Australian Pesticides &
Veterinary Medicines Authority

The Reconsideration of Approvals of the Active Constituent Diuron, Registrations of Products containing Diuron and their Associated Labels

PRELIMINARY REVIEW FINDINGS

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Veterinary Medicines Authority**

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FOREWORD

The APVMA* is an independent statutory authority with responsibility for the regulation of agricultural and veterinary chemicals in Australia. Its statutory powers are provided in the Agvet Code scheduled to the *Agricultural and Veterinary Chemicals Code Act, 1994*.

The APVMA can reconsider the approval of an active constituent, the registration of a chemical product, or the approval of a label for a container for a chemical product, at any time. This is outlined in Part 2, Division 4 of the Agvet Code.

The basis for the reconsideration is whether the APVMA is satisfied that continued use of the active constituent diuron and products containing diuron in accordance with the instructions for their use:

- would not be likely to have an effect that is harmful to human beings; and
- would not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment.

The APVMA also considered whether product labels carry adequate instructions and warning statements.

A reconsideration may be initiated when new research or evidence has raised concerns about the use or safety of a particular chemical, a product, or its label.

The process for reconsideration includes a call for information from a variety of sources, a review of that information and, following public consultation, a decision about the future use of the chemical or product.

In undertaking reviews, the APVMA works in close cooperation with advisory agencies including the Department of Health and Aging Office of Chemical Safety (OCS), the Department of Environment and Heritage (DEH), and State Departments of Agriculture as well as other expert advisors, as appropriate.

The APVMA has a policy of encouraging openness and transparency in its activities and community involvement in decision-making. The publication of review reports is a part of that process.

The APVMA also makes these reports available to the regulatory agencies of other countries as part of bilateral agreements. Under this program it is proposed that countries receiving these reports will not utilise them for registration purposes unless they are also provided with the raw data from the relevant applicant.

This document is *'The reconsideration of approvals of the active constituent diuron, registrations of products containing diuron and their associated labels, Preliminary Review Findings'* and relates to approvals of the active constituent diuron and products containing diuron and their labels that have been nominated for review by the APVMA. The review's preliminary findings and recommendations are based on information collected from a variety of sources. The information and technical data required by the APVMA to review the safety

* Prior to March 2003, the APVMA was known as the National Registration Authority for Agricultural and Veterinary Chemicals (NRA). In this report, the name APVMA is generally used even when referring to the organisation prior to March 2003.

of both new and existing chemical products must be derived according to accepted scientific principles, as must the methods of assessment undertaken.

Volume 1 summarises the APVMA's preliminary assessments and Volume 2 contains the technical reports for all registrations and approvals relating to uses of diuron. Both documents are available from the APVMA website:
http://www.apvma.gov.au/chemrev/chemrev.shtml

ACRONYMS AND ABBREVIATIONS

ac	active constituent
ACPH	Advisory Committee on Pesticides and Health
ADI	Acceptable Daily Intake
ai	active ingredient
ANZECC	Australia and New Zealand Environmental and Conservation Council
APVMA	Australian Pesticides and Veterinary Medicines Authority
ARfD	Acute Reference Dose
BA	2-bromoacrolein
CRP	Chemistry and Residues Program
ChE	Cholinesterase
CODEX	FAO/WHO Codex Alimentarius Commission
DEH	Department of Environment and Heritage (previously Environment Australia)
EHC	Environmental Health Criteria
EPA	Environmental Protection Agency
F0	parental generation
F1	filial generation, first
F2	filial generation, second
FSANZ	Food Standards Australia and New Zealand
GAP	Good Agricultural Practice
HG	Home Garden
HV	Home Veterinary
ha	hectare
IRED	Interim Re-registration Eligibility Decision
GLP	Good Laboratory Practice
JMPR	Joint FAO/WHO Meeting on Pesticide Residues
LD_{50}	median lethal dose
LOEL	Lowest Observable Effect Limit
LOEC	Lowest Observable Effect Concentration
MoS	Margin of Safety
MRL	Maximum Residue Limit
mg/kg bw/d	milligrams/ kilogram of bodyweight/day
NEDI	National Estimated Dietary Intake
NESTI	National Estimated Short-Term Intake
NHMRC	National Health and Medical Research Council
NOEL	No Observed Effect Level
NOAEL	No Observable Adverse Effect Level
NOHSC	National Occupational Health and Safety Commission
NRS	National Residue Survey
OCS	Office of Chemical Safety
OHS	Occupational Health and Safety
PACSC	Pesticide and Agricultural Chemical Standing Committee
PHED	Pesticide Handlers Exposure Database
POEM	Predictive Operator Exposure Model
PHI	Post Harvest Interval
PPE	Personal Protective Equipment
ppm	parts per million
RAC	Raw Agricultural Commodity
RBC	Red Blood Cell
SC	Suspension Concentrate
SUSDP	Standard for Uniform Scheduling of Drugs and Poisons
TCAB	3,3',4,4'-tetrachloroazobenzene
TCAOB	3,3',4,4'-tetrachloroazoxybenzene
WHP	Withholding Period

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8. TOXICOLOGY ASSESSMENT

8.1 Assessment of Data

8.1.1 Introduction

Diuron is a broad-spectrum residual herbicide acting through the inhibition of plant photosynthesis. It is primarily absorbed through plant roots and has a soil half-life of the order of one hundred days.

The current toxicology report consolidates data on metabolism, subchronic and chronic toxicity, reproductive and developmental toxicity and genotoxicity. The toxicities of two impurities in the active, namely 3,3',4,4'-tetrachloroazobenzene (TCAB) and 3,3',4,4'-tetrachloroazoxybenzene (TCAOB) have been assessed. A list of the toxicological abbreviations used in the report is included in Appendix 6.

8.1.2 History of Public Health Considerations of Diuron In Australia

Australian public health standards for agricultural and veterinary chemicals that may enter the food chain include the Poisons Schedule, First Aid and Safety Directions (FAISDs), the human acceptable daily intake (ADI) and the acute reference dose (ARfD). A further regulatory standard called the maximum residue level (MRL) is a measure of the residues present in unprocessed food (eg. grain, meat etc.) and hence is an indicator of good agricultural practice.

From the mid 1950s until 1992, Australian public health standards were set by committee process under the auspices of the NHMRC. "Pesticide Tolerances" in food were first set in 1956 by the Food Additives Committee. Between 1962 and 1966, the Food Additives Committee maintained a Sub-Committee on Pesticides and Agricultural Chemical Residues In Or On Foods (later re-named the Pesticide Residues in Food Sub-Committee), which adopted the then Canadian scheme as a basis for establishing tolerances. From 1967 onwards, Australian MRLs and ADIs for pesticides were established by the Pesticide and Agricultural Chemicals Committee (PACC), until the Department of Health and Ageing became directly responsible for setting ADIs in November 1992. Responsibility for pesticide and veterinary chemical MRLs in food was transferred to the APVMA in June 1994, after which the PACC was removed from the control of the NHMRC and re-constituted as the Advisory Committee on Pesticides and Health (ACPH). The ACPH provides the Department of Health and Ageing, the TGA and the APVMA with advice on issues of policy and practice having possible implications for public health and the proper use of chemicals in agriculture and elsewhere.

Poisons Schedules for agricultural and veterinary chemicals, drugs and some other hazardous substances are set by the National Drugs and Poisons Schedule Committee (NDPSC). Originally known as the Committee on Poisons Scheduling, the NDPSC was established in 1955 as a sub-committee of the NHMRC Public Health Committee. The NDPSC publishes its decisions in the Standard for the Uniform Scheduling of Drugs and Poisons, which recommends controls on availability, labelling, packaging and advertising. These are incorporated into and enforced by the various Australian State and Territory legislative systems. In 1994, the NDPSC was transferred from the NHMRC to the Australian Health Ministers' Advisory Council, and was re-constituted again in 1999 as a Statutory Committee of the Therapeutic Goods Administration.

A third committee formerly involved in chemicals management was the NHMRC Standing Committee on Toxicity (SCOT), which was active between 1985 and 1994. SCOT was responsible for providing specialised advice on complex toxicological matters to all the NHMRC Public Health Committee subordinate committees, including the PACC and NDPSC. In response to referrals from these committees, SCOT undertook evaluation of some drugs, pesticides, food additives, poisons, consumer products, chemicals and other hazardous substances relevant to public health.

