held between 19.8^{o}C and 20.0^{o}C (mean 19.9^{o}C) and were unaerated. A 16 h:8 h light:dark photoperiod was maintained.

Temperature was measured daily while dissolved oxygen and pH were measured at the beginning and the end of the test. Immobility (mortality) was recorded at 24 and 48 h. The 24-hour and 48-hour EC50 and the 95% confidence interval were estimated using probit analysis.

Findings

At the start of the test, the dilution water had a total hardness of 78 mg/L $CaCO_3$. Dissolved oxygen ranged from 8.6-8.7 mg/L at the start of the test and was 8.2-8.6 mg/L at the end of the study, while pH ranged from 8.2-8.3 at the start of the test and was 8.0-8.1 at the end of the study.

Measured test concentrations (once aquaria had settled) showed that, while concentrations remained relatively steady over the test period, the amount of diuron in the water was much lower than nominal concentrations. Average measured levels of diuron for the nominal 5.0, 8.4, 14, 23, 39, 65, 108, 180 and 300 mg product/L were 3.8, 6.3, 9.7, 13.1, 15.6, 17.5, 19.1, 19.9 and 24.4 mg ac/L.

The following results are summarised:

Table A2.16: Summary of the observed immobility at each time interval and concentration

Nominal Concentrations (mg ac/L)	***Observed Immobility (%)***							
	24 hours				***48 hours***			
	Aa	***Ba***	***Ca***	***Da***	***Aa***	***Ba***	***Ca***	***Da***
Water Control	***0***	***0***	***0***	***0***	***20***	***0***	***20***	***0***
4.0	***0***	***0***	***0***	***0***	***0***	***0***	***0***	***0***
6.7	***0***	***20***	***0***	***0***	***20***	***20***	***0***	***40***
11.2	***20***	***0***	***0***	***0***	***60***	***40***	***60***	***100***
18.4	***0***	***0***	***0***	***20***	***100***	***100***	***100***	***100***
31.2	***20***	***20***	***20***	***0***	***100***	***100***	***100***	***100***
52.0	***40***	***40***	***60***	***20***	***100***	***100***	***100***	***100***
86.4	***60***	***80***	***80***	***80***	***100***	***100***	***100***	***100***
144.0	***100***	***100***	***60***	***100***	***100***	***100***	***100***	***100***
240.0	***100***	***100***	***100***	***100***	***100***	***100***	***100***	***100***

[b]A, B, C and D refer to replicates containing five daphnids at the beginning of each test

A total of 5% immobility was observed in the water controls at the 48 h exposure period. After 48 hours, there was 100% immobility for the exposure groups containing 23 mg/L and above. While no sub-lethal effects were observed in the control group, two were found in the treatment groups. After 24 hours, most of the non-control daphnids were sluggish. After 48 hours, all daphnids in 5.0 mg formulation/L were on the bottom of the vessels, but became mobile when prodded with a glass rod.

Conclusion

The study authors conclude a 48 h EC50 of 12 mg formulation/L with a 95% confidence interval of 10 to 13 mg/L. Based on measured diuron levels in water, DEWHA has calculated (TOXCALC) the 48h EC50 to be 9.7 mg ac/L (with a 95% confidence interval of 8.6-10.6 mg ac/L). However, based on sub-lethal effects, the study NOEC would be <3.8 mg ac/L.

Metabolites

The following study has been submitted testing acute toxicity of the mCPDMU metabolite to *Daphnia*.

Daphnids

Title	***Assessment of Toxic Effects of the Diuron Metabolite mCPDMU on Daphnia magna using the 48 h Acute Immobilisation Test***
Authors	***Heintze, A***
Date	***2002b***
APVMA Data ID	***9002***
Test Guideline	***OECD 202 "Daphnia sp., acute immobilisation test and reproduction test, part 1: The 24 h EC50 Acute Immobilisation Test"***
Data Validity	***1 (GLP)***
Data Relied On	***Yes - the data was considered to be critical and was relied on in this assessment.***

Test System

Acute toxicity of the diuron metabolite mCPDMU (99.5% pure, white powder) to *Daphnia magna* (aged between 6 and 24 h) was tested in a static system. The test followed a standard OECD guideline and was conducted to GLP. No major deviations from the current US EPA test guideline were noted.

Six test concentrations, a control with test medium, a solvent control and two positive controls (containing potassium-dichromate at concentrations of 0.9 mg/L and 1.9 mg/L) were used. Based on the results of a range finding study, at which 15% immobilisation was observed for 100 mg/L, nominal concentrations in the definitive test were 10.0, 15.9, 25.1, 39.8, 63.1 and 100 mg ac/L. The recovery concentrations were determined analytically. Tests were performed in 100 mL glass beakers with 50 mL test solution. Four replicates of each concentration with 5 daphnids per replicate were used. Test solutions were held between 18.6^{o}C and 19.4^{o}C and were unaerated. A 16 h:8 h light:dark photoperiod was maintained. The test medium was not renewed.

Temperature, pH and oxygen saturation were measured at 0, 24 and 48 h. Immobility (mortality) was recorded at 24 and 48 h. The 24-hour and 48-hour EC50 and the 95% confidence interval were estimated from the nominal concentrations using statistical evaluation.

Findings

The dilution water was aerated before use. At the start of the test, the dilution water had a total hardness of 196 mg/L $CaCO_3$. Dissolved oxygen ranged from 92-96% saturation at the start of the test and 94-96% saturation at the end of the study, while pH ranged from 8.45-8.47 at the start of the test and was 8.46-8.48 at the end of the study.

The EC50 of the reference substance potassium-dichromate was estimated to be between 0.9 mg/L and 1.9 mg/L, as expected.

Measured test concentrations showed that concentrations remained relatively steady over the test period, and the amount of diuron in the water was consistent with the nominal concentrations, although slightly elevated. Average measured levels of diuron for the nominal 10.0, 15.9, 25.1, 39.8, 63.1 and 100 mg ac/L were 12.2, 15.5, 24.9, 44.8, 75.3 and 120 mg ac/L at 48 h.

The following results are summarised:

Table A2.17: Summary of the observed immobility at each time interval and concentration

Nominal, Total mCPDMU Concentrations (mg/L)	***Number of Immobilised Daphnids***	
	24 hours Replicate	***48 hours Replicate***

	1	2	3	4	1	2	3	4
Test Medium Control	***0***	***0***	***0***	***0***	***0***	***0***	***0***	***0***
Solvent Control	***0***	***0***	***0***	***0***	***0***	***0***	***0***	***0***
10.0	***0***	***0***	***0***	***0***	***0***	***0***	***0***	***0***
15.9	***0***	***0***	***0***	***0***	***0***	***0***	***0***	***0***
25.1	***0***	***0***	***0***	***0***	***1***	***2***	***0***	***0***
39.8	***0***	***0***	***0***	***0***	***2***	***1***	***3***	***3***
63.1	***0***	***0***	***0***	***0***	***1***	***3***	***2***	***3***
100.0	***0***	***0***	***0***	***1***	***4***	***2***	***3***	***3***

No sub-lethal effects were reported in the control groups or the treatment groups.

Conclusion

The authors calculated a 48 h EC50 of 67.4 mg ac/L with a 95% confidence interval of 48.7 to 125 mg ac/L and a NOEC of 15.9 mg ac/L.

3.2 Reproductive/Chronic Exposure

Two chronic aquatic invertebrate studies have been submitted:

Active Constituent

Daphnids

Title	***Diuron (DPX-14740) technical: 21-day chronic, static-renewal toxicity test to Daphnia magna***
Authors	Samel A
Date	2006
APVMA Data ID	9015
Test Guideline	US EPA Ecological Effects Test Guidelines OPPTS 850.1300 (1996)
Data Validity	1 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

Chronic toxicity of diuron (99.1% pure powder, Haskell Number 27779) to *Daphnia magna* (initially ≤ 24 h old) was tested in a static system. The test followed a standard US EPA guideline and was conducted to GLP. No major deviations from the test guideline were noted.

Six test concentrations and a dilution water control were used. Based on the results of an acute toxicity study, at which the 48 h EC50 was 1.4 mg/L, nominal concentrations in the definitive test were 0.06, 0.12, 0.24, 0.45, 0.9 and 1.8 mg ac/L. The measured concentrations were determined analytically. Tests were performed in 250 mL pyrex beakers with 200 mL test solution. Ten replicates of each concentration with 1 daphnid per replicate were used. New and old test solutions were held between 20.0^{o}C and 20.5^{o}C (mean 20.3^{o}C) and were unaerated. A 16 h:8 h light:dark photoperiod was maintained. Test solutions were renewed three days per week and daphnids were fed daily.

Temperature, dissolved oxygen and pH were measured at the beginning of the test, at test solution renewal and the end of the test. Immobility (mortality) and observations were recorded daily. The length and mass of the daphnids were measured at the end of the test (21 days). Total alkalinity, EDTA hardness and total conductivity were measured at the beginning of the test, weekly and at the end of the test. The NOEC,

LOEC and MATC were calculated with respect to mean measured concentrations, adult daphnid mobility, number of live young, number of immobile young, the body length and dry weight of surviving adults at the end of the test. The 21 day EC50 was calculated using probit analysis.

Findings

At the start of the test, the dilution water had a total hardness of 100-140 mg/L $CaCO_3$. The range of alkalinity, EDTA hardness and conductivity for the highest mean measured concentration with surviving daphnids (1.76 mg/L day 0 and 0.865 mg/L thereafter) was 52-56 mg ac/L as $CaCO_3$, 131-136 mg ac/L as $CaCO_3$ and 265-282 µmhos/cm respectively. Dissolved oxygen concentration for new and old solutions ranged from 6.4 mg/L to 8.7 mg/L throughout the test (minimum 70.3% of saturation). pH ranged from 7.2-7.6 for new solutions and from 7.4-8.1 for old solutions.

Measured test concentrations showed that concentrations remained relatively steady over the test period and the amount of diuron in the water remained comparable to the nominal concentrations. Average measured levels of diuron for the nominal 0.06, 0.12, 0.24, 0.45, 0.9 and 1.8 mg ac/L were 0.0572, 0.113, 0.229, 0.432, 0.865 and 1.73 mg ac/L.

The following results are summarised:

Table A2.18: Summary of survival, reproduction, mobility, length and body weight

Mean, measured Concentration (mg/L)	***%Adult Survival a***	***Day of firsd brood***	***Mean (Standard Deviation)***				
			First Reproduction day b	***Total Live young c***	***Total Immobile Young d***	***Adult Length (mm)***	***Dry Weight (mg) e***
Water Control	***100***	***N/A f***	***10.6 (1.0)***	***121.1 (26.4)***	***0 (0)***	***4.61***	***0.9***
0.0572	***100***	***N/A f***	***10.7 (1.0)***	***104.4 (29.5)***	***0 (0)***	***4.59***	***0.9***
0.113	***90***	***19***	***10.6 (1.0)***	***99.6 (26.8)***	***0 (0)***	***4.44***	***0.8***
0.229	***100***	***N/A f***	***10.2 (0.6)***	***106.5 (14.0)***	***0 (0)***	***4.45***	***0.9***
0.432	***100***	***N/A f***	***11.6 (1.3)***	***91.7 (33.3)***	***0 (0)***	***4.13***	***0.7***
0.865	***80***	***21***	***14.5 (1.3)***	***45.0 (13.6)***	***0 (0)***	***3.48***	***0.3***
1.73	***0***	***3***	***N/A g***	***N/A g***	***N/A g***	***N/A g***	***N/A g***

[a] Percent of live adult daphnids at the end of the test

[b] First day that reproduction was observed

[c] Sum of live young produced per surviving adult in 21 days

[d] Sum of immobile young produced per surviving adult in 21 days

[e] Mean dry weight of surviving adults at the end of the test

[f] N/A means not applicable due to no adult immobility

[g] N/A means not applicable due to complete adult immobility

There was 100% adult survival in the control during the 21 day study and 100% mortality in the 1.73 mg ac/L test group on day 3. Sub-lethal effects were observed in the control group and several were found in the treatment groups. After 5 days, one replicate in the control group contained a daphnid that was visibly smaller in size. This was also observed in the 0.113 mg/L test group in two replicates after day 2. After day 6, the 0.229 mg/L test group contained two replicates with daphnids visibly smaller in size and floating at the surface. The 0.432 and 0.865 mg/L test groups displayed the same observations above as well as lethargy and pale colouration for most replicates after day 2. Lethargy was seen in all replicates of the 1.73 mg/L test group after day 2. Ephippia was not seen at any test concentration or in the dilution water control.

Conclusion

The study authors conclude a 21 day EC50 for adult survival of 1.07 mg ac/L with 95% confidence limits of 0.844 and 1.44 mg/L, a 21 day NOEC of 0.432 mg ac/L, a MATC of 0.612 mg ac/L and a LOEC of 0.865 mg ac/L. This study NOEC relates to adult survival. However, there appeared to be significant effects on survival of offspring with >10% reduction at all tested concentrations. Even at the lowest test concentration of 0.0572 mg/L, the mean number of live offspring were reduced by 14% compared to the control.

Mysid Shrimp

Title	***Life-cycle toxicity of DPX-14740-166 (Diuron) to the Mysid, Mysidopsis bahia***
Authors	***Ward T and Boeri R***
Date	***1992b***
APVMA Data ID	***9028***
Test Guideline	***US EPA pesticide assessment guideline subdivision E, 72-4***
Data Validity	***1 (GLP)***
Data Relied On	***Yes - the data was considered to be critical and was relied on in this assessment.***

Test System

Life-cycle toxicity of diuron (96.8% pure, yellow powder Haskell number 18,921) to Mysid, *Mysidopsis bahia* (≤ 24 h old) was tested in a flow through system. The test followed a standard US EPA guideline and was conducted to GLP. No major deviations from the test guideline were noted.

Five test concentrations, a water control (filtered natural seawater) and a solvent control (DMF) were used. Based on information provided by DuPont Agricultural Products, at which the 96 h LC50 to mysids was 1.1 mg ac/L, nominal concentrations in the definitive test were 0.28, 0.60, 1.00, 2.00 and 4.00 mg ac/L. These correspond to nominal concentrations corrected for purity of 0.27, 0.58, 0.97, 1.94 and 3.87 mg ac/L. The measured concentrations were determined analytically and were used for all calculations. Tests were performed in 20 L glass aquaria with 8 L test solution. Two replicates of each concentration with 30 mysids per replicate were used. The mysids within each replicate were evenly subdivided into 6 retention chambers. After determining the sex of the mysids, male and female pairs were arranged within five of the six retention chambers while unpaired mysids were placed in the sixth chamber. The test solutions entered the test vessels intermittently via a flow proportional diluter, to result in an average of 11.9 media exchanges/24 h/test vessel. Test solutions were held between 24.0 and 26.3^{o}C and were aerated. A 16 h:8 h light:dark photoperiod was maintained. Aeration was initiated on day 6 and maintained until test completion.

Mortality and observations, dissolved oxygen, pH, salinity and temperature were recorded daily. Samples

to determined the concentrations of diuron were taken at day 0, 7, 14, 21 and 28.

Prior to the definitive test described above, three other definitive tests were attempted. The first attempt involved nominal concentrations of 0.12, 0.225, 0.375, 0.75 and 1.5 mg ac/L and was terminated due to inadequate production of young by the control. The second attempt involved the nominal concentrations of 0.32, 0.60, 1.0, 2.0 and 4.0 mg ac/L. It was terminated due to high control mortality. The third attempt involved nominal concentrations of 0.28, 0.60, 1.00, 2.00 and 4.00 mg ac/L, and was terminated due to a diluter malfunction.

Findings

Dissolved oxygen ranged from 5.4-7.8 mg/L throughout the study while pH ranged from 7.7-8.4 and salinity ranged from 19-21 ppt.

Measured test concentrations showed that concentrations remained relatively steady over the test period and the amount of diuron in the water agreed with the nominal concentrations. Average measured levels of diuron for the nominal 0.28, 0.60, 1.00, 2.00 and 4.00 mg ac/L were 0.27, 0.56, 0.96, 1.9 and 3.9 mg ac/L.

The following results are summarised:

Table A2.19: Summary of the mean survival, reproduction, length and weight of the Mysid shrimps

Mean Measured Concentration (mg/L)	***Mean % survival at day 28***	***Mean production of young by day 28***		***Mean total length (mm)***	***Mean Weight (mg)***	
		Aa	***Bb***		***Wet***	***Dry***
Water control	***90.0***	***9.6***	***0.7***	***9.7***	***5.6***	***1.0***
Solvent control	***91.7***	***9.0***	***0.6***	***9.4***	***4.8***	***0.8***
0.27	***86.7***	***9.2***	***0.7***	***9.5***	***5.2***	***0.9***
0.56	***90.0***	***7.4***	***0.5***	***9.2***	***5.4***	***0.9***
0.96	***78.3***	***6.0***	***0.4***	***9.0***	***5.2***	***0.8***
1.9	***80.0***	***4.0***	***0.3***	***8.8***	***4.6***	***0.7***
3.9	***65.0***	***0.0c***	***0.0c***	***7.6***	***3.3***	***0.5***

[a] These mean young production values are calculated as the total number of young produced divided by the average number of surviving females.

[b] These mean young production values are calculated as the number of young released per reproductive day

[c] These mean values were assumed to be different to the control and were not included in the statistical analysis

There was a minimum 90% mean survival in the control groups during the 28 day exposure period and a 65% mean survival in the 3.9 mg ac/L. No sublethal effects were observed in the control or test groups. The sex of the mysids could be determined after 14 days of exposure and the most sensitive measured effect was the number of young per surviving female.

Conclusion

The study authors conclude a LOEC of 1.9 mg ac/L, a NOEC of 0.96 mg ac/L and a MATC of 1.4 mg ac/L.

4. ALGAE, DIATOMS AND AQUATIC PLANTS

4.1 Active constituent

As might be expected, given that diuron is a herbicide, algae were much more sensitive to diuron than fish or aquatic invertebrates. The following studies were presented and are summarised in Table A2.20.

Table A2.20. Summary of algae/aquatic plant studies presented for review.

Test alga	*Test material and purity*	*EbC/ErC50 as µg/L test substance based on nominal concentrations*	*Rating for study1*	*Reference*
Technical				
Selenastrum capricornutum	***Technical (n.g.)***	***ErC50 = 11 (72 h)***	***acceptable***	***Zoltán, 2001d***
	Technical (98%)	***EbC50 = 18 (72 h) ErC50 = 22 (120 h)***	***acceptable***	***Douglas and Handley, 1988***
	Technical (96.8%)	***EbC50 = 1.8 (72 h) ErC50 = >5.2***	***reliable***	***Blasberg, Hicks and Bucksath, 1991***
Scenedesmus subspicatus	***Technical (98.5%)***	***EbC50 = 7.2 (96 h) ErC50 = 22***	***reliable***	***Heimbach, 1991a***
Synechococcus leopoliensis	***Technical 99.1%***	***EbC50 = 24.9 (72 h) ErC50 = 38.0***	***reliable***	***Dengler, 2006a***
Anabaena flos-aquae	***Technical (98.6%)***	***EbC50 = 23.2 (72 h) ErC50 = 30.9***	***reliable***	***Memmert, 1998***
Navicula pelliculosa	***Technical 99.1%***	***EbC50 = 16.2 (72 h) ErC50 = 65***	***reliable***	***Dengler, 2006b***
Lemna gibba	***Technical 99.1%***	***7 d EbC50 = 15.7 7 d ErC50 = 20.3***	***Reliable***	***Ferrell, 2006***
Formulated products				
Selenastrum capricornutum	***Karmex SC 500 (517 g ac/L)***	***EbC50 29.8 (120 h) (= 14.9 µg ac/L)***	***acceptable***	***Monma, 1988***
Scenedesmus subspicatus	***Diuron WP 80 (80.1% ac)***	***EbC50 5.9 (96 h) (= 4.8 µg ac/L)***	***reliable***	***Heimbach, 1991b***
	Karmex DF (81.2 %)	***EbC50 11.8 (72 h) (= 9.6 µg ac/L)***	***reliable***	***Dengler, 2003***
Metabolites of diuron				
Scenedesmus subspicatus	***mCPDMU (99.5%)***	***EbC50 = 246 ErC50 = 727 (72 h)***	***reliable***	***Dengler, 2002***
	DCPU (99.0%)	***EbC50 = 5660 ErC50 = 15500 (72 h)***	***reliable***	***Dengler, 2006c***
	DCPMU (99.9%)	***EbC50 = 18.4 ErC50 = 62.8 (72 h)***	***reliable***	***Dengler, 2006d***

n.g. = not given 1) Reliable = high level of confidence in the study; acceptable = study is scientifically sound and usable for regulatory purposes.

Study 1

The effect of diuron (technical, purity not given) on the growth of the green alga *Selenastrum capricornutum* was investigated under static conditions (Zoltán, 2001d). The report does not indicate that the procedure followed any Guidelines, even though a number of such guidelines are available.

The nominal test concentrations were 1.0, 2.0, 4.0, 6.0, 10.0 and 20 µg/L of test substance. At test termination, after 72 hours, there was a dose dependent inhibition of the growth of the algae. Based on nominal concentrations, the 72 hour ErC50 for growth was determined as 11 (CI 7.3-16.3) µg/L (probits) and the NOEC was <1.0 µg/L. Data of cell counts was not presented, only mean percent growth, and therefore the ErC50 value cannot be confirmed and the EbC50 cannot be calculated. From the report is not possible to determine if the percent inhibition data presented was based on percent growth rate or percentage cell counts. The study is rated as acceptable.

Study 2

The effect of diuron (technical, 98%) on the growth of the green alga *Selenastrum capricornutum* was determined following OECD Guideline 201 and US EPA Guideline 122-2 (Douglas and Handley, 1988).

Following a preliminary test, the main test used nominal concentrations of 10, 20, 40, 80 and 160 µg/L of test substance, with acetone at 0.1 µL/L in the test solutions. Based on nominal concentrations, the report gives the 72 hour EbC50 (biomass as area under growth curve) as 18 µg/L, the 120 hour ErC50 as 22 µg/L with a NOEC of 10 µg/L in each case. The EC50 values were determined by fitting a line by eye to the data. The mean cell count at time 0 h was 1.7×10^5 cells/mL, considerably higher than that recommended in current guidelines of 10^4 cells/mL. In the 40 and 80 µg/L exposures the cells were observed to be clumped and pale in colour while at 160 µg/L only cell debris was observed. However, when the 80 and 160 µg/L cultures were recultured in clean media (no diuron), regrowth occurred and the report indicates that the test substance was considered to be algistatic.

DEWHA has recalculated the results using nominal concentrations. The 72 and 120 h EbC50 (cell count using absorbance) was calculated as 19.4 (CI 17.8-21.2) and 32.2 (CI 26.7-35.9) µg/L with the NOEC as <10 µg/L. The 72 ErC50 was calculated as 38.0 (CI 36.6-39.8) µg/L using linear interpolation of the specific rate (Toxcalc).

As the high number of cells used was significantly higher than recommended in the Guidelines, the study is rated as acceptable.

Study 3

The effect of diuron (technical, 96.8%) on the growth of the green alga *Selenastrum capricornutum* was determined following US EPA Guidelines 122-2 and 123-2 (Blasberg, Hicks and Bucksath, 1991).

Following a preliminary test, the main test used nominal concentrations of 0.33, 0.65, 1.3, 2.5 and 5.0 µg/L of test substance with acetone at 0.1 µL/L in all the test solutions. The initial measured concentrations (analysed by HPLC) were 0.30, 0.61, 1.3, 2.5 and 5.2 µg/L, which correspond to between 91 to 104% of nominal. After 120 hours, the measured values were 0.24, 0.44, 0.99, 2.0 and 4.4 µg/L, which correspond to 68 to 88% of nominal. The mean measured results were 0.27, 0.53, 1.15, 2.25 and 4.8 µg/L. The NOEC was 1.3 µg ac/L using initial measured concentrations (1.15 µg ac/L for 120 h mean measured). The report gives EbC50s as 2.3, 3.0 and 2.9 µg/L for 72, 96 and 120 hours respectively using nominal concentrations and a quadratic regression model fitted to the data (% difference from vehicle blank vs concentration or % difference from vehicle blank vs ln concentration). But in Table V of the report the EbC50s are given as 1.8, 2.5 and 2.3 µg/L respectively, without any explanation if these are measured or nominal. DEWHA has recalculated the results using mean measured concentrations (linear interpolation) as EbC50 = 1.9 (CI 1.7-

2.2), 2.8 (CI 2.1-3.3) and 2.1 (CI 1.9-2.3) µg/L for 72, 96 and 120 hours respectively. Using the initial measured concentrations the EbC50s are 2.2 (CI 1.9-2.4), 3.1 (CI 2.3-3.6) and 2.2 (CI 1.7-2.4) µg/L respectively. The NOEC for specific growth rate was 0.61 µg/L and the 72-h ErC50 was calculated (linear interpolation: Toxcalc) using initial measured concentrations as >5.2 µg/L as the highest test concentration did not inhibit specific growth rate by >50%. The maximum growth rate inhibition was 31% of control. However, an unreliable estimate of the ErC50 can be calculated using probits as 10.3 µg/L (fit of the data to probit curve was good but still considered unreliable as growth rate only reached 31% not ≥50% required for an acceptable ErC50).

The study as presented is rated as reliable using the EbC50 of 1.8 and 2.3 µg/L for 72 and 120 hour exposure respectively, as given in the report. Its assumed that these are mean measured as they are similar to the values calculated by DEWHA for mean measured values.

DEWHA notes that one entry for *Selenastrum capricornutum* in the US EPA Pesticide Ecotoxicity database (see below) is possibly the same study as this report as it is from the ABC laboratories, as is this study, the dates are the same, 1991, and the endpoints (2.4 and 2.3 µg/L) are all but identical.

Study 4

The effect of diuron (technical, 98.5%) on the growth of the green alga *Scenedesmus subspicatus* was determined following OECD Guideline 201 (Heimbach, 1991a).

The nominal test concentrations used were 0.1, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6, 10 and 32 µg/L of test substance. The test solutions were analysed by HPLC and initially were 0.1, 0.33, 0.56, 0.9, 1.7, 2.3, 6.0, 11 and 30 µg/L, corresponding to between 72 to 110% of nominal. Based on nominal concentrations, the report gives the 96 hour EbC50 as 7.9 µg/L (probits), the ErC50 was 22 µg/L and NOEC was 3.2 µg/L. DEWHA recalculated the biomass results using measured concentrations as EbC50 = 7.2 (CI 4.5-11.9) µg/L with a NOEC of 2.3 µg/L. The study is rated as reliable using the measured EbC50 and NOEC.

Study 5

The effect of diuron (technical, 99.1%) on the growth of the blue-green alga *Synechococcus leopoliensis* (Cyanpoohyta) was determined following EC Directive (92/69/EEC), C.3 and OECD Guideline 201 (Dengler, 2006a).

Following a range-finding study, the main test used nominal concentrations of 0.4, 1.23, 3.7, 11, 33, 100 and 300 µg/L of test substance. The four highest test concentrations, 0.4, 1.23, 11 and 100 µg/L nominal, were analysed by HPLC every 24 hours and mean concentrations were 0.39, 1.14, 9.9 and 86 µg/L respectively, corresponding to between 90 to 98% of nominal. There was little change in the measured concentrations over the duration of the test.

The results of pH and temperature measurements for all test solutions showed an increase in pH from an initial range of 7.4-7.6 to pH 7.9-9.8 after 72 hours and the initial temperature was 22 to 23°C and increased to 24-25°C at termination. The initial values are within the guidelines and the observed increase in pH for the blank control is within the new proposed OECD Guideline 201 (pH change is 1.47 pH units) proposed in 2002.

Based on nominal concentrations, the report gives the 72 hour EbC50 as 26 µg/L (logistic) and the ErC50 was 380 µg/L and NOECs for biomass and growth were 3.7 and 11 µg/L respectively. DEWHA has confirmed the EbC50 as 25.6 (CI 20.2-28.9) µg/L using the logistic probability distribution, and an EbC50 of 24.9 (CI 24.4-25.3) µg/L with linear interpolation. The study is rated as reliable.

Study 6

The effect of diuron (technical, 98.6%) on the growth of the blue-green alga *Anabaena flos-aquae* (Cyanophyta) was determined following EEC Directive 92/69/EEC, C.3 and OECD Guideline 201 (Memmert, 1998).

Following a range-finding study, the main test used nominal concentrations of 1.0, 3.2, 10, 32 and 100 µg/L of test substance. The 3 highest test solutions were analysed by HPLC and were 10, 31.5 and 104 µg/L at test initiation, corresponding to between 98 to 113 % of nominal. At test termination, after 72 h, there was little change in the measured concentrations, these values were 10.2, 30.4 and 103 µg/L, some 95-103% of nominal. Based on nominal concentrations, the report gives the 72 hour EbC50 as 23.2 µg/L (probits), the ErC50 as 30.9 µg/L and NOEC as 10 µg/L. The study is rated as reliable.

Study 7

The effect of diuron (technical, 99.1%) on the growth of the freshwater diatom *Navicula pelliculosa* was determined following EC Directive (92/69/EEC), C.3 and OECD Guideline 201 (Dengler, 2006b).

Following a range-finding study, the main test used nominal concentrations of 0.4, 1.23, 3.7, 11, 33, 100 and 300 µg/L of test substance. The four highest test concentrations, 0.4, 3.7, 33 and 300 µg/L nominal, were analysed by HPLC every 24 hours and mean concentrations were 0.35, 3.23, 26 and 240 µg/L respectively, corresponding to between 90 to 98% of nominal. The initial concentrations were between 87 to 100% of nominal and at test termination the measured results were 73 to 88% of nominal.

The results of pH and temperature measurements for all test solutions showed an increase in pH from an initial range of 8.2-8.3 to pH 8.3-10.0 after 72 hours and the initial temperature was 22 to 23°C and increased to 24°C at termination. The initial values are within the guidelines and the observed increase in pH for the control is just within the new proposed Guideline (for control pH change was 1.5 pH units).

Based on nominal concentrations, the report gives the 72 hour EbC50 as 22 µg/L with CI of 9-56 µg/L (normal distribution) and the ErC50 was 65 (CI 33-160) µg/L, and NOECs were 11 µg/L for both biomass and growth. DEWHA has recalculated the results to give EbC50 as 16.2 (CI 13.3-21.8) µg/L using probit distribution, 16.0 (CI 14.2-18.8) ug/L using logit distribution and an EbC50 of 19.7 (CI 17.9-20.7) µg/L with linear interpolation. The NOEC was determined as 3.7 µg/L (Wilcoxon Rank Sum test; Shapiro-Wilk's test indicated normal distribution). The study is rated as reliable using the EbC50 = 16.2 µg/L and NOEC of 3.7 µg/L.

Since the initial review, the following growth inhibition and recovery test has been provided with *Lemna gibba*:

Title	***Diuron (DPX-14740) Technical: Static, 7-Day Growth Inhibition Toxicity Test with Lemna gibba G3***
Authors	***Ferrell, B***
Date	***2006***
APVMA Data ID	***9001***
Test Guideline	***US EPA, OPPTS draft Ecological Effects Test Guidelines: 850.4400 (1996)***
Data Validity	***1 (GLP)***
Data Relied On	***Yes - the data was considered to be critical and was relied on in this assessment.***

Test System

Acute toxicity of diuron (99.1% pure) to the freshwater vascular plant *Lemna gibba* G3 was tested in a static system. The test followed a standard US EPA guideline and was conducted to GLP. Both a definitive and a recovery test were performed as described below. The test guideline requires the frond number and

appearance to be recorded on day 0, 3, 5 and 7 of the study. However, in this test the observations were recorded on day 0, 2, 5 and 7. The test guidelines also require the test concentrations to be in a geometric series in which the ratio is between 1.5 and 2.0. The concentrations used in this study have a ratio of 3. No other major deviations from the test guideline were noted.

Definitive Test:

Five test concentrations, an abiotic control and a blank control (twenty-strength synthetic algal-assay-procedure (20X AAP)) was used. Based on the results of a range finding study, nominal concentrations in the definitive test were 0, 1.25, 3.75, 11.3, 33.9 and 102 µg ac/L (4 replicates for each) and the nominal concentration of the abiotic control was 102 µg ac/L. The respective concentrations of measured diuron after 7 days were 75, 81, 90, 100, 97 and 97% of the day 0 measured diuron concentrations. Tests were performed in 250 mL flasks with 100 mL test solution. Four replicates of each concentration and the blank control were used. The abiotic control did not have replicates. Each replicate of the test and control solutions initially contained 3 plants with 4 fronds (total of 12 fronds per replicate). Test solutions were held between 24.3^{o}C and 24.8^{o}C (mean 24.7^{o}C) and were not renewed. A 24 h photoperiod was maintained with a lighting intensity range of 5570 to 6870 lux (mean 5956 lux).

Healthy fronds were recorded at 0, 2, 5 and 7 days. pH was measured on day 0 and day 7 of the study while abnormal fronds were recorded at day 7. Frond count, frond count yield, biomass, biomass yield, growth rate based on frond count and growth rate based on biomass were determined after 7 days.

Initial biomass was determined using a sample of the inoculum culture containing the same number of plants and fronds that was used in each replicate. Final biomass was determined by using 3 randomly selected replicates from each test solution and control after day 7. The biomass was based on the dry mass of the fronds and roots.

The EC50, EbC50, ErC50, LOEC and NOEC were calculated using the geometric mean, measured concentration of diuron. The EC50, EbC50 and ErC50 values and their respective 95% confidence limits were estimated using regression analysis. The LOEC and NOEC were estimated using the Jonckheere-Terpstra test.

Recovery Test:

The recovery test used a blank control and test concentrations exhibiting ≥50% inhibition of healthy frond counts compared to the blank control after 7 days of exposure. This corresponded to test solutions with a geometric mean measured diuron concentration of 25.8 and 79.1 µg ac/L. Each blank control and test solution was tested without replicates. The plants in the selected control and test solutions were exposed to untreated 20X AAP nutrient medium without test medium renewal. 12 healthy fronds were then chosen from each recovery test treatment and aseptically transferred to the appropriate test vessel.

Test solutions were held between 24.7^{o}C and 25.3^{o}C (mean 24.7^{o}C). A 24 h photoperiod with a lighting intensity range of 6360 to 6840 lux (mean 6570 lux) was maintained. Observations and counts were recorded at 0 and 7 days.

Findings

Definitive test

pH ranged from 7.87-8.11 at the start of the test and 8.52-9.01 at the end of the test. Day 7 concentrations of diuron ranged from 75-100% of the day 0 concentrations.

Inhibition of frond count for test solutions containing 0.795, 2.47, 8.11, 25.8 and 79.1 µg/L was -1, -5, 9, 74 and 89% respectively. Inhibition of biomass was -2, 0, 17, 83 and 96% while inhibition of growth rate based on frond count was 0, -2, 4, 54 and 90% respectively. Inhibition of growth rate based on biomass was -1, 0, 7, 70 and 100% respectively.