The regulatory history of public health considerations of diuron by Australian regulatory committees is summarised in Table 17 below.

Table 17: History of public health considerations of diuron.

Date	Regulatory Activity
February 1980	PACSC: MRL recommended for water (0.04 mg/L).
May 1986	PACSC: Recommended maximum levels for TCAB and TCAOB.
November 1987	NDPSC: Considered review of submission with significant toxicological data from Du Pont and Koor Intertrade, and confirmed the scheduling status (exemption, Appendix B) of diuron.
February 1988	NDPSC: Considered the NHMRC's recommendation and agreed the limits of impurity levels of TCAB (20 mg/kg) and TCAOB (2 mg/kg) be included in Appendix L.
August 1990	NDPSC: Considered each of the applications for diuron TGAC clearance based on the levels of microcontaminants TCAB and TCAOB. Suspended consideration of Bayer's application due to bladder hyperplasia and carcinoma in 26-week and 2-year rat studies, and equivocal results from an *in vitro* UDS test in rat bladder epithelium, and a potential association with TCAB and TCAOB.
August 1990 – August 1992	PACSC: Repeatedly considered and finally accepted the applicant's statements on levels of impurities TCAB and TCAOB, and agreed to TGAC clearance.

PACCS – Pesticides and Agricultural Chemical Standing Committee; NDPSC - National Drugs and Poisons Scheduling Committee.

8.1.3 Metabolism and Toxicokinetics

Following oral administration to rats, diuron was rapidly and extensively absorbed (Tmax 1.7-1.9 h), and an enterohepatic circulation was evident by biliary fistulae technique. Elimination of diuron and its metabolites was complete, with the majority excreted within the first 24 h, mainly into the urine, and to a lesser extent into the faeces (1: 5-10 for faeces:urine). The highest residue levels were generally found in the blood, liver and kidneys, four days after dosing. No significant tissue accumulation was evident after repeated dosing.

The metabolism of diuron was extensive with only a small amount (< 2%) of the parent compound being present in the faeces. Eight metabolites in the urine and four in the faeces were characterised, as well as some unknown metabolites. Biotransformation of diuron consisted of N-demethylation, oxidation, hydroxylation and conjugation. The main metabolites, 3-(3,4-dichlorophenyl)-1-methyl urea and 3-(3,4-dichlorophenyl) urea, as well as 3,4-dichloraniline, were also detected in excreta following inhalation of diuron (Wu, 1996; Pauluhn & Eben, 1986; Weber & Abbink, 1988; Weber & Abbink, 1988).

8.1.4 Acute Studies

In lethal-dose studies, due to its low solubility in water (~ 40 mg/L), the oral toxicity of diuron was low in rats (LD50 3000 - 9087 mg/kg bw) when an aqueous vehicle was used. However, the acute oral toxicity in rats was higher when diuron was prepared in an oil vehicle (LD50 1017 - 5000 mg/kg bw). The oral LD50 in mice was 8590 mg/kg bw for males and 8244 mg/kg bw for females. Clinical signs following an oral dose of 50 mg/kg bw or higher consisted of lethargy, low posture, ocular/nasal/oral discharge, appearance, behaviour, motility and respiratory disorders, and/or weight loss.

Limit tests indicated that the acute dermal toxicity was very low. Several studies in rats showed no deaths at 2000, 2500 or 5000 mg/kg bw, and hence the dermal LD50 was greater than 5000 mg/kg bw. Similarly, the inhalation toxicity in rats was low (LD50 > 7100 mg/m^3). Diuron as a dust was a slight eye irritant in rabbits. It did not induce skin irritation in two studies with rabbits, but in another study, it was a moderate skin irritant on intact and scarified skin of rabbits, which was pre depilated with sodium sulphide and neutralised with acetic acid (Kasa, 1986). It was not considered to be a skin sensitiser in two independent tests with the Magnusson Kligman Maximisation method.

8.1.5 Short-Term Repeat-Dose Studies

Oral administration – rats
In order to test immunotoxicity of diuron, 25, 250 or 2500 mg/kg bw/day was given to rats in the diet for 3 weeks. Diuron at 250 mg/kg bw/day and above increased the spleen weight, and induced extramedullary hemopoiesis and haemosiderin deposition. No immunotoxicity was indicated (Vos et al, 1983).

Dermal application - rabbits
Rabbits received dermal applications of diuron at 0, 50, 500 or 1200 mg/kg bw/day on intact skin of the back for 6 h per day, 21 consecutive days. No deaths occurred during the study. A higher incidence of skin irritation was observed at 1200 mg/kg bw/day. No biologically significant alterations were observed in haematological or clinical chemistry parameters, mean organ weights, gross- or histo-pathology at any dose levels. The NOEL for systemic changes was 1200 mg/kg bw/day (McKenzie, 1992).

Rabbits received dermal applications of diuron at 0, 50 or 250 mg/kg bw/day on intact or abraded skin of the dorsal and flank for 6 h per day, 5 days per week for 3 weeks. No deaths occurred during the study. Slightly more severe and longer lasting skin responses (erythema, skinfold thickness) were observed on the abraded skin site of some treated rabbits without a dose-relationship. There were no treatment-related findings in haematology, clinical chemistry and urinalysis. No abnormal observations were revealed in organ weights, gross and histo-pathology. The NOEL for systemic changes was 250 mg/kg bw/day (Mihail & Schilde, 1984).

Inhalational administration - rats
Rats were exposed head/nose only to the air, the solvent (lutrol/ethanol), 6.6, 48 or 311 mg/m^3 of diuron aerosol for 6 h per day, 5 days per week for 3 weeks. All rats survived to the termination. Males at 311 mg/m^3 had lower body weight gains. Rats at 48 and 311 mg/m^3 exhibited haemolytic anaemia including slight falls in erythrocyte count, increases in MCV and MCH with simultaneous reticulocytosis, as well as concentration-related Heinz body formation. Rats at 311 mg/m^3 showed slightly reduced plasma protein concentrations and

lower T3 and T4 levels, accompanied by increased thyroxine binding capacity, more marked in males than in females. There was also a reduced trend in plasma urea and creatinine levels at 48 mg/m^3 and above. The liver N-demethylase activity was slightly induced at 311 mg/m^3. Spleen weights were significantly higher at 48 (female) and 311 mg/m^3 with dark, swollen and congestion at 311 mg/m^3. The NOEL was 6.6 mg/m^3 based on haemolytic anaemia observed at higher concentration (Pauluhn, 1986a).

Rats were exposed head/nose only to 0 (lutrol/ethanol), 4.1, 37 or 268 mg/m^3 of diuron aerosol for 6 h per day, 5 days per week for 4 or 8 weeks. All rats survived to the termination. Rats at 268 mg/m^3 showed transient lassitude and ungroomed coat post exposure. Heinz body formation, reticulocytosis and a light fall in erythrocytes were induced at 37 (female) and 268 mg/m^3, accompanied by increased MCV at 268 mg/m^3 indicating slight haemolytic anaemia. Slightly lower AST, ALT and LDH activities at 37 and 268 mg/m^3 might be relevant to a lower level of total plasma protein or albumin. Reduced thyroid activity was indicated by a lower T4 level at 268 mg/m^3. O-demethylase activity in the liver was induced at 268 mg/m^3. Histology did not however detect any pathological changes in thyroid or liver. Dark and swollen spleens were observed at 37 and 268 mg/m^3, correlated to increased spleen weight at 268 mg/m^3, and iron accumulation in the spleen at 37 (female) and 268 mg/m^3. Changes in urothelium of renal pelvis, urinary bladder and ureter were not dose-related, and could not simply attributed to the treatment. The NOEL was 4.1 mg/m^3 based on haemolytic anaemia observed at higher concentration (Pauluhn, 1986b).

8.1.6 Subchronic Studies

Oral administration - rats

Rats received diuron at 0, 75, 250 or 500 mg/kg bw/day by gavage over 5 days/week for 13 weeks. There were no treatment-related deaths or clinical signs. Lower body weight gain was seen in males at 250 and 500 mg/kg bw/day. Laboratory examinations revealed haemolytic anaemia-related changes, including reduction in RBC counts, haemoglobin and haematocrit, and increase in MCV. Dose-related increases in total serum bilirubin and blood urea nitrogen of all treated groups might be indicative of liver and kidney damage. Splenomegaly at all treated groups was consistent with haematological findings. A NOEL was not established and the LOEL was 75 mg/kg bw/day (Wandrag, 1996a).

Rats received a daily dose of diuron at 0, 55, 168, 225, 335 or 450 mg/kg bw/day in the diet for 90 days, followed by a 30-day recovery period at 0, 335 and 450 mg/kg bw. The extremities became pale, bloodless after 3-4 weeks treatment, but this had regressed by the end of recovery period. Body weight was significantly lower at 225 mg/kg bw/day and above. Reduced RBC count, haemoglobin and haematocrite, and increased bilirubin and methemoglobin, increased spleen and pituitary weights were reported (no data). The insufficient data does not allow to establish a NOEL (Beres, 1986).

Dermal application - rats

Rats received dermal applications of diuron at 0, 250, 500 or 1000 mg/kg bw/day on clipped skin of the dorsal area of the trunk over 5 days per week for 13 weeks. No treatment-related deaths or clinical signs were defined. There was a reduction in RBC count, haemoglobin and haematocrit, and an increase in MCV and MCH at all dose levels. Increased total serum bilirubin was also observed in all treated groups. No treatment-induced organ weight changes or histopathological changes were observed. A NOEL could not be established and the LOEL was 250 mg/kg bw/day (Wandrag, 1996b).

8.1.7 Chronic Studies

Mice

Mice received diuron 0, 25, 250 or 2500 ppm in the daily diet for 12 or 24 months. There were no treatment-related increases in mortality, clinical signs and changes in food consumption. Body weight was significantly lower at 2500 ppm. At various occasions, platelet counts were higher in all treated male groups, and total leucocyte counts were higher at 2500 ppm. Mice at 2500 ppm had consistently increased plasma ALT activity and bilirubin levels, together with historical changes in the liver such as hepatopathy (males), increased rates of mitosis and cell necrosis, indicating liver injury. A trend to an increased incidence of liver cell enlargement was observed dose-dependently in all treated females groups. Haemosiderin accumulation (iron pigment) in the liver, spleen and kidneys was higher at 2500 ppm. Females at 2500 ppm exhibited an increased incidence of epithelial hyperplasms of the bladder at 12 and 24 months, some associated with extension of the lamina propria mucosae and mucosal oedema. Some females at 2500 ppm showed dilation of the uterine horn, and a significant increase in the incidence of ovary luteoma and breast carcinoma, but not the combined sex cord-stromal tumours. There were no significant differences in the number of animals with neoplasms, the total number of neoplasms, number of malignant or benign neoplasms. The NOEL was 250 ppm (51/78 mg/kg bw/day for M/F) based on hepatotoxicity and haemosiderin at the higher dose. The NOEL for bladder epithelial hyperplasms was 250 ppm (Eiben et al, 1990).

Rats

Rats received diuron 0, 25, 250 or 2500 ppm in the daily diet for up to 24 months. The mortality rate was generally low and not affected by treatment. Body weight was lower at 2500 ppm. Dose-related changes in erythrocyte parameters which indicated haemolytic hyperchromic anaemia occurred in all treated female groups, and in males at 250 and 2500 ppm, accompanied by increased incidences of erythrocyte precursors (reticulocytes) and pathological erythrocytes (anulocytosis, anisocytosis, polychromasia, Jolly bodies and Heinz bodies). In addition, leucocyte counts were increased at 250 (males) and 2500 ppm. Plasma bilirubin concentration was consistently higher at 2500 ppm. The blood urea nitrogen concentration was also increased at 2500 ppm, and sometimes at 250 ppm. Urinalysis revealed a higher blood/erythrocyte content at 2500 ppm, and the urine from the males of this group showed a reddish colour. Liver and spleen weights were significantly increased in males at 250 and 2500 ppm, and in all treated female groups after 24-month dosing. Swelling/enlargement and black coloration of the spleen were found in these groups. Increased haemosiderin accumulation and fibrosis were found in the spleen at 25 ppm (females) and above, and the deposition of iron-containing pigments were also in the liver, kidneys and lungs, in particular at 2500 ppm. Heightened medullary haematopoiesis was also observed in the femoral bone marrow at 250 and 2500 ppm, as well as activated bone marrow cells in females at 25 ppm. Hardness and/or thickening of the urinary bladder wall appeared at 2500 ppm, corresponding to hyperplasia of the urinary bladder epithelium and the renal pelvis epithelium at 250 and 2500 ppm.

Some of the changes in the spleen, liver and bladder were also seen at interim sacrifice, but to a lesser extent. The total incidence and number of animals with neoplasms was higher at 2500 ppm, in particular, a higher incidence of transitional carcinomas of the urinary bladder epithelium in males and females at 2500 ppm, some with hornification of differentiation from squamous epithelial carcinoma. Benign neoplasms of urinary bladder, papillomas were slightly higher in males at 2500 ppm. It was suggested that severe urothelial hyperplasms was a possible precursor of the neoplastic alteration. The number of adenocarcinomas in the

uterus was higher at 2500 ppm compared to the concurrent control, but within the range of historical control provided by the sponsor. A NOEL for anaemia was not established, and the LOEL was 25 ppm. The NOEL for hyperplasm of the urinary bladder epithelium was 25 ppm (1.0/1.7 mg/kg bw/day for M/F) (Schmidt, 1985).

Dogs

Dogs received 0, 50, 300 or 1800 ppm of diuron in the daily diet for 12 months. Slightly reduced food consumption in females and lower body weight gains were observed at 1800 ppm. Signs of anaemia occurred at 1800 ppm, characterised by a reduction in haemoglobin and erythrocyte count, a rise in MCV, slight polychromasia and anisocytosis, and an increased incidence of anulocytes, polychromatic and oxiphile normoblasts, Jolly bodies, and great quantities of Heinz' inclusion bodies in the erythrocytes. Consequently, reticulocyte, leucocyte and platelet counts were increased, and the highly reactive fat-deficient bone marrow occurred with increased siderin content in this group. Serum protein electrophoresis revealed a slight fall in α-1 and α-2 globulin proportions, and a corresponding increase in the β-globulin proportion. At 1800 ppm, the activity of ALP in the plasma was consistently higher. There were no treatment-related changes in urinalyses. Liver, spleen and testicular weights were increased at 1800 ppm. Corresponding to colour and/or surface changes in the liver (bile), spleen, kidneys and bone marrow, histopathology detected higher incidences of iron-containing pigments in Kupffer stellate cells of the liver and the bone marrow with reactive fat-deficient at 1800 ppm, and in the red pulp of spleen and the basal region of the epithelial cells near the nucleus in the proximal tubule contorti of kidneys at 300 and 1800 ppm. The NOEL was 50 ppm (1.25 mg/kg bw/day) based on haemosiderin deposition at higher doses (Hoffmann & Schilde, 1985).

Dogs received 0, 25, 125, 250 and 1250 ppm (reduced from 2500 ppm due to food refusal and body weight loss) of diuron as a 80% wettable powder in the daily diet for 24 months. Body weight loss was observed at 1250 ppm. Significantly decreased RBC counts, haemoglobin and haematocrit values were noted at 250 and 1250 ppm, associated with abnormal blood pigments at 125 ppm and above. At 1250 ppm, bone marrow exhibited a statistical increase in erythrogenic activity/erythroid hyperplasia, and a moderate reduction in marrow fat, and hepatic Kupffer cells had increased brown haemosiderin pigment. Absolute and relative liver weights were higher in dogs at 1250 ppm. No treatment-related neoplasia findings were reported. The highest residue level was detected in the liver at termination. The NOEL was 25 ppm (0.6 mg/kg bw/day) based on haemolytic anaemia and haemosiderin deposition at higher doses (Hodge & Downs, 1964).