The following results are summarised:

Table A2.21: Summary of the number of healthy and abnormal fronds at each time interval and concentration for the definitive test

Geometric Mean, Measured Diuron Concentrations (µg/L)	***Healthy Frond Count by Test Daya***				***Abnormal Frond countb***
	Day 0	***Day 2***	***Day 5***	***Day 7***	***Day 7***
Blank Control	***12***	***97***	***309***	***580***	***3***
0.795	***12***	***94***	***309***	***584***	***0***
2.47	***12***	***104***	***313***	***608***	***3***
8.11	***12***	***103***	***275***	***586***	***0***
25.8	***12***	***79***	***117***	***150***	***7***
79.1	***12***	***62***	***61***	***62***	***1***

[a] Healthy frond count refers to the total sum of healthy fronds observed in the four replicates per control or test solution

[b] Abnormal frond count refers to the total sum of abnormal fronds observed in the four replicates on day 7

Table A2.22: Summary of the biomass yield and growth rate based on biomass data for the definitive test

Geometric Mean, Measured Diuron Concentrations (µg/L)	***Day 7***		
	Test end Lemna Biomass (mg)a	***Growth Rate Based on Biomass day 0-7 (ln Fronds)b***	***Growth Rate Based on Healthy frond count day 0-7 (ln Fronds)c***
Blank Control	***39.91***	***1.080***	***1.428***
0.795	***40.77***	***1.087***	***1.426***
2.47	***39.89***	***1.079***	***1.450***
8.11	***33.18***	***1.001***	***1.367***
25.8	***6.84***	***0.324***	***0.649***
79.1	***1.68***	***0.000***	***0.141***

[a] *Lemna* biomass refers to the total sum of the three replicates for each test concentration and blank control

[b]Growth rate based on biomass refers to the total sum of the three replicates for each test concentration and blank control.

[c]Growth rate based on healthy frond count refers to the total sum of the four replicates for each test concentration and blank control.

No mortalities were observed in the control group during the 7 day exposure period. Sub-lethal effects were observed in the control group as well as the 2.47, 25.8 and 79.1 µg/L treatment groups after day 7. These sub-lethal effects were chlorosis and necrosis and were observed in the abnormal fronds.

Recovery Test

The recovery test was terminated after 7 days due to evident frond growth in all test vessels. From the highest exposure group, there was a 7X increase in healthy fronds after 7 days. During exposure, this increase was only 1.3X. Meanwhile, in the control group, the increase during the exposure phase was around 12X compared to around 14.5X in the recovery period. This suggests inhibition resulting from diuron exposure is phytostatic.

The following results during the 7 d recovery period are summarised:

Table A2.23: Summary of the healthy frond count for the recovery study

Geometric Mean, Measured Diuron Concentrations (µg/L)	***Healthy Frond Count by Recovery Test Day***	
	Day 0	***Day 7***
Blank Control	***12***	***174***
25.8	***12***	***125***
79.1	***12***	***85***

Conclusion

The study authors concluded the most sensitive parameter was a biomass yield with a 7-day E_yC50 of 14.4 µg/L with a 95% confidence interval of 9.26 to 19.6 µg/L, a LOEC of 8.11 µg/L and a NOEC of 2.47 µg/L, based on geometric, mean measured concentrations. The following conclusions for the definitive test are summarised below:

Table A2.24: Summary of the EC50, 95% confidence interval, LOEC and NOEC for various parameters

7 day EC50 (95% confidence interval) for diuron, based on mean, measured concentrations (*µg/L*)	**EC50 Frond count: 19.1 (13.4 to 24.8)**
	EbC50 Biomass: 15.7 (10.6 to 20.8)
	ErC50 Growth Rate, Frond Count: 26.9 (21.2 to 32.6)
	ErC50 Growth Rate, Biomass: 20.3 (14.6 to 26.0)
7 day NOEC for diuron, based on mean, measured concentrations (*µg/L*)	**Frond Count: 8.11**
	Biomass: 2.47
	Growth Rate, Frond Count: 8.11
	Growth Rate, Biomass: 2.47

The study authors concluded from the recovery test that the effect of diuron on growth and reproduction of *Lemna gibba* was found to be phytostatic within 7 days for mean measured concentrations ≤79.1 µg ac/L

Other duckweed data

There are no duckweed studies reported in the US EPA RED (US EPA 2003), but there are 3 reports listed for diuron on the US EPA ECOTOX database with duckweed, showing results as follows:

Lemna minor (duckweed): 7 d EC50 = 25 µg/L;

Lemna perpusilla (duckweed): 7 d EC50 = 15 µg/L;

Spirodela polyrhiza (giant duckweed): 7 d EC50 = 41 µg/L.

Lemna gibba and *Lemna minor* are the only species recommended for testing under the OECD test guideline – these are described as species representative of temperate areas and commonly used for toxicity tests, both species having a floating or submerged discoid stem (frond) and a very thin root emanating from the centre of the lower surface of each frond.

Lemna perpusilla appears to be similar to the standard test species *Lemna gibba* and *Lemna minor*, whereas *Spirodela polyrhiza* (giant duckweed) is a larger plant with more roots per frond. These literature studies are reviewed below.

Liu and Cedeno-Maldanado (1974) considered the toxicity to aquatic non-target species of a range of herbicides including diuron. Although not a GLP report and conducted prior to the development of the relevant test guideline, the design and conduct of the study appear satisfactory – four replicates of seven test concentrations (2×10^{-5} M to 1×10^{-8} M) for each herbicide, under controlled laboratory conditions from cultures maintained in exponential growth. The test species were *Spirodela polyrhiza* and *Lemna perusilla*.

The tests were initiated with 10 fronds per dish and transferred to fresh media (static-renewal) on days 2 and 4. Counts taken on day 7 were used to calculate the frond multiplication ratio. The herbicide concentrations

causing 50% inhibition of growth were estimated graphically from plots of increase in frond number as a % of the control against concentration (data for the four replicates are not available, hence DEWHA has not recalculated these according to standard methods). The resulting estimates for *S. polyrhiza* and *L. perusilla* were 1.75 X 10^{-7} M (41 µg/L) and 6.4 X 10^{-8} M (15 µg/L), respectively.

Teisseire *et al* (1999) compared the toxicity of diuron alone and in combination with two other toxicants, copper and folpet to duckweed (*L. minor*) (). Although not a GLP report, the design and conduct of the study appear satisfactory – three replicates of seven test concentrations (5 to 100 µg/L), semi-static conditions (solution renewed after 4 days of the 7 day tests) under controlled laboratory conditions from cultures maintained in exponential growth. Results were based on nominal concentrations.

The results for diuron were IC50 of 25±3 µg/L, IC90 of 60±2 µg/L and the LOEC was 5 µg/L, the lowest test concentration. A NOEC was not determined. Measurements of total chlorophyll content of the duckweed showed that the concentration of chlorophyll increased for 10 and 20 µg/L test solutions to be 40% above control, then decreased with increasing concentrations of diuron and was no longer significantly different to control at 100 µg/L. When diuron was used in combination with copper and folpet, the effects of the other two toxicants was slightly antagonistic or independent.

The effects of diuron and its metabolites (from demethylation) on the PSII complex in *L. gibba* were determined using pulse-amplitude modulated (PAM) chlorophyll fluorescence (Dewez, *et al*, 2002). The metabolites used were the mono-demethylated DCPMU [N'-(3,4-dichlorophenyl)-N-methylurea], DCPU [N-(3,4-dichlorophenyl)urea] and DCA [3,4-dichloroaniline].

The duckweed was exposed to diuron or its metabolites at test concentrations of 1 to 50 µg/L (diuron and DCPMU) with a level of 100 µg/L also tested for DCPU and DCA. The PSII operational quantum yield[3] was determined 5, 24 and 48 hours later using PAM. In addition, rapid fluorescence induction of the plants was determined (this allows information on the site where the PSII system is inhibited), with results assessed by use of a fluorescence toxicity index. The results show that after 48 hours (the 5 and 24 hour results will not be considered as these there are not important in discussing the relative toxicity of the metabolites) the effective quantum yields of the duckweed were reduced compared to control. Compared to the control, operational quantum yield was reduced by 90% in the diuron treatment at 50 µg/L, and by 73% in the DCPMU treatment at 50 µg/L. Lower inhibition was seen in the DCPU and DCA treatments with reductions of 21 and 5.6% at 100 µg/L respectively.

The fluorescence toxicity index for *L. gibba* was shown to be highly dependent on the concentrations of diuron and DCPMU (and DCPU to an extent), and to the time of exposure. Based on this index, the toxicity of DCPMU at 48 h (50 µg/L) was shown to be about 75% that of diuron, which is in relatively good agreement wih the the operational quantum yield results above. It is concluded that both DCPU and DCA are unlikely to have significant herbicidal activity based on the fluorescence toxicity results (~25 and <10% that of diuron), or the operational quantum yield results..

Formulated Products

Study 1

[3] The steady-state (F_s) and maximum (*F'm*) fluorescence levels in the light-adapted plant are used to calculate the effective quantum yield by (*F'm/Fs)/F'm*, This is another parameter that represents the efficiency with which excitation energy captured by the chlorophyll antenna is used in electron transport."

The effect of Karmex SC 500 (several similar formulations are registered in Australia), containing diuron at 517 g ac/L, on the growth of the green alga *Selenastrum capricornutum* was determined following IBAMA Guidelines (Monma, 1998).

Based on the results of a preliminary test, the main test used nominal concentrations of 6.0, 10, 20, 30, 40, 60 and 100 µg/L of test substance. The test solutions were not analysed and all results were based on nominal concentrations. At test termination, after 120 hours, there was a dose dependent inhibition of the growth of the algae. The report gives the 120 hour EbC50 as 33.1 µg/L (determined by exponential regression) and the NOEC was 10 µg/L. The EbC50s at 24, 48, 72 and 96 hours were 16.8, 19.1, 20.3 and 26.9 µg/L test substance respectively. DEWHA recalculated the results using probits as EbC50 = 29.8 (CI 19-44-12.8) µg/L after 120 hours with NOEC of 30 µg/L (Steel's test). The 72 h EbC50 was calculated by DEWHA as 17.8 (CI 12.2-24.0) µg/L and the NOEC was 20 µg/L. There were large variations in the controls, which affected the sensitivity of the NOEC in the statistical analysis.

The algistatic/algicidal effect of the test substance was determined by transferring algae from the 40, 60 and 100 µg/L growth medium after 72 hours to fresh algae growth medium. These algae cells showed exponential growth and an algicidal effect was not found. The study is rated as acceptable.

Study 2

The effect of diuron WP 80 (formulated product at 80.1% ac) on the growth of the green alga *Scenedesmus subspicatus* was determined following OECD Guideline 201 (Heimbach, 1991b).

Following a preliminary test, the main test was conducted using nominal concentrations of 1.0, 1.8, 3.2, 5.6, 10, 18, 32, 56 and 100 µg/L of test substance. The test solutions were analysed by HPLC and were 0.46, 2.4, 4.1, 9.0, 15, 28, 48 and 85 µg/L of test material, corresponding to between 58 to 113% of nominal (average was 97.8% of nominal). Based on nominal concentrations, the report gives the 96 hour EbC50 as 3.7 µg/L (probits) and the ErC50 was 30 µg/L and the NOEC was 1.0 µg/L in both cases. DEWHA recalculated the results using measured concentrations at 96 hours as EbC50 = 4.8 (CI 3.5-6.6) µg ac/L with a NOEC of 2.3 µg ac/L, the EbC50 is equivalent to 5.9 (CI 4.4-7.9) µg product/L. The study is rated as reliable.

Study 3

The effect of Karmex DF containing diuron at 81.2% (Karmex in Australia is formulated at 900 g ac/kg), on the growth of the green alga *Desmodesmus subspicatus* (formerly *Scenedesmus subspicatus*) was determined following OECD Guideline 201 and EEC Directive 92/69/EEC, C.3 (Dengler, 2003).

Based on the results of a preliminary test, the main test used nominal concentrations of 3.1, 6.3, 12.5, 25, 50 and 100 µg/L of test substance. The test solutions were analysed by HPLC at the start, 24, 48 and 72 (termination) hours later and the mean concentrations were 2.4, 4.4, 8.6, 17.5, 36.1 and 71.5 µg ac/L, corresponding to between 84.3 to 95.6% of nominal. The analytical method used was satisfactory except for the 3 µg/L of test material where the recovery was just 76% of nominal. Based on the nominal concentrations of test substance, the report gives the 72 hour EbC50 as 15.3 µg formulation/L (probits), the ErC50 as 37.2 µg formulation/L and NOEC as 6.3 µg formulation/L (corresponds to 12.4, 30.2 and 5.1 µg diuron/L respectively). DEWHA recalculated the results using measured concentrations as EbC50 = 9.6 (CI 7.5-12.8) µg ac/L with NOEC of 4.4 µg ac/L; the EbC50 is equivalent to 11.8 µg formulation/L. The study is rated as reliable.

Metabolites of Diuron

Study 1

The effect of the diuron metabolite m-CPDMU (3-(3-chlorophenyl)-1,1'-dimethyl urea; 99.5% purity) on the growth of the green alga *Desmodesmus subspicatus* (formerly *Scenedesmus subspicatus*) was determined following OECD Guideline 201 and EEC Directive 92/69/EEC, C.3 (Dengler, 2002).

Based on the results of a preliminary test, the main test used nominal concentrations of 0.05, 0.09, 0.16, 0.29, 0.52, 0.94 and 1.7 mg/L of test substance. The test solutions were analysed by HPLC at the start, 24, 48 and 72 (termination) hours later and the mean concentrations were 0.053, 0.96, 1.8, 0.32, 0.58, 1.04 and 1.85 mg/L, corresponding to between 107 to 112 % of nominal. At test termination, after 72 hours, there was a dose dependent inhibition of the growth of the algae. Based on nominal concentrations, the report gives the 96 hour EbC50 as 0.246 mg/L (probits) and the ErC50 was 0.727 mg/L and NOEC was 0.16 mg/L. The study is rated as reliable.

Study 2

The effect of the diuron metabolite DCPU (1-(3,4-Dichlorophenyl)-urea; 99.0% purity) on the growth of the green alga *Desmodesmus subspicatus* (formerly *Scenedesmus subspicatus*) was determined following OECD Guideline 201 and EEC Directive 92/69/EEC, C.3 (Dengler, 2006c).

Based on the results of a preliminary test, the main test used nominal concentrations of 0.78, 1.56, 3.13, 6.25, 12.5, 25, 50 and 100 mg/L of test substance. Selected test solutions were analysed by HPLC at the start, 24, 48 and 72 (termination) hours later and the mean concentrations were 0.72, 1.55, 12.6, 47.8, and 89.0 mg/L for 0.78, 1.56, 12.5, 50 and 100 mg/L respectively. These correspond to between 92 to 101% of nominal. Based on nominal concentrations, the report gives the 72 hour EbC50 as 5.66 (CI 3.7-7.7) mg/L and the ErC50 was 15.5 (CI 9.6-24.2) mg/L and the NOECs were 1.56 and 3.13 mg/L for biomass and growth rate respectively. The study is rated as reliable.

Study 3

The effect of the diuron metabolite DCPMU (3-(3,4-Dichlorophenyl)-1-methyl urea; 99.9% purity) on the growth of the green alga *Desmodesmus subspicatus* (formerly *Scenedesmus subspicatus*) was determined following OECD Guideline 201 and EEC Directive 92/69/EEC, C.3 (Dengler, 2006d).

Based on the results of a preliminary test, the main test used nominal concentrations of 2.05, 5.12, 12.8, 32, 80, 200 and 500 µg/L of test substance. Selected test solutions were analysed by HPLC at the start, 24, 48 and 72 (termination) hours later and the mean concentrations were 2.5, 5.6, 33 and 525 µg/L for 2.05, 5.12, 32 and 500 µg/L respectively. These correspond to between 102 to 122% of nominal. Based on nominal concentrations, the report gives the 72 hour EbC50 as 18.4 (CI 11.1-30.1) µg/L and the ErC50 was 62.8 (CI 53-74) µg/L and the NOEC was 5.12 µg/L for both biomass and growth rate. DEWHA has confirmed these calculations. The study is rated as reliable.

Pesticide EcoToxicity Database

According to the available data from Pesticide Ecotoxicity database and US EPA RED (US EPA 2003), this indicates that diuron can generally be classified as very highly toxic to aquatic plants, including algae and diatoms. The EC50s for green algae (Chlorophyceae) ranged from 2.4 to 37 µg ac/L, similar to that for the reviewed studies above, making these algae the most sensitive but the brown and red algae species tested also fell into this range.

Table A2.25. Summary of aquatic toxicity studies with diuron – algae and diatoms available from the US EPA RED (US EPA 2003). All studies were conducted to US EPA Guideline 122-2 except where indicated.

Species	Comments	Toxicity µg/L (95% confidence limits)	Year reported[1]	US EPA category[2]

Chlorophyceae (green algae)				
Selenastrum capricornutum	Guideline 123-2; 96.8% ac	96 h EC50 = 2.4 (2.0-2.8); NOEC = 0.44	1991	Core
Chlorella sp.	95% ac	72 h EC50 = 19	1986	Supplemental
Chlorococcum sp.	95% ac	72 h EC50 = 10	1986	Supplemental
Dunaliella tertiolecta	95% ac	240 h EC50 = 20	1986	Supplemental
Neochloris sp.	95% ac	72 h EC50 = 28	1986	Supplemental
Platymonas sp.	95% ac	72 h EC50 = 17	1986	Supplemental
Chlamydomonas sp	95% ac	72 h EC50 = 37	1986	Supplemental
Bacillariophyceae (diatoms)				
Achnanthes brevipes	95% ac	72 h EC50 = 24	1986	Supplemental
Navicula incerta	95% ac	72 h EC50 = 93	1986	Supplemental
Nitzschia closterium	95% ac	72 h EC50 = 50	1986	Supplemental
Phaeodactylum tricornutum	95% ac	240 h EC50 = 10	1986	Supplemental
Stauroneis amphoroides	95% ac	72 h EC50 = 31	1986	Supplemental
Thalassiosira fluviatilis	95% ac	72 h EC50 = 95	1986	Supplemental
Cyclotella nana	95% ac	72 h EC50 = 39	1986	Supplemental
Amphora exigua	95% ac	72 h EC50 = 31	1986	Supplemental
Rhodophyceae (red algae)				
Porphydriium cruentum	95% ac	72 h EC50 = 24	1986	Supplemental
Prymnesiophyceae (haptophytes marine algae)				
Monochrysis lutheri	95% ac	72 h EC50 = 18	1986	Supplemental
Isochrysis galbana	95% ac	240 h EC50 = 10	1986	Supplemental

1) Only the year date of the study has been cited; 2) Category listed on the US EPA Pesticide EcoToxicity Database.