8.1.8 Reproduction Studies

Rats

In a two-generation reproduction study, rats received 0, 10, 250 or 1750 ppm of diuron in the daily diet through breeding, gestation and lactation. At 1750 ppm, food consumption and mean body weight gains were lower in P and F1 parents during premating and gestation, with a rebound during lactation. No treatment-related effects were detected on mating and fertility indices of P and F1 parental rats. Enlarged spleens were observed in some P and F1 females at 1750 ppm which microscopically correlated with congestion. Litter size and pup survival rates were normal in all groups. Mean F1 and F2 litter and pup weights were lower at 1750 ppm. No treatment related gross abnormalities were observed in F1 or F2 pups. The NOEL was 250 ppm (15/16 mg/kg bw/day for M/F) for general and reproduction toxicity based on reduced food consumption and body weight gain, and lower pup weights at the higher dose (Cook, 1990).

8.1.9 Developmental Studies

Rats
Diuron was administered by gavage at 0, 16, 80 or 400 mg/kg bw/day to presumed pregnant female rats on gestation days 6 – 15 and killed on day 20. Pregnant rats at 80 and 400 mg/kg bw/day had significantly lower food consumption and reduced body weight gain during dosing. There were no treatment-related effects on litter size, resorptions or the foetal sex ratio. Foetal body weights were significantly lower for litters at 400 mg/kg bw/day. Skeletal examinations revealed a higher incidence of foetuses with delayed ossification of the vertebrae and sternum (sternal centres) at 400 mg/kg bw/day. The NOEL was 16 mg/kg bw/day for maternal toxicity, and 80 mg/kg bw/day for foetal developmental toxicity (Dearlove, 1986a).

Rabbits
Artificially inseminated female rabbits received diuron at 0, 2, 10 or 50 mg/kg bw/day by gavage on gestation days 7-19 and killed on day 29. Pregnant rabbits at 50 mg/kg bw/day had lower food consumption, and reduced body weight gain. No clinical signs or gross lesions were attributed to treatment. The mean foetal weight, number of live foetuses and incidences of resorption and/or foetal death were comparable across all groups. No external, soft tissue or skeletal alterations demonstrated either a significant or dose-related incidence, as compared with control. The NOEL was 10 mg/kg bw/day for maternal toxicity and was 50 mg/kg bw/day for developmental toxicity (Dearlove, 1986b).

8.1.10 Genotoxicity Studies

A number of *in vitro* and *in vivo* experiments have tested the genotoxic potential of diuron. Diuron was negative *in vitro* in a series of Ames test (11 studies, 1984-2000), in the mutagenic assay on CHO/HPRT cells (2 studies), and in a chromosomal aberration test and a sister chromatid exchange test on CHO-K1 cells. Diuron did not show genotoxic effect *in vivo* in a cytogenetic assay, a chromosomal aberration assay, a sister chromatid exchange assay and micronucleus test (3 out of 4 studies, 1983-1998). Diuron 2000 – 2500 mg/kg bw did not show a genotoxic effect in the germ cells of male mice in a dominant lethal test.

In an *in vitro* cytogenetic study (1 out of 3), diuron showed clastogenic effect on human lymphocytes at the concentration range of 125 to 500 μg/mL in the absence of S9 activating system, and 500 to 1000 μg/mL in the present of S9. However, diuron was uniformly negative in 2 other *in vitro* and 4 *in vivo* chromosomal aberration/sister chromatid exchange assays.

In an *in vitro* UDS test in primary rat hepatocytes, a trend towards slight increases in the average net nuclear was attributed to slight reduction in the cytoplasmic grain counts with increasing concentrations of diuron. However, in an *in vivo* UDS assay, diuron at 250 ppm and the above caused an induction of UDS and reduction of DNA repair of urinary bladder epithelial cells.

In a published study of micronucleus test (1 out of 4 tests, Agrawal *et al* 1996), diuron 170 and 340 mg/kg bw significantly increased micronuclei, compared to the negative control. However, the magnitude of increase in micronuclei induced by the positive control cyclophosphamide was relatively low (4-6 MNPCE/1000) compared to data from other laboratories (10 – 20), and only similar to that of diuron in this study. Since the study

provided only limited information on the test substance and study conditions, it is difficult to make further assessment. However, negative results were produced from 3 other micronuleus tests.

8.1.11 Human Studies

No exposure-induced clinical problems were found by medical surveillance in a manufacturing site of diuron during 22 years (Xavier & Pereira, 2002). No cases of chloracne (March Mil, 1992) or mild chloracne with increased triglyceride and cholesterol values (Scarisbrick & Martin, 1981) were reported.

In a poisoning incident, 2 workmen who received an intense spray exposure to 2,4-D or Karmex (a product of diuron) developed itching and burning in oral and nasal mucosa and conjunctiva, small ulceration in the skin area contacted to, chest discomfort with cough and mucoid sputum, mild headache, muscle twitching and throat soreness within 24 hours, and recovered within 4-5 days (Torrington, 1983).

In poisoning incidences involving accidental ingestion of diuron, the metabolites 3-(3,4-dichlorophenyl)-1-methyl urea, 3-(3,4-dichlorophenyl) urea and/or 3,4-dichloraniline were detected in the blood and/or urine, (Geldmacher *et al*, 1971; Boven *et al*, 1990; Verheij *et al*, 1989). Based on the information, the metabolic pathway in the human is similar to that in the rat (Boven et al, 1990).

8.1.12 Mechanism Studies

Mice-oral
The aim was to investigate the haemotoxic effects observed at a low dose range of diuron in a carcinogenic study on mice during the first 6 months of the study. Mice received diuron 0, 5, 25 or 250 ppm in the daily diet for up to 6 months. Lower body weight occurred in all treated groups lacking a clear dose-relationship. During and up to dosing for 6 months, there were no treatment-related changes in haematology parameters, and no evidence of injury to the hemopoietic system, i.e. neither increased medullary/extramedullary hemopoietic activity, nor increased haemosiderin deposition in the spleen or liver were found. No treatment-related pathological alterations were detected at termination (Eiben, 1988).

Rats-oral
The purpose of the study was to investigate the high mortality, depression of body weight and RBC counts at 250 and 2500 ppm observed in a 2-year rat feeding study. Rats at weaning received diuron as a 80% formulation at 0, 250 or 2500 ppm of the active ingredient in the diet for 90 days. There were no treatment-related deaths. Rats at 2500 ppm showed significantly reduced food consumption and lower body weight. This group also exhibited lower RBC, haematocrit and haemoglobin values, and an elevated cell population of femoral marrow; the later suggesting compensatory bone marrow hyperplasia (Sherman, 1962).

In order to establish a NOEL for diuron in relation to its effects on the erythrocytes, rats received diuron at 0, 4, 10 or 25 ppm (0/0, 0.3/0.3, 0.7/0.8 or 1.6/1.8 mg/kg bw/day for M/F) in the diet for up to 26 weeks. There were no treatment-induced deaths, clinical signs or changes in food consumption and body weight. At 25 ppm, lower haemoglobin in females and higher reticulocyte counts in both sexes were observed at various times, and slightly increased accumulation of ferriferous pigments occurred in the spleens. The haematology

NOEL was 10 ppm (0.7/0.8 mg/kg bw/day for M/F) based on haemolytic anaemia at the higher dose (Schmidt & Karbe, 1986a).

To gain knowledge in morphogenesis of the urothelium tumours, the time of origin and the reversibility of precancerosis, in diuron-treated rats, male rats received 0 or 2500 ppm of diuron in the daily diet for 2, 4, 12 or 26 weeks, or for 4 or 26 weeks followed by a recovery period of 4 or 8 weeks respectively. No rats died and no notable clinical signs were observed during the study. Lower body weight gain was observed in treated rats throughout the dosing period, and was still apparent after the period of recovery. Swelling or enlargement of the spleen with red-black discolouration was observed in all treated groups. To an increasing extent with longer treatment duration, urinary bladders from treated rats showed increased consistency, reduced transparency, dilated blood vessels, and hyperplasia of epithelium (4-week or longer) sometimes associated with connective tissue proliferation and granulocyte infiltration. Hyperplasia with exo- and endophytic growth (after 4 weeks) and marked squamous epithelial metaplasia (after 26 weeks) were found. Distinct thickening of the urinary bladder wall in treated rats was largely the result of an increase in connective tissue, mainly in the subepithelial area. Recovery groups showed more or less a trend to reversion of above alterations on cessation of treatment. An increased incidence of epithelial hyperplasia in the renal pelvis was also seen after 26-week dosing (Schmidt & Karbe, 1986b).

8.1.13 Pharmacology study

Oral or intraduodenal administration of diuron up to 1000 mg/kg bw showed no effects on the CNS in mice, the respiratory and circulatory systems in dogs, the autonomic nerve system, and skeletal muscle. Oral doses of diuron up to 2000 mg/kg bw had essentially no effect on rat blood parameters including thromboplastin time and in vitro haemolytic effect. Diuron at 1000 mg/kg bw, but not 300 mg/kg bw and lower dose significantly inhibited intestinal motility in mice (Algate et al, 1989).

8.1.14 Impurity studies

3,3',4,4'-tetrachloroazobenzene (TCAB) and 3,3',4,4'-tetrachloroazoxybenzene (TCAOB) are two impurities formed as unwanted by-products in the manufacture of diuron. Both chemicals also formed from the degradation of chloranilide herbicides and by the photolysis and biolysis of 3,4-dichloroaniline.

TCAB

TCAB showed low acute oral toxicity (LD50 $\geq$ 5000 mg/kg bw), and moderate inhalation toxicity (LC50 880-920 mg/m^3) in rats. In a dermal study in rabbits, it did not cause any death (1 rabbit/dose) up to 1000 mg/kg bw, the highest dose tested.

Dermal effects of 0.002% to 2% TCAB and 0.01% to 10% 3,4-dichloroaniline were compared by applying to the skin of rabbit ear for 5 days/week over 4 or 6 weeks. Slight to severe sloughing, plug formation, ear thickening and hair lose were observed, more severe at 2% TCAB than 10% 3,4-dichloroaniline. Both are strong acnegens (Morrow, 1976).

Rats were exposed to volatilised TCAB 190 mg/m^3 for 4 h/day, 5 day/week over 2 weeks. Following the exposure, increased RBC counts and decreased MCV and MCH were detected, as well as dark urine with higher pH and sugar positive (Trochimowicz, 1976).

The US National Toxicology Program (NTP) has published technical reports on the toxicity of TCAB and TCAOB (Toxic Rep Ser 1998 Nov; 65:1-F6. Toxic Rep Ser 1998 Nov; 66:1-G4.). The data are outlined as the following.

In the 16-day gavage studies (5 day x 3 week), TCAB 0, 1, 3.2, 10, 32 or 100 mg/kg bw/day in corn oil was given to B6C3F1 mice. No effects were found on survival or mean body weight gains of rats and mice. Liver, lung and spleen weights were increased and thymus weight was reduced. Female mice at 100 mg/kg bw/day had atrophy of the thymus. Haematopoietic cell proliferation in the spleen was increased at 100 mg/kg bw/day.

In the 16-day gavage studies (5 day x 3 week), TCAB 0, 12.5, 32, 80, 200 or 500 mg/kg bw/day in corn oil was given to F344/N rats. Thymus weight was reduced. Haematopoietic cell proliferation in the spleen was increased in all male groups, and in females at 32 mg/kg bw/day and above. Renal tubule hyaline droplet accumulation in the cytoplasm of renal cortical epithelial cells and chronic nephropathy were observed microscopically in males at 80 mg/kg bw/day and above.

In the 13-week studies, mice received TCAB in corn oil at 0, 0.1, 1, 3, 10 or 30 mg/kg bw/day by gavage. Mice showed increased liver and spleen weights at 10 and 30 mg/kg bw/day, an increased incidence of hyperplasia of the forestomach at 1 mg/kg bw/day and above. A decrease in thymus weight of males at 30 mg/kg bw/day, an increase in centrilobular hypertrophy of hepatocytes and a higher incidence of haematopoietic cell proliferation in the spleen in males at 3 mg/kg bw/day and above, and a significant decrease in epididymal spermatozoal concentration in males at 3 and 30 mg/kg bw/day. The NOEL was 1 mg/kg bw/day in mice.

In the 13-week studies, rats received TCAB in corn oil at 0, 0.1, 1, 3, 10 or 30 mg/kg bw/day by gavage. The major effects included a decrease in body weight at 30 mg/kg bw/day, decreased thymus weights accompanied by thymic atrophy, increased incidence of haematopoietic cell proliferation in the spleen, a responsive anaemia, decreased platelet counts, increased liver (also in males at 1 and 3 mg/kg bw/day) and spleen weights at 10 and 30 mg/kg bw/day. Hepatic cytochrome P-450 1A staining presence and intensity were increased at 30 mg/kg bw/day. Sharp decreases in circulating thyroxine levels at all dose groups, and thyroid-stimulating hormone were marginally increased. The incidence of hyperplasia of the forestomach was increased in males at 3 mg/kg bw/day and above and in females at 30 mg/kg bw/day. A NOEL was not established in rats.

TCAB was mutagenic in *S. typhimurium* strain TA97 in the presence of rat liver S9, but not mutagenic in TA98, TA100, TA1535 or TA1537 with or without S9. *In vivo*, the frequency of micronucleated erythrocytes was significantly increased in peripheral blood samples from mice give TCAB at 10 and 30 mg/kg bw/day by gavage for 13 weeks. However, results of a 3-day exposure of up to 200 mg/kg bw by ip did not demonstrate induction of micronuclei in bone marrow erythrocytes of male mice.

TCAOB

In the 16-day gavage studies (5 day x 3 week), TCAOB 0, 1, 3.2, 10, 32 or 100 mg/kg bw/day in corn oil was given to B6C3F1 mice. Effects in mice included increases in liver weights and decreases in thymus weights, thymic atrophy, splenic haematopoietic cell proliferation, and hepatic foci of inflammation and necrosis in mice.

In the 16-day gavage studies (5 day x 3 week), TCAOB 0, 12.5, 32, 80, 200 or 500 mg/kg bw/day in corn oil was given to F344/N rats. Major effects in rats included reduced body

weight gain, increases in liver and lung weights and decreases in heart and thymus weights, cytoplasmic alteration of hepatocytes, splenic haematopoietic cell proliferation, thymic atrophy, and nephropathy in rats and thymic atrophy, splenic haematopoietic cell proliferation, and hepatic foci of inflammation and necrosis in mice.

In the 13-week studies, mice received TCAOB in corn oil at 0, 0.1, 1, 3, 10 or 30 mg/kg bw/day by gavage. Liver weights of mice was increased in males from 3 mg/kg bw/day and females from 1 mg/kg bw/day. Increased incidences of centrilobular hypertrophy of hepatocytes were observed at 10 and 30 mg/kg bw/day, and of haematopoietic cell proliferation in the spleen in males at 30 mg/kg bw/day and females at 10 and 30 mg/kg bw/day. The incidence and/or severity of splenic pigmentation were increased in all treated groups. Thymus weights were decreased in males from 3 mg/kg bw/day and females at 10 and 30 mg/kg bw/day, and the incidence of thymocyte necrosis was increased in males at 10 mg/kg bw/day and females at 10 and 30 mg/kg bw/day. Hyperplasia of the forestomach and dilatation of hair follicles were observed in males at 10 and 30 mg/kg bw/day and females at 30 mg/kg bw/day. The NOEL was 0.1 mg/kg bw/day for mice.

In the 13-week studies, rats received TCAOB in corn oil at 0, 0.1, 1, 3, 10 or 30 mg/kg bw/day by gavage. Deaths occurred in 10/10 males (from weeks 6 to 9) and 7/10 females (weeks 8 to 12) at 30 mg/kg bw/day. The causes of deaths were not specified, and lower body weight gain or weight loss, pale extremities and eyes, ruffled fur, thinness and lethargy were observed prior to deaths. Decreased body weight gains were observed in males from 3 mg/kg bw/day and females from 10 mg/kg bw/day. Decreased thymus weights accompanied by thymic atrophy, and increased liver weights were observed at 1 mg/kg bw/day and above. Hepatic cytochrome P(450)1A staining was increased in males at 1 and 3 mg/kg bw/day and in females at 3 mg/kg bw/day and above. All treated groups showed a responsive anaemia and decreases in platelet counts, a sharp decrease in circulating thyroxine levels accompanied by marginally increased thyroid-stimulating hormone levels, as well as a decrease in epididymal spermatozoal motility, increased incidences of centrilobular degeneration and haematopoietic cell proliferation in the liver, chronic active inflammation of the lung vasculature and haematopoietic cell proliferation in the spleen, increased incidence and/or severity of cardiomyopathy and nephropathy. The oestrous cycle length was increased in females at 10 mg/kg bw/day. There was a higher incidence of hyperplasia of the forestomach in males from 3 mg/kg bw/day and in females from 10 mg/kg bw/day. No NOEL was established in rats.