The most sensitive result was an 96 hour EC50 of 2.4 µg/L (likely to be the same study as listed as study 3 above by Blasberg*et al*, 1991) for the green algae *Selenastrum capricornutum* (renamed *Raphidocelis subcapitata* and more recently, *Pseudokirchneriella subcapitata*), and the range is from 2.4 to 95 µg ac/L (results not converted to active consistent), based on the purity of test material. The EC50 value for the prolonged 10 day data shown in Table A2.25 is also within a similar range of 10-20 µg/L.

4.2 Algae and aquatic plants - Literature reports

Marine Algae

Study 1

Title	Comparative effects of herbicides on photosynthesis and growth of tropical estuarine microalgae
Authors	Magnusson et al
Date	2008
APVMA Data ID	N/A – literature paper
Test Guideline	OECD TG 201; US EPA OPPTS 850.5400
Data Validity	2* (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

This research is valuable in that it provides a basis for comparing non-standard PAM results with more

traditional algae toxicity end-points of growth and biomass. The study involved a 3 day (72 h) exposure period using two tropical benthic microalgae; *Navicula sp*. (Heterokontophyta) and *Nephroselmis pyriformis* (Chlorophyta). Replicate mother cultures for both organisms (n=5) in exponential growth phase were dosed with a dilution series of seven concentrations of herbicide (diuron, hexazinone or atrazine) and a DMSO carrier control.

A 3-day (72 h) exposure was chosen as the main experimental time frame for endpoint comparison and determination of EC50 concentrations following standardized ecotoxicology test guidelines (USEPA, 1996; OECD, 2006). Comparison before 3 days was not feasible as growth rate could not be reliably measured in a single day, and the cultures were too dilute to measure a reliable fluorescence signal with the mini-PAM. The actual test concentrations are unclear, but appeared to cover seven test concentrations between 10^{-1} and 10^{2} nM (0.023 to 23 µg/L)

Findings

The following results were obtained:

Table A2.26: 72 h growth rate (µ), biomass increase and effective quantum yield [Y(II)] values (µg/L)

	Navicula sp.			Nephroselmis pyriformis		
	µ	Biomass	Y(II)	µ	Biomass	Y(II)
EC50						
Diuron	7.8**	3.7	5.5	8**	5.8	5.9
Atrazine	130*	65	99	50	35	28
Hexazinone	27*	14	16	10	8.4	6.2
EC10						
Diuron	2.4**	0.5	1.0	5.2**	2.2	1.1
Atrazine	35*	26	19	23	11	6.8
Hexazinone	6.5*	3.4	3.3	4.8	3.8	2.1

* n=4; ** n=3; otherwise, n=5

Conclusion

These results indicate that the PAM methodology would appear to give outcomes not dissimilar to the standard toxicity endpoints. Growth was less sensitive than reduction in quantum yield for both species and all chemicals tested, and this is important as the growth endpoint is the preferred one for reporting and use in the risk assessment of a standard regulatory assessment over results determined through biomass measurements. In this sense, use of PAM results may slightly overestimate toxicity compared to growth results, but nonetheless, the outcomes are in relatively good agreement. We note that the PAM exposure period in this study was 3 days, which allowed it to be directly comparable to the growth and biomass results. However, many PAM studies seem to be for a shorter exposure period (24 h). To confidently use results generated using PAM methodology, such 24 h results would need to be related to standard 72 h standard growth and reproduction studies.

Study 2

The effect of diuron on crustose coralline algae (CCA) from the Great Barrier Reef area has been examined (Harrington, *et al*, 2005). [CCA are 'hard' marine substrata with calcareous crusts and are important elements that help bind reefs together. These algae induce the settlement of benthic organisms, including corals (there is evidence that some corals species will only settle on selected species of CCA) and

consequently changes in CCA abundance can result in changes in the structure, function and abundance of corals in reef ecosystems.] The paper studied the synergistic effects of sedimentation and diuron exposure of several 'clean' sediments and diuron with sediment, and investigated the effects of such exposures on photosynthesis and survival of these organisms. Three species of CCA were collected from midshelf reefs and subjected to sediments (*Hydrolithon reinboldii*, *Neogoniolithon fosliei* and *Porolithon onkodes*). One of these secies (*P. onkodes*) was then exposed to diuron and sediments in combination. The primary response of interest were altered photophysiology (quantified using PAM fluorometry), bleaching and survival.

Four types of sediments were used. Estuarine sediment (upper 5 cm of a mud bank) from the Herbert River was sieved into fine (<63 µm) and medium (63-250 µm). Fine offshore sediments were collected from Otter Reef and sieved to retrieve the <63 µm fraction, and a fine calcareous sediment was prepared as sawdust by cutting dried skeletons of *Porites* corals. Analysis of the first three sediments revealed diuron contamination at 0.20, 0.28 and 0.16 µg/kg respectively, showing even in the offshore sediments, diuron is a low level contaminant.

Sediment exposure studies: CCA fragments were transferred to 25 L aquaria (2 per sediment type). The sediments were stirred to ensure uniform distribution and allowed to settle. Measured levels of sediment deposition were 96-105 mg/cm^2. Flow through sea water was provided during the exposure period (84 h) after which the fragments were subsequently transferred back to sediment free aquaria to recover (84 h). Sedimentation adversely affected all species with all sediment types. Following removal to sediment free aquaria, recovery was observed for all species. The most significant effects were found for the Herbert River fine sediment, and the most sensitive species was *P. onkodes*, which after 84 h recovery, still only had photosynthetic activity around 80% of control levels.

Combined diuron and sediment exposure: This part of the experiment was performed to determine whether sedimentation stress is altered by the presence of diuron and was performed with the sediment shown to cause the greatest stress and the CCA species shown to be the most susceptible. *P. onkodes* was exposed to four diuron concentrations (measured at 0 and 105 h with mean values of 0, 0.79, 2.27, 6.36, 21.3 µg/L) for 105 hours. In addition, diuron was added to aerated Herbert River fine sediments suspended on sea water at mean (0 and 105 h) concentrations of 0, 0.79, 2.50, 7.86, 24.65 µg/L. *P. onkodes* was exposed to this mixture sufficient to give a final sedimentation rate of 96 mg/cm^2. Following exposure, CCA were transferred back to sediment and contaminant free aquaria for a recovery period of 9 days.

In the diuron only experiment, the only concentration to reduce photosynthetic activity was the highest test concentration with around 65% inhibition at the end of the exposure period. Recovery continued after cessation of exposure and photosynthetic activity for this group was the same as control values after 9 days. In the combined diuron/sedimentation experiment, at the end of the exposure period, all treatments (including the uncontaminated sediment treatment) showed similar reduction in photosynthetic activity (around 20% of control values) indicating the stress was caused by sedimentation rather than diuron. However, during the recovery period, the uncontaminated sediment group showed stronger recovery and after 9 days, had recovered to within about 75% of control levels. Meanwhile, all the diuron treatment groups showed a statistically similar recovery and ranged from between 40 and 60% of control values at the end of the recovery period. The implication of this is that while initial stress is caused by sedimentation, the occurrence of additional stress (in this case, diuron), can impede the recovery of the CCA, even though in this case, diuron did not cause any lasting adverse effects on the test organism when exposed in water alone up to 21 µg/L.

In the sediment only experiments, the most sensitive species, *P. onkodes* had parts of the fragments showing loss of pigmentation, although no mortality occurred after the treatments. With the additional stressor of diuron, some fragments were considered dead (17%) with 59% bleached.

These results can not be used in a standard risk assessment approach. No dose/response relationship can be determined, although it could be noted that diuron in absence of sedimentation exhibited a LOEC of 21.3 µg/L and a NOEC of 6.36 µg/L to *P. onkodes*. As concluded in the paper, sediment deposition can

negatively affect the photosynthetic activity of CCA and this stress can be significantly enhanced by the presence of diuron. In actual fact, the presence of diuron did not enhance the stress caused by sedimentation during the period of sedimentation. However, it did appear to adversely affect the ability of the CCA to recover.

Corals

Several non-standard test results are described below for various coral species. The results are primarily based on effects on chlorophyll fluorescence, and it is unclear how this end-point relates in terms of biological significance compared to traditional end-points such as growth or reproduction. Following further consideration, DEWHA now considers the following results can not be applied in the standard risk assessment approach being used in this report. However, it appears from the following information that impacts on chlorophyll fluorescence to the range of corals is not remarkably different to growth/reproduction toxicity data for a range of algal/diatom results described above that were obtained following standard test guidelines.

It appears from these results that should sustained sufficient levels of diuron occur in water (10 µg/L, appears to be a representative value based on the following information), coral bleaching could result, and for some species, this process could be irreversible.

It should be noted that effects of herbicides such as diuron on coral bleaching are further complicated by interactions with other stressors, such as sediment, ocean warming, nutrients and changes in salinity.

Study 1

Cantin *et al*., (2007) examined the importance of energy derived from photosynthesis to the gametogenisis of corals following long-term experimental exposures to diuron. Two broadcast spawning corals, *Acropora tenuis* and *A. valida*, and a brooding coral, *Pocillopora damicornis*, were exposed to 0 (controls), 1.0 (low) and 10 µg/L (moderate) diuron concentrations for 2 to 3 months prior to spawning on planulation. Each treatment was performed outdoors in 500 L tanks with unfiltered oceanic seawater that was settled in a header tank before flowing into experimental tanks at 3 L/min. Seawater temperatures in the tanks ranged from 26^{o}C in the spring and autumn to 29^{o}C in the summer months. For each of the three treatments, 2 tanks were used and 4 large reproductive colonies of each species were maintained within each tank during the 3 separate exposure experiments.

The photosynthetic efficiency (maximum quantum yield and effective quantum yield) of *Symbiodinium* spp. within host tissues of the 3 coral species was estimated from chlorophyll fluorescence measurements taken with a pulse amplitude modulated (PAM) chlorophyll fluorometer. The following findings were reported:

Diuron caused photoinhibition in each species, with PAM recording consistent declines in effective quantum yields of 20% and 75% at 1 and 10 µg/L respectively;

A. valida and *P. damicornis* were both sensitive to this photoinhibition, becoming severely bleached at 10 µg/L.

At 10 µg/L, *A. valida* sustained both partial and full colony mortality. However, *A. tenuis* was more resistant and neither bleached or sustained mortality at any treatment.

Polyp fecundity was reduced by 6-fold in *A. valida* and both *A. valida* and *P. damicornis* were unable to spawn or planulate following long term exposures to 10 µg/L diuron.

The LOEC from this study appeared to be 10 µg/L with a NOEC of 1.0 µg/L based on polyp fecundity.

Study 2

Negri et al, (2005): In this research, effects of diuron on the early life history stages of broadcast spawning and brooding corals were examined in laboratory experiments. Exposure periods were 96 h (4 d) and a 14 d recovery period was included.

The experiments were conducted using ethanol as carrier (concentration not given) and preliminary experiments showed that after 24 hours in either glass or polystyrene cell culture plates the concentration of diuron remained within 30% of nominal. The diuron solutions were renewed daily for the 96 hour exposures. Nominal concentrations were 0.1, 1, 10, 30, 100, 300 and 1000 µg/L. All results were presented as nominal concentrations.

Diuron did not affect fertilisation of the broadcast spawning species *Acropora millepora* and *Montipora aequituberculata* at concentrations of up to 1000 µg/L. Metamorphosis of symbiont-free *A. millepora* larvae was only significantly inhibited at 300 µg/L of diuron. *Pocillopora damicornis* larvae, which contain symbiotic dinoflagellates, were able to undergo metamorphosis after 24 h exposure to diuron at 1000 µg/L. Two-week old *P. damicornis* recruits on the other hand were as susceptible to diuron as adult colonies, with expulsion of symbiotic dinoflagellates (bleaching) evident at 10 µg/L diuron after 96 h exposure, and there was no recovery after 14 days in clean seawater. Recruits were as sensitive as adults to effects of diuron on photosynthesis as measured by fluorescence (maximum quantum yield (*Fv/Fm*), and effective quantum yield (∆*F/F'm*) using a PAM fluorometer. The recruits and adults recovered in uncontaminated seawater but *P damicornis* was severely bleached at 10 µg/L of diuron or higher and remained so after the recovery period. Table A2.27 summarises the results (taken from paper).

Table A2.27. NOECs and LOECs (µg/L) for each of the life stages of the corals tested.

Life history transition/stage	Diuron exposure, µg/L	Duration	Species	NOEC (µg/L)	LOEC (µg/L)
Fertilisation	1-1000	4 h	A. millepora	1000	
		6 h	M. aequituberculata	1000	
Metamorphosis	1-1000	24 h	A. millepora	100	300
		24 h	P. damicornis	1000	
Recruit survival	30-1000	96 h	A. millepora	1000	
	1-1000	96 h	P. damicornis	1000	
Recruit tissue retraction	0.1-1000	96 h	P. damicornis	10	100
No recovery from tissue retraction		14 d	P. damicornis	10	100
Recruit bleaching		96 h	P. damicornis	1	10
No recovery from bleaching ("living ghosts")		14 d	P. damicornis	1	10
Recruit ΔF/F'm	0.1-100	96 h	P. damicornis	0.1	1.0
Recruit Fv/Fm			P. damicornis	0.1	1.0
Adult ΔF/F'm	0.1-100	96 h	P. damicornis	0.1	1.0
			A. millepora	0.1	1.0
Adult Fv/Fm	0.1-100	96 h	P. damicornis	0.1	1.0
			A. millepora	0.1	1.0
Adult survival exposure	0.1-100	96 h	P. damicornis	100	
			A. millepora	100	

The study should be considered as a range finding study but still clearly shows that the coral *P. damicornis* is sensitive to diuron with irreversible bleaching of coral recruits first occurring at 10 µg/L after 4 days exposure, and the NOEC was 1.0 µg/L. The photo-inhibition of the coral symbiotic dinoflagellates occurred at 1 µg/L of diuron as determined by PAM fluorometery.

While this research reports NOECs from recruit coral PAM findings of 0.1 µg/L, the study also investigated recovery. This is an important aspect, and showed that following cessation of exposure, recovery was complete with quantum yields at exposure groups of 0.1, 1.0 and 10 µg/L being equivalent to controls within 1 day. Recovery was somewhat slower at the highest 30 µg/L tested, but was still complete within 7 days of exposure ceasing.

Study 3

Jones and Kerswell (2003) reported a study of the toxicity of diuron and various other Photosystem II (PSII) herbicides to reef-building corals, or more specifically to the dinoflagellate (unicellular algae) that live symbiotically in the gastrodermis of the coral organisms[4]. Pulse-Amplitude Modulated (PAM) chlorophyll fluorescence techniques were used to examine changes in the maximum effective quantum yield (∆*F/F'm*) of symbiotic dinoflagellates within the host tissues of the coral.

Diuron was one of several PSII inhibiting herbicides to which the coral *Seriatopora hystrix* was exposed in short-term toxicity tests (24 h static toxicity tests at 25ºC under a 10 h light:14 h dark cycle – chlorophyll fluorescence parameters determined at 10 h for ∆*F/F'm* and 24 h for *Fv/Fm*). The EC50 for ∆*F/F'm* was determined as 2.3 µg/L, the NOEC <0.3 µg/L and LOEC = 0.3 µg/L. Another coral *Acropora formosa* gave an EC50 for ∆*F/F'm* of 2.7 µg/L and NOEL and LOEC as before (NOEC <0.3 µg/L and LOEC = 0.3 µg/L). This, together with the information below, suggests comparable toxicity to coral dinoflagellates to that shown to sensitive algae species such as *Selenastrum capricornutum* in standard algal toxicity tests. However, the endpoints used for the dinoflagellates were altered phytophysiology (reduction in maximum quantum yield) and are not directly related to growth or mortality of the algae species.

Time course experiments that were conducted with *S. hystrix* and *A. formosa* using diuron showed that:

∆*F/F'm* was reduced within minutes by exposure to diuron but recovered quickly on return to fresh running seawater; after 5 hours, ∆*F/F'm* recovered to within 5% of control value.

the effects of diuron (3 µg/L for up to 8 h) on ∆*F/F'm* of *Seriatopora hystrix* were inversely related to temperature over the range 20-30ºC, although initially the effects were less at the lower temperatures. In the control coral there was little difference in ∆*F/F'm* between different temperatures.