TCAOB was not mutagenic in *S. typhimurium* strain TA97, TA98, TA100 or TA1535 with or without S9. It did not induce significant increases in micronucleated erythrocytes in a 3-exposure male mouse bone marrow micronucleus test up to 200 mg/kg bw, but results of a 13-week peripheral blood micronucleus test in mice at 10 and 30 mg/kg bw/day were positive.

8.2 Hazard Assessment

The toxicological database for diuron is extensive and consists of unpublished reports generated by industry, as well as a range of published studies including NTP technical reports for TCAB and TCAOB. The data package is adequate to assess the potential hazard of diuron to humans. There were no studies conducted on any diuron products registered in Australia.

Metabolism studies in rats indicated that diuron is rapidly and completely absorbed, and subsequently metabolised within 24 - 48 hours. The metabolism of diuron was extensive and

involved in N-oxidation, some ring hydroxylation, demethylation, dechlorination, and conjugation to sulphate and glycuronic acid. The metabolic pathways in rats, cows and humans were similar. Diuron and its metabolites were almost completely eliminated, mainly by the renal route. A comparison of excretion following single and repeat dose(s) at low and high doses showed no evidence of accumulation. Radioactive residues in the tissues of rats were low at the time of sacrifice (4 days), and the highest residue levels were found in the blood, liver and kidneys.

Diuron has low acute toxicity by the oral dermal or inhalation exposure routes. Diuron is neither a skin irritation nor a skin sensitiser, but it is a slight eye irritant owing to its crystalline form at room temperature.

Effects involving haemoglobin were the primary toxicological target of diuron administration. Erythrocyte damage resulting in haemolytic anaemia (depressed erythrocyte counts, reduced MCHC and elevated MCV values, low haematocrit figures, reduced haemoglobin values, increased spleen and liver weights, abnormal blood pigment, Heinz bodies, and haemosiderin in the spleen, liver and kidneys) and compensatory haematopoiesis (in the spleen and bone marrow) were observed. Consistent observations of erythrocytic regeneration were obtained in chronic toxicity studies in rats, mice and dogs. Many of these haematological changes were shown to occur following a duration of oral exposure as short as 2 weeks in the rat, the most sensitive species. Based on the time course and the nature of the haematological effects, it is anticipated that these changes could be induced by a single dose of diuron. Hence, this endpoint is considered suitable to establish an ARfD.

Abnormal blood pigments induced by diuron were associated with the formation of methemoglobin and sulphemoglobin (Stevens JT & Sumner DD, 1991; Wang et al, 1992). Methemoglobin is formed when the iron atom in haemoglobin is oxidised from the ferrous to the ferric state by the superoxide ion. The oxidative change also causes denaturation of haemoglobin to form insoluble deposits that attach to the red cell membrane (formation of Heinz bodies). The haemotoxic effect of diuron has been attributed to aromatic amine metabolites including 3,4-dichloroaniline (Wang et al, 1992).

Unlike linuron, a structural analogue of diuron that induced testicular adenomas and adverse effects on the developing male rat reproductive system, diuron effects were limited to reduced pup body weights and delayed ossification of the vertebrae and sternebrae in rats. The foetal effects occurred at the maternal toxic dose of diuron, and accompanied by the poor nutritional state of the dams (reduced food consumption and body weight gain) during pregnancy and lactation. No foetal malformations or changes of other developmental parameters were associated with diuron. Diuron was not considered as to be a reproduction / developmental toxicant.

A concern regarding the carcinogenicity potential of diuron was the finding of an increased incidence of urinary bladder carcinomas and kidney carcinomas in the Wistar rat. After 24-month dosing with diuron at 2500 ppm, a higher incidence of urinary bladder transitional epithelial carcinomas, and occasional squamous cell carcinomas was found in both sexes (males: 67% *vs* 2%; females: 22% *vs* 0 in control), as well as papillomas in male rats (benign neoplasias, 6% *vs* 0%). Hyperplasia of the urothelium which may be regarded as preliminary stages of the carcinomas occurred at 2500 ppm after 12-month dosing, and at 250 and 2500 ppm (but not 25 ppm) after 24-month dosing. A 6-month rat dietary study (2- to 26-week treatment) (Schmidt & Karbe, 1986b) with special attention to urothelial alterations demonstrated the chronology of neoplasm development and the reversibility of precancerous

alterations of the urothelium. More pronounced hyperplasia of the epithelia developed in distinctly greater number of rats treated with 2500 ppm diuron for 4 weeks and longer, and the incidence and degree increased with the duration of treatment. An increase in thickness of the bladder wall which appeared to derive from an increase in the subepithelial connective tissue appeared from 2-week treatment onwards. These changes were partially reversed during a recovery period of 4 or 8 weeks. The presence of a no effect level at 25 ppm for the urinary bladder hyperplasia and neoplasms (Schmidt & Karbe, 1986a) suggests a threshold for these changes.

The sponsor has proposed that the hyperplasia and neoplasm effect of diuron on rat bladder epithelium was possibly mediated by alkaline urinary pH that was resulted from a specific rat diet (Altromin 1321 diet) uniquely used by the testing laboratory. Under this diet, a relatively high incidence of urinary bladder hyperplasia (>20%) also occurred in control group of the 2-year rat study. Furthermore, it is noteworthy that positive results were also observed in an UDS test with urinary bladder epithelial cells from rats treated with diuron and fed with Altromin 1321, in spite of negative responses from a battery of *in vitro* and *in vivo* genotoxic studies including an *in vitro* UDS test on rat hepatocytes.

Similar hyperplasia and carcinomas in the rat urinary bladder epithelium have been reported on another well studied, but chemically unrelated, insecticide propoxur. Propoxur (8000 ppm) was tumorigenic to the rat urinary bladder when administered in Altromin 1321 diet, but not when administered in a casein-based semi-synthetic diet. This difference is believed to arise from urinary pH, which is slightly alkaline in rats (approximate pH 8) consuming Altromin 1321 but acidic in rats fed a casein-based diet. Cohen SM et al (1994) have demonstrated that a reduction of 1 pH unit or more for urine pH is enough to inhibit urothelial proliferation and tumour formation in rats treated with propoxur. Thus, the urothelial effects of propoxur in the rat are dependent on high urinary pH and high administered doses.

There is no direct evidence to measure the influence of diet on the urinary bladder effects of diuron. Although, as pointed out by the sponsor, the hyperplasia and carcinomas were not observed in the urinary bladder epithelium in another 2-year rat study fed with a standard rat diet (rather than Altromin 1321) (Hodge & Downs, 1964). The results of this study were considered unreliable for regulatory purposes due to the respiratory infection rates that induced high mortality rates. A parallel *in vivo* UDS study with diuron on rats fed with normal diet was not available. Nevertheless, it is reasonable to accept the argument that carcinogenic and genotoxic effects observed in rat urinary bladder epithelium are probably associated with some specific metabolite(s) of diuron in alkalised rat urine. In addition, diuron-induced urinary bladder carcinomas were not observed in the 2-year mice feeding study, although epithelial hyperplasia, thickened mucosa of urinary bladder with oedema developed in female mice.