Study 4

Another paper by the same principal researcher (Jones, *et al*. 2003) reported studies with the herbicides diuron and atrazine and four species of coral (those above, plus *Montipora digitata* and *Porites cylindrica*), again using PAM chlorophyll fluorescence techniques. The measured EC50s of diuron (10 hours exposures, 100 µmol quanta/m^2/s) for effective quantum yield (∆*F/F'm*) were 5.1, 4.3 and 5.9 µg/L for *A. formosa*, *P. cylindrica* and *M. digitata* respectively. After 24 hours of exposure (at the end of a 14 hour dark period), the maximum fluorescence (*Fv/Fm*) was significantly different to controls corals exposed to 1.0, 3.0 and 30 µg/L respectively. The coral *S. hystrix* was used to test the effect of light levels. The EC50 was 3.7 µg/L at 'normal' light levels (100 µmol quanta/m^2/s) but when exposed to lower light intensities (20 µmol

[4] The dinoflagellate (zooxanthellae) symbiont provides nutrients and food through photosynthesis, pigments providing UV-protection of both the coral (coelenterate) and algae, and enhances the rate of carbonate accumulation (reef building). The polyps can survive for a few months without zooxanthellae but will eventually die unless favourable conditions return and the surviving zooxanthellae repopulate the corals, then the corals return to their normal colours and continue growing. If conditions remain unfavourable (eg temperatures too high) or if there are too few surviving zooxanthellae, the coral polyps cannot recover and they die. http://ag.arizona.edu/azaqua/algaeclass/symbios.htm; http://www.wfu.edu/users/braukm0/coralsymbiosis.html; Levy et al (2003) and Salih, Hoegh-Guldberg and Cox (1998).

quanta/m^2/s) the EC50 decreased to 2.9 µg/L. The effect of reduced salinity was also examined (35 to 27 part per thousand); there was no significant interaction between diuron and the reduced salinity levels.

Included in the study was an examination of exposure of algae *in hospite* (in host; in the coral tissue) in *M. digitata* to higher concentrations of diuron (0.1, 1.0, 10, 100 and 1000 µg/L) for 96 h (compared to the short term ∆*F/F'm* EC50 of diuron ~6 µg/L) with a 96 hour recovery period. Exposure to the concentrations of 1, 10, 100, 1000 µg/L caused a reduction in the fluorescence parameters ∆*F/F'm* and *Fv/Fm*, compared to controls. There was loss of symbiotic dinoflagellates and bleaching at 10 µg/L and there was significant loss of symbiotic dinoflagellates and pronounced tissue retraction causing the corals to pale and bleach at 100 and 1000 µg/L. One day after being transferred to clean seawater, *Fv/Fm* remained suppressed in the corals exposed to 100 and 1000 µg/L only.

The ∆*F/F'm* in freshly isolated dinoflagellates from *S. hystrix* was rapidly reduced on exposure to diuron and the LOEC was 0.25 µg/L and the EC50 was 5.5 µg/L. In the previous test, the EC50 of this coral *in hospite* was 3.7 µg/L.

Study 5

The effect of diuron (and 2,4-D) on the hermatypic coral *Porites cylindrica* was investigated (Råberg *et al*, 2003). The corals were exposed to diuron concentrations of 10, 50 and 100 µg/L and effects measured were changes to fluorescence (maximum quantum yield (*Fv/Fm*), effective quantum yield (∆*F/F'm*) and non-photochemical quenching[5]) using PAM fluorometer and changes to respiration (O_2 used per m^2) using an oxymeter. All parameters measured were affected at 50 and 100 µg/L compared to control whereas at 10 µg/L there were significant effects on gross primary production rate, effective quantum yield (∆*F/F'm*) and non-photochemical quenching but no effects (p = 0.05) on maximum quantum yield and respiration compared to control values.

Seagrasses

Study 1

The effect of diuron on three species of seagrasses has been studied using PAM fluorometer (Haynes, 2001). The seagrasses were wild collected together with sediment (Moreton Bay, Australia) and were identified as *Halophila ovalis*, *Cymodocea serrulata* and *Zostera capricorni*. The author notes that both Halophila and Cymodocea species are important food resources for the endangered dugong.

The seagrasses (together with their associated sediments) were exposed to a single dose of diuron at 0.1, 1.0, 10 and 100 µg/L applied to the aqueous phase for a 5 day period (2 replicates per test concentration). The grasses were then rinsed and replaced for 5 days in clean seawater for recovery. The changes in chlorophyll fluorescence were measured daily using the PAM fluorometer at a fixed distance from the leaf surface and at a standard position on the leaf. There were 2 plants tested per replicate and the study was conducted in duplicate. The results were expressed as effective quantum yield.

Water concentrations were measured at the start and end of the exposure period in all replicates. Average concentrations for each test concentration were 0.12, 0.9, 7.8 and 85 µg/L.

[5] The non-photochemical quenching is measured from (Fm-F'm)/(Fm-Fs) which shows the light energy dissipation via heat.

There was a rapid response in all seagrasses to the two highest test concentrations with effective quantum yield decreasing to be approximately <50% of control after the first 2 hours. Within the first day, the most sensitive grass species, *H. ovalis* showed significant declines in effective quantum yield for all test exposures. After 5 days of exposure, the quantum yield for *H. ovalis* depressed for all test concentrations (30 and 35% of control at 0.1 and 1.0 µg/L respectively), and *Z. capricorni* was depressed but only at 10% of control for both 0.1 and 1.0 µg/L. The quantum yields for *C. serrulata* were only depressed at the two highest test concentrations. Effective quantum yield was significantly lower (50-75% of control) for all plants at the two highest concentrations (10 and 100 mg/L) for all seagrass species (Dunnet's Test). The author did not calculate EC50 values based on the results. DEWHA has undertaken these calculations using results determined from graphs, so the results should be treated with caution. Nonetheless, they provide a good guide. Calculations were done by TOXCALC using probit analysis, but without individual replicate data, confidence intervals were not calculated. The results indicate a 5 day EC50 (based on chrorophyll fluorescence) of 15.6 µg/L for *C. serrulata*; 7.6 µg/L for *H. ovalis*; and 27.7 µg/L for *Z. capricorni*.

There was rapid recovery in all species following return to clean seawater but recovery was not sustained with all species exhibiting fluctuations in effective quantum yield over the 5 day recovery period. *H. ovalis* was the most sensitive species during the recovery period with the ANOVA analysis showing this species as significantly different to the other two and the quantum yield did not improve as much as the other two species.

It is concluded that the study shows that there is a statistically significant effect on the quantum yield of *H. ovalis* and *Z. capricorni* with exposure to diuron at 10 µg/L in the water column, however the small sample size used in this study means results should be used with caution. DEWHA notes that while photosynthesis could be affected, this limited effect on its own would be unlikely to lead to mortality of seagrasses unless additional environmental stressors were involved, for example, storm damage, sedimentation, or over grazing. The seagrasses in the Great Barrier Reef Lagoon are likely to experience sedimentation from terrestrial sources, grazing from dugongs and turtles as well as periodic tropical storms and hence there is concern as to the potential additional adverse effect of diuron on seagrass meadows.

Study 2

In a study on the effect of antifouling herbicides on the seagrass *Zostera marina* (eel grass), diuron (at 0.5, 1.0, 2.5, 5, 10 and 25 µg/L) and in mixtures with Irgarol was tested (Chesworth, *et al*, 2004). The effect of diuron alone and in mixtures with Irgarol on chlorophyll fluorescence (*Fv:Fm*) and leaf specific biomass ratio (determined by examining new growth during the 10-day period to old growth before the trial) were examined after a 10-day exposure. For the study on mixtures, one herbicide was fixed with the other variable, for example, Irgarol at a fixed concentration of 0.23 µg/L (= EC20 for fluorescence) with diuron at concentrations of 0.5, 1.0, 2.5, 5, 10 and 25 µg/L. The study used field collected plants (collected from an estuary in the UK) with 9 plants per test concentration (3 plants per replicate).

The paper gives the LOEC and NOEC for diuron as 1.0 and 0.5 µg/L respectively based on reduction in fluorescence (*Fv:Fm*), with the 10-day EC50 of 3.2 µg/L for *Fv:Fm*. However, none of the concentrations tested reached 50% inhibition (of *Fv:Fm*), minimum *Fv:Fm* was approximately 58% of control (taken from graph) at 25 µg/L, and therefore DEWHA considers the EC50 as >25 µg/L. Further, DEWHA cannot confirm the NOEC/LOEC results as the raw replicated data was not presented in the paper. Plants exposed to diuron showed a significant reduction in growth at a concentration of 5.0 µg/L and there was statistically significant effect on growth (leaf biomass) at 2.5 µg/L. When *Z. marina* was exposed to mixtures of diuron and Irgarol, there was no significant further reduction in photosynthetic efficiency at any concentration when compared to plants exposed to the individual herbicides alone at similar concentrations, that is, with Irgarol fixed, plant responses closely corresponded to those of diuron alone. However, there were significant reductions in *Fv:Fm* noted at an earlier stage. The lowest observable significant effect concentration for growth decreased to 0.5 µg/L for the mixtures but a NOEC was not determined (NOEC <0.5 µg/L of diuron in mixture). The paper notes that Irgarol 1051 and diuron have been shown to occur together in concentrations

above 0.5 µg/L, suggesting that seagrasses may be experiencing reduced photosynthetic efficiency and growth as a result if such concentrations were sustained.

This paper has been criticised by Dulka and Samel (2006) as it was not conducted according to GLP, test solutions were not analysed, test conditions were atypical of a rooted macrophyte study and results were presented in graphical form only. Dulka and Samel also recalculated the EC20 and EC50 for growth as assessed by biomass as 2.4 (CI 0.83-6.8) and 14.3 (CI 8.6-23.6) µg/L using the standard probit model and 5.0 (CI 3.3-6.7) and 9.6 (CI 3.9-15.3) µg/L using a non-linear nested model (OECD model 5, OECD 2006). They also recalculated the EC20 and EC50 for chlorophyll fluorescence as 3.4 and 54.4 µg diuron/L. DEWHA notes that similar criticisms can be levelled against a significant number of reports - if not the majority – published in the open scientific literature. Given the uncertainties around the above results, it is not possible to use them in the standard risk assessment. It is noted, however, that the LOEC for inhibition of growth (biomass) with diuron of 5.0 µg/L provided in the report is similar to the EC20 recalculated by Dulka and Samel, - and a NOEC of 2.5 µg/L and this indicates that the inhibition of fluorescence is similar to inhibition of algal growth. It is also apparent from these data that sensitivity of the tested seagrasses are not dissimilar to those found for sensitive algae species where tests were performed to standard guidelines with standard end-points.

Higher Tier Testing

Study 1

Knauert et al., (2008) report on an outdoor mesocosm study undertaken to evaluate if effects of a mixture of similar acting compounds on the photosynthetic activity of phytoplankton could be described by concentration addition. Only the results relating to the diuron only treatment are considered here. The test ran in outdoor mesocosms for a period of seven months and included a six week pre-exposure, five week constant exposure and five month post exposure period. In the diuron only experiment, the test concentration for diuron was 5 µg/L, which was expected to equate to a 30% hazardous concentration (HC30) based on an SSD of available EC50 data on photosynthetic effects of diuron. To maintain roughly constant exposure concentrations during the 5 week exposure period, diuron was reapplied on days 12 and 20. In addition, a third of this rate was tested. To elucidate if the HC30 would elicit similar effects on photosynthetic activity of the phytoplankton from the mesocosms, short term dose-response relationships were established in the laboratory, testing diuron at concentrations of 1.25, 2.5, 5 and 10 µg/L.

In the short term laboratory study, the HC_{30} was shown to elicit similar effects accounting for 40.6% inhibition of photosynthesis, while the $1/3HC_{30}$ resulted in around 17.5% inhibition. Analysis of the mesocosm water during the exposure period indicated diuron was maintained at a relatively constant level. During the post exposure period, diuron moved out of the water column with a half life of 43 days.

Within two days after application, exposure to diuron alone induced around 57% inhibition of photosynthetic activity. Over the constant exposure period, the average inhibition of photosynthetic activity was 47.7%. However, compared to control ponds, the authors conclude that effects on photosynthetic activity had completely disappeared after 140 days (compared to atrazine where statistically significant effects could be determined until the end of the experiment on day 173). Values provided graphically in the report suggest the diuron concentration in the water at this time was around 1.2 µg/L. In this system, DCPMU was measured and was found at a maximum level of 15% applied diuron.

Study 2

Knauert et al., (2009) addressed the question of whether equitoxic concentrations of three herbicides (atrazine, isoproturon and diuron), and their equitoxic mixture resulted in similar effects on a phytoplankton community structure. Herbicide effects were evaluated using principal component analysis (PCA) and principal response curve (PRC) in addition to common community parameters, such as total abundance,

number of species, diversity, dominance patterns (with respect to the level of classes), and dynamics of the most dominant species. Only the diuron only component of the study is considered here. The test concentration for diuron was 5 µg/L. The mesocosms treated with diuron were redosed twice on days 12 and 20. The phytoplankton community as well as herbicide concentrations were monitored over a period of seven months and the entire mesocosm experiment was thus subdivided into a six week pre-exposure period, a five week constant-exposure period, and a five month post treatment period.

For the taxonomic determination, aliquots of the fixed phytoplankton samples were taken and cells allowed to settle in a sedimentation chamber. Quantitative evaluation was done using an inverted microscope and taxa were identified at the species level or to the lowest possible taxonomic level.

Prior to application, total abundance in all ponds was similar. During the five week constant exposure, the mean total abundance reached approximately 6000 individuals/mL in the control treatment. In the diuron treatment, total abundance was reduced by a factor of approximately three, resulting in 1500 individuals/mL on day 26. At the end of the experiment (day 173), total abundance in all treatments ranged from 3,000 to 5,000 individuals/mL, and was significantly lower only in the diuron treatment.

Regarding community structure and succession, at day 5 after commencement of exposure, the species compositions of the treatment communities were not significantly different from those of the control communities. From days 12 to 40, differences in species composition between the control and treated mesocosms were observed. However, during the post treatment period, the communities treated with diuron recovered and were similar to the control communities, with exceptions on days 82 and 140 according to PCA. While PCA coordinates data for each sampling date separately, PRC attempts to explain the data by considering time and treatment. PRC analysis indicated that communities in all treatments could recover within three to five weeks.

In terms of number of different taxa, the number of taxa in the diuron treated mesocosms were comparable to the control during the period of constant exposure, and this remained during the post treatment phase of the study.

Study 3

A recent report gives the 96 h EbC50 for *R subcapitata* 0.7 µg/L using diuron formulated as 50% WP (wettable powder) (Ma *et al*, 2006). It is assumed that the EC50 is expressed as active constituent, although this was not clear from the paper. The paper was a comparison of the toxicity of 40 herbicides to algae and diuron was by far the most toxic herbicide considered. The paper also showed that the EC50 for *R subcapitata* was approximately 10 times more sensitive to diuron than *Scenedesmus obliquus* and *Chlorella vulgaris* (ratio of EC50s [*R subcapitata/S. obliquus* or *C. vaulgaris*] = 0.171 and 0.163 respectively), but was of similar sensitivity to *Chlorella pyrenoidosa* (ratio EC50 = 0.538).

Study 4

The effect of interaction between diuron and other antifoulants has been examined using the marine diatom *Chaetoceros gracilis* (Koutsaftis and Aoyama, 2006). The paper examined the effect of diuron in mixtures with zinc pyrithione or Irgarol 1051. Test conditions used diuron at 25, 50 or 100% of its EC50 (EC50 was 36 µg/L) with the other two actives at 50, 100 or 200% of their EC50s. It was shown that with diuron at 25% of the EC50 and either zinc pyrithione (EC50 for *C. gracilis* = 3.2 µg/L) or Irgarol 1051 (EC50 for *C. gracilis* = 1.1 µg/L) at concentrations equal to their EC50, there was a 50% increase in toxicity to *C. gracilis* above additive effects only, that is, there was a slight synergistic effect.

Mangroves

Laboratory Studies - Plants

Duke *et al* (2003) reported the results of some preliminary trials of the toxicity of PS II-inhibiting herbicides to four mangrove species (*Avicennia marina*, *Aegiceras corniculatum*, *Rhizophora stylosa* and *Cerios australis* – the first two species are described as "salt excretors" and the others as "salt excluders"). The nature of the plants used meant that *A. marina* and *R. stylosa* received only root exposure to treated water, while some or all leaves of some plants of *A. corniculatum* and *C. australis* were below the high water mark, giving foliar as well as root exposure. Seedlings of the four species were grown in pots containing a commercially prepared sediment mixture and grown in a planting house. The pots were placed in tank units which enabled high and low tide to be simulated by pumping saline (16‰) water from a lower storage tank up into the upper holding tank for one hour periods twice per day, temporarily flooding the plants (the holding tanks were replenished [rather than replaced] as necessary to compensate for evaporative loss).

After an initial adjustment period for the mangroves, evaluations were made of the toxicity of diuron as well as ametryn and atrazine compared to an untreated control, with each herbicide at four treatment rates (4, 40, 400 and 4000 µg/kg dw of sediment), using herbicide dissolved in water (with acetone as co-solvent) to which "commercially bought" clay was then added (0.1 mg dw/2 L test solution) and mixed to simulate natural run-off conditions. The test solution was added evenly over the surface of each pot on a single occasion as the simulated tide was receding (60 mL solution/~1.7 kg dw sediment per pot). This resulted in the upper layer of clay containing all the diuron for each pot.

A potentially confounding effect on treatments in this preliminary study was that for each replicate of each herbicide, all four treatments were contained within the same tank, receiving the same simulated tidal water. For diuron, water samples taken at day 21 had a mean concentration of 7.71 µg/L (the concentrations for atrazine and ametryn were 13.7 and 7.75 µg/L, respectively). This represents a composite of leached herbicide from pots containing different rates of the herbicide. The concentrations of diuron in sediment (top 1 cm), taken at intervals up to 71 days after dosing, are given in Table A2.28.

The measured values were initially patchy and up to 3 X the (notionally) applied concentration. The authors suggested that this was due to accumulation in the top few centimetres of the sediment, rather than being distributed evenly through the profile. DEWHA comments that this is due to the initially applied clay retaining significant amounts of diuron. The concentration of diuron in the sediments then declined over the period of the study for all test concentrations except the lowest concentration. This is probably due to mobilisation of diuron from high treatments and then being re-adsorbed onto the lower treatments.