Based on available observations, the development of urothelial tumours appears to be a multistage process, involving hyperplasia progressing through to tumours if diuron exposure is not stopped. The NOEL was 25 ppm for urothelial hyperplasia and 250 ppm for tumours. In other words, the proliferative histological response to diuron that leads to tumour formation occurs only when exposure is continuous. Its reversibility after withdrawal from exposure is consistent with a mitogenic mode of action. A mitogen is not DNA reactive, and not cytolethal at carcinogenic doses. It induces direct mitogenic stimulation of growth, causes mutations secondary to cell proliferation and may provide a selective growth advantage to spontaneously initiated precancerous cells. Initiation and promotion events occurred secondary to a variety of associated activities such as regenerative cell proliferation

(Butterworth et al, 1995). Hence, the hyperplasia induced by diuron appears to result from a direct mitogenic effect of the chemical or its metabolite on the urothelium due to a chronic local stimulation by the alkaline urine, rather than from genotoxicity of the chemical and subsequent regeneration.

In summary, diuron is considered unlikely to be a genotoxic carcinogen. The development of urinary carcinoma in rats appeared to be dependent on long term administration of high doses of diuron and a specific rat diet (Altromin 1321 diet) which leads to an alkaline urinary pH. These two factors have little relevance to likely human exposure. Hence, it is considered that at anticipated human exposure levels tumour induction in humans is unlikely.

Since the residues of diuron are not found in the diet for Australian, exposure to diuron by the general population through food is not a concern. The main human exposures are likely to be to agricultural workers, with some exposure to the public through contact with ornamental plants and landscaping. Given that diuron has poor dermal absorption characteristics, the occupational risk is considered to be low.

8.3 DOSE Levels Relevant For Risk Assessment

To identify the lowest NOELs for the establishment of an ADI and ARfD, a summary of the NOELs determined in those studies considered adequate for regulatory purposes are shown in Table 18.

The current Australian ADI for diuron is 0.006 mg/kg bw/day. It was established in 1987 using the NOEL of 0.6 mg/kg bw/day (25 ppm) in a 2-year dog dietary study (Hodge & Downs, 1964) for the abnormal blood pigments at the next higher dose (125 ppm, approximate 3 mg/kg bw/day), and using a 100-fold safety factor. However, in the current submission, a more recent 1-year dog study (Hoffmann & Schilde, 1985) indicates a higher NOEL of 1.25 mg/kg bw/day (50 ppm) for haemosiderin deposition in the spleen and kidneys.

Another 2-year rat study (Schmidt, 1985) was evaluated as part of the current submission. In the absence of a NOEL, this study established a LOEL of 1.0/1.7 mg/kg bw/day (25 ppm) for males/females due to haematological changes. A supplementary 6-month rat dietary study (Schmidt & Karbe, 1986) specifically designed to monitor for haematological effects at low doses gave a NOEL of 0.7/0.8 mg/kg bw/day (10 ppm) for the reduced haemoglobin concentration and increased reticulocyte counts. Since the rat was the most sensitive species with the lowest effect level of 1 – 2 mg/kg bw/day, an ADI of 0.007 mg/kg bw/day can be established using the NOEL of 0.7 mg/kg bw/day and a 100-fold safety factor.

The ARfD has not been established previously. In single dose/short term studies, above haematological changes as the most sensitive endpoints in rats occurred following a duration of oral exposure as short as 2 weeks (at 2500 ppm, Schmidt & Karbe, 1986b) or 4 weeks (at 25 ppm, Schmidt & Karbe, 1986a), the shortest term sampled for testing in the study. Based on the nature and the time course of haemolysis, it is reasonable to anticipate that the effect could be induced by a single oral dose of diuron exposure, although no such tests have been conducted. Hence, this endpoint is suitable to be used for setting an ARfD. An ARfD of 0.007 mg/kg bw/day is hence established using the NOEL of 0.7 mg/kg bw/day in the 6-month rat dietary study and a 100-fold safety factor.

Table 18: Studies relevant for the establishment of an ADI and ARfD

Species	NOEL (mg/kg bw/d)	LOEL (mg/kg bw/d)	Toxicological Endpoint	Reference
Subchronic Studies				
Rats 13-wk, po gavage	Not established	75	Haemolytic anaemia: reduced RBC, Hgb and Hct, and increased MCV, blood bilirubin and urea nitrogen.	Wandrag (1996a) [QA/ GLP]
Rats 6-month dietary	0.7/0.8 (10 ppm) for M/F	1.6/1.8 (25 ppm) for M/F	Reduced haemoglobin (females) and increased reticulocyte counts	Schmidt & Karbe (1986a) [QA/GLP]
Chronic studies				
Mice 2-y dietary	51/78 (250 ppm) for M/F	640/876 (2500 ppm) for M/F	Increased leucocytes, blood ALT and bilirubin, haemosiderin accumulation in the liver, spleen and kidneys, urothelium hyperplasia, neoplasia in ovary and mammary.	Eiben et al (1990) [QA/ GLP]
Rats 2-y dietary	Not established.	25 ppm (1.0/1.7 for M/F)	Changes in haematology, clinical chemistry, organ weights, and pathology of spleen, bone marrow, urothelium hyperplasia and neoplasia in the urinary bladder.	Schmidt (1985) [QA/ GLP]
Dogs 1-y dietary	1.25 (50 ppm)	7.5 (300 ppm)	Haemosiderin accumulation in the spleen and kidneys.	Hoffmann & Schilde (1985) [QA/ GLP]
Dogs 2-y dietary	0.6 (25 ppm)	3.1 (125 ppm)	Haematological changes and blood pigments.	Hodge & Downs (1964)
Reproduction studies				
Rats 2-generation	15/16 (250 ppm) for M/F	101/116 (1750 ppm for M/F	General toxicity: lower food consumption and body weight gain and fibroadenoma in the mammary gland	Cook (1990) [QA/ GLP]
	101/116 (1750 ppm for M/F	-	No reproduction toxicity in all dose levels tested.	
	15/16 (250 ppm) for M/F	101/116 (1750 ppm for M/F	Foetal/pup toxicity: lower pup weight.	
Developmental studies				
Rats po gavage	16	80	Maternal toxicity: lower food consumption and body weight gain.	Dearlove (1986a) [QA/ GLP]
	80	400	Developmental toxicity: lower pup weight and developmental retardation of skeleton.	
Rabbits po gavage	10	50	Maternal toxicity: lower food consumption and body weight gain.	Dearlove (1986b) [QA/ GLP]
	50	-	No developmental toxicity at all dose levels tested.	

QA = quality assured study; GLP = statement of compliance with principles of good laboratory practice

8.4 Human exposure

8.4.1 Residues in food and drinking water

Products containing diuron are intended to be used in agricultural food and non-food crops, ornamental trees, flowers, and shrubs, paints and coatings, ornamental fish ponds, and catfish production, some industrial and residential sites including ponds, aquariums and paints.

In the MRL Standard for Maximum Residue Limits in Food and Animal Feedstuff (APVMA, November 2004), MRL of diuron is defined as "the sum of diuron and 3,4-dichloroaniline, expressed as diuron". MRLs for diuron have been established for cattle meat, cattle milk, edible offal of cattle, cereal grains, asparagus, field pea (dry), fruits, pineapple, sugar cane, oilseed and crude cotton seed oil, as well as primary feed commodities for animals.

The 19th and 20th Australian Total Diet Surveys (ATDS) (2002 and 2003, respectively) performed under the auspices of Food Standard Australia New Zealand (FSANZ) detected no diuron in any of the food surveyed. Furthermore, the Department of Agriculture, Fisheries and Forestry's Australia National Residue Survey which monitor the residues found in food destined for human consumption do not include diuron, indicating no detectable residues of diuron in sampled commodities. Therefore, the dietary exposure for the population was estimated to be nil as the concentration of diuron was less than the limit of detection.

Current Health Value of diuron is established at 0.03 mg/L which is based on 10% of ADI. According to Australian Drinking Water Guidelines (NHMRC, 1996), diuron and some other chemicals have either been detected on occasions in Australian drinking water or their likely use would indicate that they may occasionally be detected.

8.5 Consideration of the active constituent

8.5.1 Approval Status

There is no objection on toxicological grounds to the ongoing approval of currently approved diuron active constituent.