Table A2.28. Concentration of diuron (mg/kg dw) in the upper 1 cm layer of sediment from the mangrove study. Samples pooled from 6 pots.

Initial dosage µg/kg dw	Day 7	Day 14	Day 21	Day 71
Control	nd	nd	nd	nd
4	170	290	410	198
40	830	690	550	500
400	1200	4600	780	600
4000	12000	8500	5100	2000

nd = not detected,

Plant responses were assessed with the use of PAM chlorophyll fluorescence techniques. Diuron was the most toxic herbicide tested after 71 days (all responses refer to the maximum exposure concentration of 4000 µg/kg; there were no significant effects on fluorescence at lower doses) and none of the mangroves species that were affected showed any signs of recovery after this period. *Avicennia marina* was the most sensitive to diuron as measured by inhibition of photosynthesis. All of the mangroves showed some physical symptoms of injury (chlorosis and necrosis) and all of the *A. corniculatum* (river mangrove) were dead. *A. marina* had the highest measured concentrations of diuron in leaf tissues after 11 days of exposure, measured at ~340 µg/kg leaf (dry weight) and *A. corniculatum* was the second highest with ~230 µg/kg, both salt excretors, while *C. australis* and *R. stylosa* had significantly lower levels at 40 and 50 µg/kg leaf dw

respectively. Note that *A. corniculatum* and *C. australis* received the highest exposure to the herbicides as the roots and leaves were submerged during the simulated high tide whereas *A. marina* and *R. stylosa* were only exposed via the roots.

The research suggested that regardless of whether exposure to the herbicides tested was through root exposure only or also through foliage, that salt-excreting mangrove species were more vulnerable than salt-excluding ones.

The report focussed on data for the highest rate (nominal 4000 µg/kg sediment) and indicated that there were statistically significant effects of herbicide rate. However, it did not make clear what the effects of the lower rates were. In an honours thesis (Bell, 2001), based on this work, it is clear that none of the other test concentrations showed statistically significant effects compared to control.

Field Studies

Duke *et al* (2003) examined the dieback of mangroves in the Pioneer estuary and similar estuaries and compared these results to diuron in sediments. *Avicennia marina* was the main mangrove affected by the dieback. The report indicates that the dieback of mangroves in the Mackay region was first noted early in the 1990s but dramatically increased during the wet years in 1997-99. Duke initially examined the area in 2000 and noted that there was a correlation with the concentration of diuron in sediment and the health of the mangroves (only 3 analysis of diuron in sediment undertaken). He returned in 2002 and collected further information as well as additional analyses of the sediments including metal analysis and nutrients. It is this second field study that is reported in the 2003 manuscript.

In areas where there was dieback of *A. marina* the concentrations of diuron in the sediments (0-2 cm) ranged from 1.2 to 8.2 µg/kg. The reports also notes that there was evidence of a dose response relationship between the concentration of diuron in sediment and the amount of dieback observed, expressed as percentage of healthy trees, although the data set is very limited. Other factors considered included toxic metals, excessive sedimentation or nutrients, none of which showed a correlation with the level of dieback observed.

The report indicates that there is a correlation with the concentration of diuron in the sediments and the overall health of the mangrove *A. marina* as measured by percentage of healthy trees in plots and transects (in Pioneer River–Barnes Creek $r^2 = 0.892$, ($n = 4$, $P < 0.02$), Bakers Creek $r^2 = 0.8179$ ($n = 4$, $P < 0.05$) and in all plots together $r^2 = 0.4803$, $n = 11$, $P < 0.02$). For one site, McCreadys Creek, there was no relationship between concentration of diuron in sediment and mangrove dieback. The report also indicates that there is a correlationship with the levels of diuron and declining levels of chlorophyll in mature leaves (Barnes Creek $r^2 = 0.8995$, $n = 4$ and Bakers Creek $r^2 = 0.9915$, $n = 3$) and decreasing numbers of healthy seedlings (in Barnes Creek $r^2 = 0.8069$, $n = 4$, $P < 0.05$, Bakers Creek $r^2 = 0.9524$, $n = 4$, $P < 0.05$ and in all plots together $r^2 = 0.3352$, $n = 11$, $P < 0.05$) in the surveyed plots.

However, the dose response between the concentration of diuron in sediment and the amount of dieback observed has been questioned by Kennedy and Crossan (2005). Kennedy notes that one of the data points used by Duke has been graphed incorrectly from the table of data and as a result the linear fit reported by Duke ($r^2 = 0.4803$, $P < 0.02$, $n = 11$) is no longer significant ($r^2 = 0.270$, $n = 11$). DEWHA agrees that dose response based on the tabulated data is not statistically significant. In a similar vein, when the reported relationship between the number of healthy seedlings and concentration of diuron was examined for all sites, it is also not significant ($r^2 = 0.1465$, $n = 10$ {at one site there were no data for seedling health}).

However, an erratum has been issued by Duke (2006) that relates to two typographical errors in the data presented in his report. The data point noted by Kennedy as being incorrectly graphed is one such point, the data in the table is incorrect and with the corrected point, the r^2 is = 0.4175 ($n = 11$, $P < 0.05$) for all data points. The other data point was in the seedling health data that was tabulated wrong but was correct in the

graph for seedlings versus diuron (r^2 = 0.3352, n = 11, P <0.05). With these corrections, both the health of trees and seedlings are statistically significantly negatively correlated with the concentration of diuron in sediments.

In the estuaries where there was no dieback (Daintree and Johnstone Rivers), the concentrations of diuron measured were either <1.2 µg/kg in the sediments (0-2 cm) or *A. marina* did not grow in the contaminated sediments. In the 3 estuaries with dieback, diuron levels were >2 µg/L and in the areas where *A. marina* was found. Transects conducted through the mangroves showed that *A. marina* increased in health away from the river edges and towards the landward areas of the mangroves (except where drainage came from cane fields). High levels of diuron in sediments and healthy *A. marina* mangroves were mutually exclusive.

Other mangroves species were also showing some symptoms of stress with yellowing of leaves. *Aegiceras corniculatum* (river mangrove) was also affected with dead branches and yellowing leaves in some plots in the Pioneer River area associated with the higher levels of diuron (7.9 and 8.2 µg/kg) and *Ceriops australis* (yellow mangrove) showed significant dieback in 2 small areas but not in all and was not wide spread. This was considered due to localised effects.

Other possible causative agents that were considered include heavy metal contamination, excessive nutrients, pneumatophore burial (as suggested by Kirkwood and Dowling, 2002) and accessory factors. There was no correlation with the concentrations of toxic heavy metals in the sediments, excessive nutrients or sediment accumulation (measured as height from cable root to surface) and the presence of dieback.

While the field studies in the Duke report suggest that where diuron concentrations in sediment were >2 µg/kg, the mangrove species *Avicennia marina* (the common mangrove) may show symptoms of dieback, this was not strongly statistically correlated and the result is insufficiently validated to use in the risk assessment. The result is in contrast to the preliminary laboratory trial where effects were only noted at 4000 µg/kg. DEWHA acknowledges other possible interpretations of the data are valid, for example, under field conditions there are additional stressors not taken into account by the laboratory trial or that diuron is a marker for another unknown factor. Further, as noted by Duke (2005), "…the timing of when sites might have received high doses of herbicide would greatly affect the residual concentrations where these are expected to degrade and diminish at different rates depending on differences in arrival date, tidal flushing, water currents and soil type. Accordingly, accurate dose response studies are only considered possible under controlled experimental conditions rather than *ad hoc* field sampling of irregularly contaminated estuarine sediments."

At this stage there are insufficient data to categorically state that diuron has affected mangroves at Mackay and this is supported by the following field data.

2004 Field Study

Following on from the work of Duke *et al* (2003), the mangrove health in the Pioneer River estuary was studied during December 2004 (Wake, 2005). Plots were established at 9 locations from the top to the mouth of the Pioneer River estuary and in the Bassett Basin to collect baseline data. As there had been an extended dry period for the last years in the catchment and the study was in December before the start of the wet, there should minimum runoff into the system. The report indicates that this provided an opportunity to document the baseline levels of nutrients, chemicals and sediment over the length of the estuary from the most upstream extent of the tide to the mouth of the Pioneer estuary. During this period there has been an apparent improvement in the health of the mangroves, particularly in some of the areas most severely affected by dieback of *Avicennia*. Four plots previously sampled as part of the Mangrove Dieback Project by Duke *et al* (2003) were also sampled to determine changes in herbicide and nutrient levels and mangrove health in the absence of significant runoff.

The mangrove communities in this study were dominated by *Avicennia marina* and/or *Aegiceras corniculatum*. There was evidence of previous dieback in many sites, but there was a noticeable absence of the wilted yellow leaves that were noted between 2000 and 2002. There was significant recruitment of *Avicennia* seedlings at Barnes Creek, one of the most severely affected dieback locations, but there were very few seedlings in some of the other badly affected locations such as Fursden.

The concentration of diuron in the sediment, together with other herbicides, was determined at each site within the mangroves. In addition, the concentration of heavy metals was determined as well as the mineralogy of the sediments. The sediments were cored on 6 and 7 of December 2004 using a hand operated, 1 metre long corer to give 3 samples for analysis, the surface level, the root zone (as determined by inspection of the core) and the maximum depth of the core. The length of the core varied between sites as did the size of the root zone. Table A2.29 gives the concentrations of diuron in sediment found at 6 sites. At the other 3 sites surveyed (Fursden, Hodder St and Barnes Creek Bridge) the report states that the level of diuron was low but does not give measured concentrations.

Table A2.29. The depth and size of core and concentration of diuron (µg/kg dw sediment) at that depth on 6 and 7 December 2004.

Location	Surface		Root zone		Maximum depth	
	Depth, cm	Conc. µg/kg dw	Depth, cm	Conc. µg/kg dw	Depth, cm	Conc. µg/kg dw
Dumbleton	4-7	1.5	8-12	2.3	20-50	2.7
Pioneer Fursden	4-7	11	30-35	5.3	92-95	10
Macalister St	3-6	2.3	22-26	1.9	40-45	0.2
Barnes Creek	4-7	2.1	12-16	2.1	50-55	0.3
STP creek	1-4	1.2	9-12	1.1	50-53	0.8
Sandfly creek	2-6	3	17-21	5.1	55-60	1.7

The results show that the concentrations of diuron were similar down the soil core to the bottom of the core at 5 sites except for Macalister St and Barnes Creek, where the concentrations of diuron were lower. It is unlikely that the entire sediment core down to ~90 cm would be mixed during flood event/tidal movements - if this was so the mangroves themselves would have been uprooted. The pattern of diuron concentrations don't seem typical of leaching events where the concentrations would be expected to decline with increasing depth. Therefore, DEWHA considers that the diuron concentrations at the different depths is the remaining concentrations from previous runoff and subsequent deposition events. This implies that at each site a similar concentration of diuron is deposited each time, which may not be unreasonable, and that diuron is very stable in these estuarial sediments with very slow degradation.

In general the levels of diuron have declined compared to those found by Duke but the levels in the sediments at Pioneer Fursden (on the Pioneer River upstream from the confluence of Fursden Creek) were higher than for any sediment samples analysed in 2000 and 2002. The mangroves at this site did not appear to be affected by these levels. Importantly, mangroves appear to have been exposed to these levels for a considerable period of time at Pioneer Fursden given similar concentrations found at almost 1 m sediment depth. The author notes that the levels in Sandfly Creek suggest that there are also non-agricultural sources of diuron in the Pioneer River estuary, which was not shown in the work of Rohde *et al* (2006).

Diuron concentrations in pore water were much higher at Fursden (between Fursden Creek and Pioneer River) than in 2002 (see Table A2.30). The pore water collected was the water that flowed into the core after the soil core removed for those sites where a core was taken or the water that flowed into a hole dug with a shovel for the other sites (Fursden, Barnes Ck bridge and Hodder St).

Table A2.30. Concentration of diuron in pore water and index of stress on mangroves.

Location	Pore water concentration, µg/L	Index of stress on mangroves
Dumbleton	0.06	156
Pioneer Fursden	0.02	189
Macalister St	Not detected	203
Barnes Creek	0.01	106
STP Creek	0.02	166
Sandfly Creek	0.02	271
Fursden	0.1	253
Barnes Ck bridge	0.01	250
Hodder St.	0.02	165

There does not appear to be any relation between sediment concentrations and pore water concentrations between levels in Table A2.30 and A2.29. The pore water levels would be dependent on the sediment characteristics such as amount of organic carbon present, and this information is not available for the individual sites.

An index of stress for *Avicennia* mangroves was developed and found to be highest at Sandfly Creek although this location had the lowest proportion of dead trees (see Table A2.30). The stress index was calculated by the percentage of trees multiplied by the number of positive stress parameters. Sandfly Creek also had the highest proportion of leaf damage. Barnes Creek had the lowest value for the stress index although 42% of adult trees were dead. This was probably because this location was severely affected by dieback in the past but now had a large number of young trees. The index of stress did not correlate with diuron concentrations in sediment or with pore water concentration of diuron, ie bioavailable diuron. DEWHA notes that the index relates to total stress of the mangroves, not just that due to diuron exposure, and diuron is not the only stressor in the system.

Looking at individual sites, the site with the highest percentage of yellowing leaves in Avicennia, Fursden (100% of leaves yellow/green colour), did correspond with the highest concentration of diuron in the pore water. However, no conclusion can be drawn from this as other sites with a high stress index value were found to contain low levels of diuron in pore water. In contrast, the site with the highest concentration of diuron in sediment, Pioneer Fursden, did not correspond with highest impact on the health of the mangroves.

The report states that all the locations sampled had similar mineralogical composition. The proportions of quartz, feldspar and illite/smectite were similar at all locations except Sandfly Creek which had a higher proportion of feldspar in the root zone and a higher proportion of illite/smectite at maximum depth. The source of sediments for Sandfly Creek will be different from those sites where flood borne sediments are deposited directly. There was also considerable clearing of mangroves upstream of the site in the past, although regeneration is occurring.

The sediments were analysed for a total of 51 metals (both total levels and biologically available) and there was no evidence that levels of heavy metals were likely to affect mangrove health within the Pioneer estuary as no site had levels that exceeded the ANZECC (2000) guidelines. Sites where median grain size was greater than about 200 microns had low levels of most metals.

It is concluded that this study does not give support the proposition put forward by Duke et al (2003) that diuron in sediment is the main causative agent for the dieback in the mangroves in the Mackay region.

2005 Field Study

The concentration of diuron in sediments was sampled on 22 and 23 November 2005 at the same sites as used in the year previous (Wake, 2006). There was one flood event in January 2005 and there was no significant rainfall between this flood and when the samples were collected. Stakes placed at the sampling sites previously were used to determine the amount of sediment deposited, which showed little variation from

site to site (ranged of ±2 cm) but that there was a consistent but slight increase in sediment in the upper reaches (Dumbleton, Pioneer Fursden and Fursden). Table A2.31 gives the results together with the stress index for the mangroves and changes in the stress index from the previous year's sampling.

Table A2.31. Concentration of diuron in sediment and pore water for 2005 sampling and index of stress on mangroves

Location	Sediment levels, µg/kg	Pore water levels, µg/L	Stress Index for mangroves	Change in stress index from 2004
Dumbleton	26	nd	137.4	-19
Pioneer Fursden	35	0.02	232.5	+43.5
Macalister St	4.1	nd	231.3	+27.8
Barnes Creek	4.8	0.01	144.1	+37.8
STP Creek	1.8	0.02	158.5	-7.8
Sandfly Creek	6.3	0.01	223.1	-48.4
Fursden	5.4	0.10	200	-53
Barnes Ck bridge	2	0	216	-33.8
Hodder St.	6.4	0.02	255	+90

The results showed that there was no statistically significant change in the stress index at any site despite that fact that at two sites the level of diuron was significantly higher. Additional sediment sampling in February 2006 at 3 sites (Dumbleton, Macalister St and Sandfly Creek) following runoff events in January gave diuron concentrations of 9.7, 3.0 and 2.3 µg/kg respectively. The concentration of diuron is lower than in the earlier samples taken in November 2005, especially at Dumbleton. The reason for this is unclear but it is possibly due to movement/ transportation and mixing of sediments surface sediments in this dynamic environment. Overall there was a general improvement in the health of the mangroves with good numbers of seedlings at most sites except Dumbleton and Pioneer Fursden, where there were no seedlings. Wake did not comment on this finding but DEWHA notes the correlation with the high levels of diuron in the sediment at these sites.

5. TERRESTRIAL INVERTEBRATES AND SOIL MICROFLORA

5.1 Bees

One study has been provided for review:

Title	Karmex DF (Diuron; DPX-14740-246) 80.0%: Acute oral and contact toxicity to the honeybee, Apis melifera L
Authors	Bocksch, S
Date	2006
APVMA Data ID	8998
Test Guideline	OECD Guideline No. 213 and No. 214 (1998)
Data Validity	1 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

The study was undertaken to determine the effect of the formulation Karmex DF (DPX-14740-246), containing nominal diuron concentrations at 80% of the formulation, on the honeybee, *Apis mellifera* in the laboratory. Both acute contact and oral toxicity were tested. It is unclear if a range finding study was used to determine nominal concentrations for the acute and oral tests of 6.25, 12.5, 25.0, 50.0 and 100.0 µg

ac/bee. Based on consumption of the test item, actual oral doses were 7.20, 14.75, 24.26, 51.47 and 72.10 µg ac/bee. A control treatment of 50% (w/v) sugar solution and tap water was used for the oral and contact tests, respectively. Perfekthion was used as a toxic control with nominal concentrations of 0.30, 0.18, 0.12 and 0.08 µg/bee and 0.26, 0.14 and 0.10 µg/bee for the oral and contact tests, respectively. The actual dose of perfekthion for the oral test was 0.30, 0.20, 0.13 and 0.09 µg/bee.

Test vessels were stainless steel cages 10 cm x 8.5 cm x 5.5 cm (length x width x height). One side contained a removable glass sheet, the bottom contained ventilation holes 1 mm in diameter and the inner walls were lined with filter paper. Five test solutions were used for the test substance and four for the toxic reference. 10 bees (young female adult workers) were placed in each test vessel (5 replicates per test solution, control and reference solution). The test conditions involved temperatures between 25.0-26.0^{o}C at 55-67% relative humidity with a 24 h dark photoperiod except during observations made under neon light.

The oral component involved a 6 hour exposure period (after a 24 h starvation period) where bees were offered test and control solutions containing 50% (w/v) aqueous sugar solution, such that each bee would consume approximately 20 µL of sugar solution. 250 µL of test solution was supplied to each cage in pre-weighed feeders (eppendorf cups). The feeders were weighed again after the test and the total amount consumed was divided by the initial number of bees in the cage to determine the actual dose.

The contact test involved topical application of the test solution or control using a 2 µL droplet on the dorsal thorax of each bee. The bees were anaesthetized with CO_2 and the needle of the micro-applicator was cleaned between each application using a solution of water and a water-wetting agent.

Mortality and abnormal behaviour were observed at 4, 24 and 48 h for both the oral and acute tests. Mortality was corrected for control mortality using the SCHNEIDER-ORELLI formula (1947).

The test was deemed valid if control mortality did not exceed 10% and if the 24 h LD50 of perfekthion (the reference toxin) was in the range of 0.10 to 0.35 µg ac/bee for the oral test and 0.10 to 0.30 µg ac/bee for the contact test.

Findings

After 48 h, 0% mortality was observed in the control group and in the test groups up to the highest dose of 72.10 µg ac/bee for the acute oral test.

No mortality was observed for the control or highest test dose of 100 µg ac/bee in the acute contact test after 48 h, while 4% mortality was observed for the 50 µg ac/bee dose after 48 h.

Sub-lethal or behavioural effects were not observed in the oral or contact test groups compared to the respective controls.

The 24 h LD50 of the reference toxin perfekthion (400 g/L methyl parathion EC) was 0.12 µg ac/bee for the oral test and 0.21 µg ac/bee for the contact test.

Conclusion

Diuron in the tested formulation did not exhibit toxicity to honey bees, and the oral 48 h LD50 is >72.10 µg ac/bee with the contact 48 h LD50 >100 µg ac/bee.

5.2 Beneficial Terrestrial Invertebrates

Laboratory Studies

Title	Karmex 80 WG: Acute Toxicity to the Aphid Parasitoid, Aphidius rhopalosiphi (Hymenoptera, Braconidae) in the Laboratory
Authors	Schuld, M
Date	2001
APVMA Data ID	9020
Test Guideline	Mead-Briggs, 1992a; Barrett et al, 1994; Mead-Briggs et al, 2000
Data Validity	1 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

The study was undertaken to determine the effect of the formulation Karmex 80 WG, containing diuron at 81.2% of the formulation, on the aphid parasitoid *Aphidius rhopalosiphi* in the laboratory. Both adult survival and effect on fertility were tested. The test article was diluted in deionised water (200 L/ha) and applied to glass plates. Based on a non-GLP range finding study, this test was undertaken as a limit test, and the only application rate was 4000 g ac/ha. A control treatment of deionised water (200 mL/ha) and perfekthion at a nominal rate of 0.12 g/ha (applied in 200 L/ha) were also included in the experiment.

Treatments were applied to glass plates, and once dry, these were used to form the floor and ceiling of shallow arenas. Ten adult wasps (5 males and 5 females) were placed in each arena (4 replicates per treatment). The test was conducted at around 20^{o}C and 50-85% relative humidity with ambient lighting for a 16 h photoperiod.

For assessment of the parasitic capacity, the fertility test, if possible, 15 randomly chosen females per group were taken. A pot containing 10 barley seedlings infested with about 50-100 *Rhopalosiphum padi* was placed on a seed tray. One female parasitoid was introduced in the each fertility cage and their condition recorded.

For the mortality component, conditions of the wasps were recorded at 0.5, 2, 24 and 48 h after their introduction. Moribund wasps were counted as dead. Mortality was corrected for control mortality. No LR50 could be calculated due to a lack of mortality. For the fertility component, the plants bearing the aphids were maintained under test conditions and the number of parasitised aphids counted after 11 days.

The test was deemed valid if control mortality did not exceed 10%, mean mortality in the reference group was at least 50%, minimum control parasitation rate was >5 aphid mummies per surviving female; and not more than two females produced no mummies in the control group.

Findings

From a total of 40 test animals per treatment, there was no mortality in the control group, 2 deaths (5%) in the diuron treatment group and complete mortality in the toxic standard, found after 24 h. Validity criteria for the mortality phase of the study were met.

For both the control and diuron treatments, 15 females were placed into individual test cages for the fertility test. There were a total of 171 mummies produced by diuron treated parasitoids (11.4 per female) compared to 266 mummies produced by control females (17.73 mummies per female). This was deemed statistically significantly different (p <0.05), and an inhibition in reproduction from the diuron treatment group of 35.7% was concluded.

Conclusion

While there were no adverse effects on mortality at 4000 g ac/ha, this rate resulted in a reduction in reproduction of around 36%. Based on IOBC classification (Boller *et al*, 2005), this makes diuron "moderately harmful" (laboratory study, reduction in beneficial capacity of 30-80%). However, it is at the lower end of this range, and the limit test was performed at a high concentration. It is concluded that diuron would not cause lasting adverse effects on *Aphidius rhopalosiphi* at up to 4000 g ac/ha.

Title	Karmex 80 WG: Toxicity of the predatory mite, Typhlodromus pyri SCHEUTEN (Acari, Phytoseiidae) in the laboratory
Authors	Adelberger, I
Date	2001
APVMA Data ID	8994
Test Guideline	LOUIS/UFER, 1995 based on OVERMEER, 1998 and Barrett et al, 1994
Data Validity	1 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

The study was undertaken to determine the effect of the formulation Karmex 80 WG, containing diuron at 81.2% of the formulation, on the predatory mite *Typhlodromus pyri* SCHEUTEN in the laboratory. Both adult survival and effect on fertility were tested. The test article was diluted in deionised water (200 L/ha) and applied to glass plates. Based on a non-GLP range finding study, the only application rate was 4000 g ac/ha (5000 g product/ha). A control treatment of deionised water and perfekthion at a nominal rate of 6 g ac/ha (applied in 200 L water/ha) were also included in the experiment.

The test vessels were composed of two glass slides attached along their longitudinal edge via two glass bars. A barrier of glue was used to form a square arena which was treated by a spray application of test solution. Once dry, the test vessels were placed on wet filter paper laid on top of water soaked foam on a plastic plate. Twenty mites (protonymphs ≤1 day old) were placed in each arena (5 replicates per treatment). The test conditions involved temperatures between 24.0-26.0^{o}C at 55-85% relative humidity with a 16:8 h light:dark photoperiod. The mites were given drinking water *ad libitum* and fed pollen.

The mortality component involved a 7 day exposure period and conditions of the mites were recorded at day 3 and 7. Mortality was defined as the number of dead and missing (not recovered or trapped by glue) mites and was corrected for control mortality. No LR50 could be calculated due to a lack of mortality.

The fecundity of surviving mites was assessed in test groups where the mortality, corrected using Abbott's formula, was ≤50% for a further 7 days. Observations for the control and test substance groups were taken 10, 13 and 14 days after treatment. The number of eggs and juveniles were counted in each test group and the cumulative number of eggs per female was determined.

The test was deemed valid if control mortality did not exceed 20% on day 7, mean mortality in the reference group was at least 50% on day 7 and the cumulative number of offspring per female in the control exceeded 4 eggs.

Findings

There was 7% mortality for the control groups and test groups exposed to 4000 g ac/ha as well as 96.0% mortality for groups exposed to the toxic control (6 g ac/ha) after 7 h. Reproduction in the Karmex 80 WG test groups were reduced by 4.48% and is not deemed statistically reduced compared to the control ($p > 0.05$). The sex of males and females could be determined by day 7 and validity criteria for the mortality and

fecundity phases of the study were met.

A summary of the findings is provided below:

Table A2.31: Effects on mortality and reproduction rate

	Control	Karmex 80 WG (4000 g ac/Ha)	Toxic Standard (6 g ac/Ha)
Mortality (%) Day 7	7.0	7.0	96.0 a
Corrected Mortality Day 7	NA	0.0	95.7
Mean cumulative No. of offspring per female Day 14	8.9	8.5	Not assessed
Reproduction factor Day 14	NA	0.96	Not assessed
% Reduction in reproduction Day 14	NA	4.48	Not assessed

[a] Value is significantly different to the control (Fisher's exact test, p≤ 0.05)

Conclusion

Based on the IOBC classification (Boller *et al*, 2005), diuron in the tested formulation is considered harmless or slightly harmful (reduction in beneficial capacity of 0-50%) based on combined mortality and reproduction effects to the predatory mite *Typhlodromus pyri* SCHEUTEN under laboratory conditions. It is concluded that diuron would not cause lasting adverse effects on *Typhlodromus pyri* at up to 4000 g ac/ha.

Title	An evaluation of the side-effects of BAY 11310H (diuron and glyphosate) on lycosid spiders
Authors	Mead-Briggs, M
Date	1992b
APVMA Data ID	9012
Test Guideline	Not Reported
Data Validity	4 (GLP)
Data Relied On	The data was considered information only and was not relied on in this assessment.

Test System

The study was undertaken to determine the effect of the formulation BAY 11310H, containing nominal concentrations of diuron at 27% of the formulation and glyphosate at 14.4%, on the lycosid spiders of the genera *Pardosa spp.* in the laboratory. The measured concentration of diuron was 27.40% and glyphosate was 15.70% of the formulation. The survival of sub-adult spiders when exposed to residues and direct spray plus residue was tested. The test article was diluted in water (30 g product/L water; 8.2 g diuron/L water). Based on the maximum recommended application rate of 15 kg product/ha, the only application rate was 15000 g product/ha (4110 g diuron/ha) with an application volume of 500 L/ha and 5 psi. A control treatment of water (500 L/ha) was also included in the experiment.

The test arenas were plastic pots of diameter 9 cm and depth of 5 cm filled to a depth of 2 cm with lime free silica sand. The test substance and control were applied at a rate of 500 L/ha for both residue and spray plus residue tests.

For assessment of residue toxicity, pots were treated with the test substance and left to dry for 60 minutes before a spider was placed in the pot. For assessment of the control and direct spray plus residue tests,

spiders were present in the pots during application.

Twenty pots containing one spider each were used for the residue, spray plus residue and control tests with no replicates. The residue and control tests contained 5 males:15 females while the spray plus residue test contained 6 males:14 females. The tests were conducted at 20 ± 2.5^{o}C and 38-70% relative humidity. This was outside the ranges specified in the un-named protocol (21 ± 2^{o}C and 50-80% relative humidity) but was deemed not important to the study outcome. The moisture of the sand was maintained at 70% of its holding capacity and spiders were not fed 3 days prior to testing.

Survival was recorded at 2 h, 24 h and daily for the following 5 days. Food (4 pea aphids) was provided after 4 days of exposure (7 days of fasting) and feeding activity was observed at 1 h, 24 h and 48 h.

Validity criteria for the study were not provided.

Findings

There was 0% mortality for the control, residue and spray plus residue tests during the 6 day exposure period.

In the feeding assessment, both the residual and spray plus residual treatments reduced the number of aphids consumed by 33-42% with respect to the control. This reduction was deemed statistically significant. The EU note with respect to this outcome that the product was applied at a rate equivalent to twice the recommended rate for diuron. However, it is not possible to distinguish between the effects of the two active substances in the formulation. The LR50 of glyphosate in itself to *Pardosa spp*. is approximately 3.7 kg/ha, which is only 1.7 times the amount applied in the study mentioned above. Therefore, it is likely that the reduction in feeding rate results from exposure to glyphosate (EFSA, 2004).

Conclusion

Under the conditions of this test, neither the residual or spray plus residual treatments were toxic to the spiders up to the rate tested of 4110 g diuron/ha. While there were impacts on feeding rates, these can not be unequivocally attributed to diuron based on this study.

Title	A Study of the Acute Toxicity to Aleochara bilineata (Staphylinidae) of Ustinex PA According to the IOBC/WPRS Guideline for Testing of Chemicals
Authors	Römbke J and Vickus P
Date	1991
APVMA Data ID	914
Test Guideline	Samsoe-Petersen, 1987.
Data Validity	4 (GLP)
Data Relied On	The data was considered to be information only and was not relied on in this assessment.

Test System

Effects of the product “Ustinex PA”, containing amitrole (29.6%) and diuron (54%) was tested on the beetle species *Aleochara bilineata* in the laboratory. Nine adult female beetles were exposed for 5 d at a concentration corresponding to 10 kg product/ha (5.4 kg diuron/ha). The product was sprayed in a green house on test vessels containing quartz sand.

Measured parameters were mortality, the behaviour and feeding rates of adult beetles. Additionally, the

number of eggs laid during the test period and the number of hatched larvae counted one week after the end of the acute test were determined.

Findings

At the end of the test, no test animals were recorded as dead. No animals died in the water control, but complete mortality was observed by day three in the toxic standard control. On the average, each beetle in the test vessels ate 114 fly eggs compared to 115.7 eggs in the water control vessels. The mean number of eggs laid per beetle in both the water controls and test vessels was 20.6. However, on average the hatching rate was 4.8% in the test vessels compared to 96.1% in the control vessels.

Conclusion

Based on the IOBC classification (Boller *et al*, 2005), the tested formulation is considered harmless or slightly harmful (reduction in beneficial capacity of 0-50%) based on mortality of adults, feed consumption and egg laying. However, when considering the impact on egg hatching (~95% non-hatched), the tested formulation is harmful (reduction >75%) to the beetles *Aleochara bilineata*. These effects cannot be attributed solely to diuron in this study due to the presence of amitrole in the test formulation.

5.3 Earthworms

One earthworm reproduction study with a formulation of diuron, and two acute earthworm studies with diuron metabolites have been provided for review.

Acute Exposure – diuron metabolites

Title	Acute Toxicity of DCPMU on Earthworms, Eisenia foetida Using an Artificial Soil Test
Authors	Stäbler, D
Date	2001a
APVMA Data ID	9022
Test Guideline	OECD Test Guideline 207 (1984)
Data Validity	1 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

The acute toxicity of the diuron metabolite, DCPMU (99.7% pure), to the earthworm, *E. foetida*, was tested in a 14 d soil exposure laboratory study. The test was conducted in agreement with the test guideline, and no major deviations to the test system were recorded.

Based on a range finding study (1 replicate per treatment, 10 worms per replicate; and included a toxic control with 2 replicates per treatment), the definitive test was conducted at nominal concentrations of 100, 178, 316, 562 and 1000 mg DCPMU/kg artificial soil. Each treatment was replicated 4 times with 10 worms per replicate.

The incubation of the test containers was carried out at around 20^{o}C with continuous artificial light. The average weight of worms was recorded at the beginning and end of the test. Mortality was assessed at 7 and 14 days. The LC50 was calculated by probit analysis, and weight change calculated with pairwise Mann & Whitney-U-Test.

Findings

In the definitive test, there was no mortality in the control group. Mortality of 0, 7.5, 42.5, 75 and 80% was recorded after 14 days in the 100, 178, 316, 562 and 1000 mg DCPMU/kg artificial soil treatment groups respectively.

There were no treatment related effects on worm weights between the start and end of the study, and no behavioural abnormalities were observed in surviving worms.

Conclusion

The 14 d LC50 was calculated to be 413 mg/kg soil dry weight. The NOEC was 178 mg/kg based on mortality.

Title	Acute Toxicity of DCPU on Earthworms, Eisenia foetida Using an Artificial Soil Test
Authors	Stäbler, D
Date	2001b
APVMA Data ID	9023
Test Guideline	OECD Test Guideline 207 (1984)
Data Validity	1 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

The acute toxicity of the diuron metabolite, DCPU (100% pure), to the earthworm, *E. foetida*, was tested in a 14 d soil exposure laboratory study. The test was conducted in agreement with the test guideline, and no major deviations to the test system were recorded.

Based on a range finding study (1 replicate per treatment, 10 worms per replicate; and included a toxic control with 2 replicates per treatment), the definitive test was conducted at nominal concentrations of 200, 299, 447, 668 and 999 mg DCPU/kg artificial soil. Each treatment was replicated 4 times with 10 worms per replicate.

The incubation of the test containers was carried out at around 20^{o}C with continuous artificial light. The average weight of worms was recorded at the beginning and end of the test. Mortality was assessed at 7 and 14 days. The LC50 was calculated by the Spearman-Kärber method due to the distribution of mortality data.

Findings

In the definitive test, there was no mortality in the control group, or the 200, 299 and 447 mg/kg treatment groups. Mortality of 5% and 100% was recorded after 14 days in the 668 and 999 mg/kg treatment groups respectively.

There were no treatment related effects on worm weights between the start and end of the study up to 668 mg/kg, and no behavioural abnormalities were observed in surviving worms.

Conclusion

The 14 d LC50 was calculated to be 801 mg/kg soil dry weight. The study authors report a LOEC of 668 mg/kg, and a NOEC <668 mg/kg. However, given mortality at this level was only 5%, and there were no

other abnormal effects observed, the study NOEC could be taken as = 668 mg/kg.

Chronic Exposure/Reproductive Studies

Title	Karmex 80 WG (Darmex DF): Assessment of Effects on Reproduction and Growth on Eisenia foetida in Artificial Soil
Authors	Stäbler, D
Date	2001c
APVMA Data ID	9021
Test Guideline	BBA Richtlinie: Teil V1, 2-2; ISO Guideline: 11268-2
Data Validity	4 (GLP)
Data Relied On	No - the document is incomplete and is for information only.

Test System

At this stage, the only document submitted is the study plan for this test. DEWHA has reviewed the plan. The proposed test system is in very good agreement with OECD test guideline 222, Earthworm Reproduction Test. The proposed rates of application are 5.3, 10.7, 26.7, 133.3 and 266.7 mg ac/kg soil, to be applied as a spray in 400 L/ha water to the soil surface once worms have been introduced to the test system.

Findings

No actual test report has been provided at this stage.

Conclusion

No actual test report has been provided at this stage.

5.4 Soil Micro-organisms

Several studies have been provided for review:

Title	Effects of KARMEX XP on Soil Microorganisms: Carbon transformation test
Authors	Raposo, M
Date	2005a
APVMA Data ID	9029
Test Guideline	OECD TG 217
Data Validity	1 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

The effects of the formulation, KARMEX XP, containing diuron at 800 g/kg, was evaluated on soil microorganisms in a carbon transformation test. Two Brazilian test soils were used. Soil 1 contained 2.38% OC, and a microbial biomass of 0.35 mg C/g soil while soil 2 contained 1.05% OC and a microbial biomass of 0.2 mg C/g soil.

A total of nine samples were required for each of the two soils (three replicates per treatment). Dose rates were 0, 4.27 mg/kg and 21.34 mg/kg, which was aimed to correspond to diuron rates of 3.2 kg ac/ha and

16 kg ac/ha respectively assuming incorporation to 5 cm in a soil with a density of 1.5 kg/m^3.

The rate of release of $^{14}CO_2$ from soil samples was determined by radiorespirometric methods, with assessments made after 3 h, 4.5 h, 6, h, 7.5 h, 9 h and 12 h of incubation. At 7, 14 and 28 days of incubation, 12 h assessments were repeated in the same way for both soil types. The level of radioactivity was assessed by LSC.

Findings

In soil 1, the values of CO_2 released ranged from -8.7% (low treatment) to 9.19% (high treatment) compared to the control. These values are provided in terms of mean release from all three replicates over the 0, 7, 14 and 28 day measurements. Further investigation of the data showed that for no individual time point, CO_2 release rates in the treatment group deviated more than 25% from control values.

In soil 2, the values of CO_2 released ranged from -10.66% (low treatment) to -15.61% (high treatment) compared to the control. These values are provided in terms of mean release from all three replicates over the 0, 7, 14 and 28 day measurements. Further investigation of the data showed that for no individual time point, CO_2 release rates in the treatment group deviated more than 25% from control values, although for the 28 day measurements, in the highest treatment, release rates were 24.6% lower than those in the control replicates.

Conclusion

The difference between control and treated soils in terms of release rates of CO_2 after 28 days was below 25% of control values. It can be considered that diuron up to 16 kg ac/ha is not likely to have a significant impact on soil microorganisms in terms of carbon transformation in soil.

Title	Effects of KARMEX XP on Soil Microorganisms: Nitrogen transformation test
Authors	Raposo, M
Date	2005b
APVMA Data ID	9029
Test Guideline	OECD TG 216
Data Validity	1 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

The effects of the formulation, KARMEX XP, containing diuron at 800 g/kg, was evaluated on soil microorganisms in a nitrogen transformation test. The soils used and treatment rates were as described in Raposo (2005a) above.

Effects on nitrogen transformation were determined through measuring changes in the nitrate concentration, which was determined by visual absorbency at 410 nm using a spectrophotometer.

Findings

In soil 1, the values of CO_2 released ranged from -1.3% (low treatment) to 0.8% (high treatment) compared to the control. These values are provided in terms of mean release from all three replicates over the 0, 7, 14 and 28 day measurements. Further investigation of the data showed that for no individual time point, nitrate concentrations in the treatment group deviated more than 25% from control values.

In soil 2, the values of CO_2 released ranged from 0.4% (low treatment) to 3.6% (high treatment) compared

to the control. These values are provided in terms of mean release from all three replicates over the 0, 7, 14 and 28 day measurements. Further investigation of the data showed that for no individual time point, nitrate concentrations in the treatment group deviated more than 25% from control values.

Conclusion

The difference between control and treated soils in terms of nitrate concentrations after 28 days was below 25% of control values. It can be considered that diuron up to 16 kg ac/ha is not likely to have a significant impact on soil microorganisms in terms of nitrogen transformation in soil.

Title	Assessment of the Side Effects of DCPU on the Activity of the Soil Microflora
Authors	Kölzer, U
Date	2001a
APVMA Data ID	9007
Test Guideline	BBA IV, 1-1; OECD TG 216; OECD TG 217
Data Validity	1 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

The study was undertaken to examine the potential for DCPU (99.8% pure) to affect soil microbial processes, specifically examining the effect of DCPU on soil short term respiration and nitrogen transformation.

The test soil was a silty sand soil (BBA soil type 2.3) with a microbial biomass of 10.08 mg C/100 g dry weight, calculated from respiration activity. The soil was treated with two rates, namely 4 and 40 kg DCPU/ha. The test soil had a density of 1330 kg/m^3, so assuming mixing through the top 5 cm soil, at these rates field concentrations would be around 6 mg DCPU/kg and 60 mg DCPU/kg for the low and high treatment rates respectively. The control consisted of soil treated with deionised water. A toxic standard was also tested under identical conditions to validate the test methods.

The effect on nitrogen turnover was assessed by monitoring the concentrations of ammonium, nitrate and nitrite in soil after adding it with ground lucerne. The effect on short term respiration was assessed by measuring the short term respiration rate of soil after addition of glucose.

Findings

After 42 days, DCPU at the low and high concentrations had no substantial effect on nitrogen turnover in soil, that is, effects were <25% that of the control (5.2% at the low concentration and 21.2% at the high concentration). By comparison, the toxic standard showed a 55% deviation in total nitrogen from the control values. For earlier observation periods, however, there were significant effects (>25% deviation from the control) at the high treatment rate. At 7, 14 and 28 days after treatment, total nitrogen levels in the high treatment soil deviated from the control by around 54%, 35% and 36% respectively.

The short term respiration rate in soil treated with DCPU was not substantially different from the control after 28 days with <5% deviation from control values at both test rates. By comparison, the toxic standard inhibited short term respiration by almost 38% after 28 days.

Conclusion

DCPU is not expected to have any substantial effect on nitrogen turnover in soils up to 6 mg/kg, or on short term respiration up to 60 mg/kg. However, at the higher rate, there may be some short term impacts on

nitrogen turnover, but these are not expected to last.

Title	Assessment of the Side Effects of DCPMU on the Activity of the Soil Microflora
Authors	Kölzer, U
Date	2001b
APVMA Data ID	9008
Test Guideline	BBA IV, 1-1; OECD TG 216; OECD TG 217
Data Validity	1 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

The same test system as reported for Kölzer (2001a) above was used to measure the effects of DCPMU on the soil respiration and nitrogen turnover. Application rates were as above for DCPU.

Findings

After 42 days, DCPMU at the low and high concentrations had no substantial effect on nitrogen turnover in soil, that is, effects were <25% that of the control (-3.1% at the low concentration and 19.1% at the high concentration). By comparison, the toxic standard showed a 55% deviation in total nitrogen from the control values. For earlier observation periods, however, there were significant effects (>25% deviation from the control) at the high treatment rate. At 7, 14 and 28 days after treatment, total nitrogen levels in the high treatment soil deviated from the control by around 37%, 20% and 37% respectively.

The short term respiration rate in soil treated with DCPMU was not substantially different from the control after 28 days with -2.2% deviation from control values at the low rate and -6.7% deviation at the high rate. By comparison, the toxic standard inhibited short term respiration by almost 38% after 28 days.

Conclusion

DCPMU is not expected to have any substantial effect on nitrogen turnover in soils up to 6 mg/kg, or on short term respiration up to 60 mg/kg. However, at the higher rate, there may be some short term impacts on nitrogen turnover, but these are not expected to last.

5.5 Non-Target Terrestrial Arthropods

Several studies have been provided for review.

5.6 Non-Target Terrestrial Plants

Two studies were provided for review:

Title	Influence of Diuron on Seed Germination, Seedling Emergence and Vegetative Vigour of Several Terrestrial Plants
Authors	McKelvey and Kuratle
Date	1992
APVMA Data ID	9011
Test Guideline	US EPA-FIFRA, 40CFT, Part 158.540; Pesticide Assessment Guidelines Subdivision J, 122-1 and 123-1
Data Validity	1 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

Testing was conducted to evaluate the effects of diuron at a maximum rate of 13.44 kg ac/ha (12 lb/A) on seed germination, seedling emergence and elongation along with vegetative growth and vigour of ten selected plant species. For those species where negative effects >25% were observed, further testing to determine a dose response curve was conducted. The first test was undertaken with 4 monocotyledons (onion, corn, wheat and sorghum) and 6 dicotyledons (sugarbeet, soybean, pea, tomato, rape and cucumber). No tier II germination studies were necessary. No tier I vegetative vigour studies were conducted as all test species were promoted to tier II. From the tier I seedling emergence study, it was decided that species with >10% significance were promoted to tier II testing.

Seedling emergence testing was undertaken with 20 seeds per tray, and 4 replicates per species. The application solution consisted of diuron dissolved in acetone. After seeds were planted, the test solution was applied as a pre-emergence soil surface application at five different rates (varied depending on the test species), and a control group of plants. Greenhouse conditions included a temperature range of 13^{o}C to 32^{o}C and a 16 h light, 8 h dark photoperiod. The test duration was 2 weeks with data collection including evaluation of seedlings emerged, seedling appearance and mean shoot height measurements taken after 1 and 2 weeks.

The vegetative vigour study was undertaken in standard 15 cm x 15 cm pots. At the time of application, a total of 6 plants per test species were exposed to a range of 5 test application rates (varied between species), and each species was replicated 4 times. Diuron dissolved in acetone was applied as a foliar spray. Greenhouse conditions included a temperature range of 17^{o}C to 35^{o}C and a 16 h light, 8 h dark photoperiod. The test duration was 3 weeks with data collection including shoot height and observations of plant appearance taken after 1 and 3 weeks. After 3 weeks, composite shoot, root and whole plant dry weight were measured.

Williams's test was used to provide a value for the NOEC at the 95% confidence level. If this indicated a normal rate response, probit analysis of the untransformed data was used to determine the EC50 and EC25 data.

Findings

In the tier 1 seed germination study, no plants advanced to tier 2 testing. The plant with the highest inhibition of germination was onion (9.1%) while sugarbeet (-13%), soybean (-7.5%) and rape (-24%) all had increased germination compared to control plants.

For the Tier II tests, the solutions were analysed to verify concentrations of diuron in the solution. Concentrations ranged from 103 to 105% of the nominal value.

The following results were reported:

Table A2.32: Seedling Emergence Tier II Results (g ac/ha)

	Seedling Emergence (height data). Results in g ac/ha	
	NOEC	EC25 (95% CI)
Onion	213	Not able to be calculated
Corn	840	6384 (5264-7504)
Wheat	<840	2912 (2016-3808)
Sorghum	840	907 (381-1456)
Sugarbeet	213	Not able to be calculated
Soybean	Not tested	Not tested
Pea	Not tested	Not tested
Tomato	51.5	202 (112->28000)
Rape	104	202 (34-258)

Cucumber	231	381 (269-504)

Table A2.33: Vegetative Vigour Tier II NOEC Results (g ac/ha)

	Shoot height	Shoot weight	Root weight	Total plant weight
Onion	<51.5	<51.5	<51.5	<51.5
Corn	840	213	213	213
Wheat	213	<213	213	<213
Sorghum	<52.6	<52.6	<52.6	<52.6
Sugarbeet	5.6	5.6	5.6	5.6
Soybean	12.3	2.24	12.3	2.2
Pea	25.8	<5.6	25.8	<5.6
Tomato	5.6	1.12	1.12	1.12
Rape	12.3	<12.3	12.3	<12.3
Cucumber	5.6	5.6	5.6	5.6

Table A2.34: Vegetative Vigour Tier II EC25 Results (g ac/ha, 95% CI in Brackets).

	Shoot height	Shoot weight	Root weight	Total plant weight
Onion	53.8 (14.6-79.5)	24.6 (CND)	28 (0-482)	25.8 (0.1-43.7)
Corn	1680 (1232-2128)	437 (269-605)	157 (43.7-302)	358 (157-549)
Wheat	672 (493-1109)	45.9 (CND)	CND	43.7 (CND-146)
Sorghum	CND	31.4 (CND)	CND	213 (CND)
Sugarbeet	31.4 (22.4-39.2)	9.7 (3.8-15.7)	4.5 (CND-12.3)	8.7 (2.7-14.6)
Soybean	31.4 (8.4-40.3)	13.4 (6.3-19)	12.3 (1.7-22.4)	13.4 (6.0-19)
Pea	CND	5.9 (1.2-13.4)	4.7 (CND-29.1)	5.7 (1.1-13.4)
Tomato	9.4 (5.7-12.3)	1.9 (0.7-3.0)	1.2 (0-2.9)	1.3 (0.3-2.4)
Rape	52.6 (44.8-59.4)	8.3 (2.9-13.4)	4.3 (0-9.9)	5.9 (0.3-11.2)
Cucumber	5.9 (4.1-7.4)	5.9 (4.1-7.5)	3.8 (2.0-5.3)	5.7 (3.9-7.2)

CND = Could Not Determine

Conclusion

Based on the vegetative vigour data, dicots were in general more sensitive than monocots. The most sensitive monocot was sorghum (EC25 = 31.4 g ac/ha; shoot weight; NOEC <52.6 g ac/ha) while the most sensitive dicot was tomato (EC25 1.2 g ac/ha, root weight; and EC25 = 1.3 g ac/ha, total plant weight; NOEC = 1.12 g ac/ha).

Title	Influence of Diuron on Seed Germination, Seedling Emergence and Vegetative Vigour of Several Terrestrial Plants
Authors	Heldreth and McKelvey
Date	1996
APVMA Data ID	9004
Test Guideline	US EPA-FIFRA, 40CFT, Part 158.540; Pesticide Assessment Guidelines Subdivision J, 122-1 and 123-1
Data Validity	1 (GLP)
Data Relied On	Yes - the data was considered to be critical and was relied on in this assessment.

Test System

This study was undertaken at the request of the US EPA following their review of McKelvey and Kuratle (1991) described above. The purpose was to re-evaluate non-target plant response to diuron on seedling emergence and

vegetative vigour on five plant species each in the absence of non-test pesticides (that is, with a solvent control) and with negative (untreated) controls.

Testing was conducted at rates up to 13.4 kg ac/ha to evaluate effects of diuron on seedling emergence following soil surface application and on vegetative vigour following foliar exposure. Seedling emergence testing was conducted on onion, wheat, sugar beet, tomato and rape. Vegetative vigour tests were performed on onion, wheat, sorghum, pea and rape. Effects on emergence, shoot height, shoot dry weight and visual response were measured.

In the seedling emergence test, for each species, 4 replicates of 10 seeds each were included for each treatment rate, the solvent control (acetone) and the negative control. The test duration was 14 days. For the vegetative vigour test, for each species, 10 replicate plants were treated with each treatment rate, the solvent control and the negative control. The test duration was 21 days.

Findings

Test solutions were verified analytically and showed measured concentrations to range from 101.7 to 106.7% of the nominal value.

Table A2.35: Seedling Emergence Tier II Results (g ac/ha). 95% CI in Brackets

	Height		Shoot dry weight	
	NOEC	EC25	NOEC	EC25
Onion	44.2	195 (153-234)	99.6	96.2 (69.9-116)
Wheat	1680	8690 (5197-20832)	1680	809 (515-1109)
Sugarbeet	>211	CND1	211	143 (79.9-189.3)
Tomato	105	204 (112-5947)	105	95 (64.4-119)
Rape	52.5	178 (144-214)	211	102 (69.8-128)

1) CND = Could not determine

Table A2.36: Vegetative Vigour Tier II Results (g ac/ha, 95% CI in Brackets).

	Height		Shoot dry weight	
	NOEC	EC25	NOEC	EC25
Onion	420	1120 (549-CND)	420	209 (28.9-326)
Wheat	840	4345 (CND)	13.1	32.9 (21.1-46.8)
Sorghum	13.1	2251 (1557-3842)	13.1	62.2 (40.7-85.8)
Pea	13.1	60.8 (39.4-115)	13.1	13.9 (9.7-18.3)
Rape	525	88.8 (66.5-109)	525	40.3 (31.2-49.3)

Conclusion

Plants were more sensitive in the vegetative vigour study. In this study, the most sensitive monocot was wheat with an EC25 of 32.9 g ac/ha (shoot dry weight) and a NOEC of 13.1 g ac/ha, while the most sensitive dicot was the pea with an EC25 of 13.9 g ac/ha (shoot dry weight) and a NOEC of 13.1 g ac/ha.

5.7 Mammals

The data in Table A2.36 are from Tomlin (2003) and DEWHA has not seen the full reports. These show that diuron has low acute toxicity to rats and the chronic toxicity to rats and dogs is also low.

Table A2.36. Summary of toxicity to mammals.

Test	Species	Result
Acute oral	Rat	LD50 > 3000 mg/kg
Chronic toxicity	Rat 2 years Dog, 2 years	NOEL = 250 mg/kg in diet. NOAEL = 125 mg/kg in diet.

APPENDIX F – REFERENCES

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