8.5.2 Impurity Limits

An integral part of the safety assessment of an active constituent is a consideration of the chemical composition of the material. Technical-grade active constituents will contain measurable levels of impurities, which can arise during manufacture and/or from subsequent degradation during storage. The chemical identity of these impurities is generally well characterised. The impurities present in the technical-grade material are usually of no particular concern since health standards are established on the basis of toxicology studies conducted using the mixture. However, for those which have high acute toxicity, genotoxicity or teratogenic potential, concentration limits need to be set, so that the toxicological profile of the technical-grade active constituent does not appreciably alter in the event of slight changes in the proportions of the impurities.

The current minimum compositional standard for active constituent diuron and the maximum for impurities are shown in Table 19.

Table 19: Current minimum compositional standard for active constituent diuron and the maximum for impurities.

Chemical	Standard
Diuron	Minimum 950 g/kg
3,3',4,4'-tetrachloroazobenzene	Maximum 20 mg/kg
3,3',4,4'-tetrachloroazoxybenzene	Maximum 2 mg/kg

The two impurities are formed as synthesis by-products in the early stage of manufacture of diuron, linuron and propanil (or present in 3,4-dichlorophenyl isocyanate), and also formed from the degradation of chloranilide herbicides and by the photolysis and biolysis of 3,4-dichloroaniline.

The maximum impurity levels for the active constituent diuron were set by Pesticides and Agricultural Chemical Committee in 1986. Although no detailed record on the toxicological basis on which the standard for the impurities was established, the major concern at the time was likely the genotoxicity/carcinogenicity potential of diuron. Urinary bladder tumours were observed in the 2-year rat study with diuron, the mechanism(s) were not extensively explored at the time, and its relevance to the impurities was uncertain. TCAB and TCAOB were chemically derived from azobenzene and azoxybenzene, and structurally resemble to 2,3,7,8-tetrachlorodibenzo-p-dioxin. The latter chemicals, in particular chlorinated dioxins, were generally considered to be environmental carcinogens. Hence, the maximum levels of TCAB and TCAOB for the active constituent diuron were probably established to limit/reduce the potential genotoxicity/carcinogenicity.

A toxicity profile for TCAB and TCAOB is now available (US National Toxicology Program). TCAB has low oral toxicity but moderated inhalational toxicity. Although acute toxicity data for TCAOB (LT50 & LC50) are not available, high mortality rate occurred following treatment with TCAOB 30 mg/kg bw/day in corn oil (as solvent) in the 13-week rat study (all males, 7/10 females, the deaths occurred from week 6, after an accumulated dose of approximate 1200 mg/kg bw). The causes of death were not specified in the report, and they were likely related to severe hemotoxicity and liver toxicity.

In the 16-day and 13-week rat and mouse studies, both chemicals caused typical dioxin-like effects, such as thymic atrophy, decreased body weight gains, increased liver weights, induction of hepatic cytochrome P(450)1A, a marked decrease in circulating thyroxine concentrations even at the lowest dose (0.1 mg/kg bw/day), a decrease in epididymal spermatozoal concentration in mice, hematopoietic effects, hyperplasia of the forestomach. However, both TCAB and TCAOB are six to two orders of magnitude less potent than 2,3,7,8-tetrachlorodibenzo-p-dioxin.

Both TCAB and TCAOB were essentially negative in an Ames test, and a micronuclei test on mice bone marrow erythrocytes following 3-day ip exposure at up to 200 mg/kg bw/day. However, both chemicals induced micronucleated mice peripheral erythrocytes after 13-week exposure with lower doses (10 and 30 mg/kg bw/day). The discordance between the short- and long-term micronucles test results has also been observed with other chemicals (phenolphthalein, salicylazosulfapyridine and diisopropylcarbodiimide). Furthermore, TCAB-induced DNA damage was observed in primary rat hepatocytes, but only after pre-treatment with hepatic mixed-function oxidase inducers (Shaddock et al, 1989). Hence, although certain metabolism requirements or total accumulated doses may be essential for the positive results, the concern on the potential genotoxicity / carcinogenicity of TCAB or

TCAOB to humans can not be totally ignored, especially no chronic toxicity / carcinogenicity and reproduction / developmental studies have been conducted with TCAB and TCAOB.

Based on the present review, diuron has low acute toxicity and low potential for irritation/sensitisation. It is neither a reproduction / developmental toxicant, nor a genotoxigen. Development of urinary bladder carcinoma following long term administration of a high dose of diuron to rats under the specific dietary condition does not cause significant concerns on carcinogenicity potential of diuron in humans. Since both impurities at levels within the maximum limit were present in the diuron active used for all toxicological studies, the risks including carcinogenic potential associated with exposure to diuron containing the impurities would have not been underestimated. However, there is no strong evidence to rule out the possibility that higher levels of TCAB and TCAOB (out of the limit) in the active constituent diuron might increase the risk of genotoxicity/carcinogenicity. Hence, establishing a limit for the impurities is considered to be appropriate since all sources of the active diuron comply with existing levels, and this standard should be retained.

8.5.3 Residue Definition

In the existing MRL Standard for Maximum Residue Limits in Food and Animal Feedstuff (APVMA, November 2004), the residue of diuron is defined as "the sum of diuron and 3,4-dichloroaniline".

3,4-dichloroaniline is used as an intermediate in the manufacture of diuron, and was also a common metabolite of diuron by hydrolysis in both rats and humans. Besides, it is also a main substance converted by diuron polar metabolites in plants and after degradation of diuron in the soil.

Toxicological information for 3,4-dichloroaniline is limited. According to the European Commission CSTEE report (November 2003), the oral LD50 of 3,4-dichloroaniline in rats is around 600 mg/kg bw, and inhalation LC50 ranges from 2800 to 4700 mg/m^3/4h. It appears to be a mild irritant, and a potential skin and respiratory sensitiser. Similar to diuron, the most notable acute toxic effect is methaemoglobinaemia (Guilhermino et al, 1998). It is toxic to the kidneys, liver and urinary bladder of rats with 24 hours after dosing (Valentovic et al, 1997). Repeated doses also caused anaemia, methaemoglobin, haemosiderin and elevated spleen weights in rats following inhalation administration, and in rabbits after dermal exposure. The limited mutagenicity testing produced equivocal results, evidence of the induction of spindle damage was observed in a sister chromatid exchange assay, while other tests including a mocronucleus test were generally negative. No carcinogenicity studies are available. No specific teratogenic effect was observed.

Since 3,4-dichloroaniline is a common metabolite of diuron in both animals and plants, toxicological studies of diuron in animals have adequately covered the potential toxicity of 3,4-dichloroaniline as a metabolite. Furthermore, field trials have shown that the proportion of 3,4-dichloroaniline is relatively low. On this basis, there is no toxicological basis to include 3,4-dichloroaniline in the residue definition.

8.6 Consideration of public health standards

8.6.1 ADI and ARfD considerations

The ADI for humans is the level of intake of a chemical that can be ingested daily over an entire lifetime without appreciable risk to health. It is calculated by dividing the overall NOEL for the most sensitive toxicological endpoint from a suitable study (typically an animal study) by an appropriate safety factor. The magnitude of the safety factor is selected to account for uncertainties in extrapolation of animal data to humans, intraspecies variation, the completeness of the toxicological database and the nature of the potential toxicologically significant effects.

The current Australian ADI for diuron is 0.006 mg/kg bw/day, based on a NOEL of 0.6 mg/kg bw/day in a 2-year dog dietary study for the abnormal blood pigments and using a 100-fold safety factor. An amended ADI of 0.007 is recommended in this review, based on a NOEL of 0.7 mg/kg bw/day in a 6-month rat dietary study for the reduced haemoglobin and increased reticulocytes and using a 100-fold safety factor, this is shown in Table 20.

The ARfD is the estimate of the amount of a substance in food or drinking water, expressed on a milligram per kilogram body weight basis, that can be ingested over a short period of time, usually one meal or one day, without appreciable health risk to the consumer on the basis of all known facts at the time of the evaluation. The ARfD has not been established previously. An ARfD of 0.007 mg/kg bw/day is established based on a NOEL of 0.7 mg/kg bw/day in the 6-month rat dietary study for the reduced haemoglobin and increased reticulocytes and using a 100-fold safety factor.

Table 20: ADI and ARfD for diuron.

ADI: 0.007mg/kg bw/day			
SF	**NOEL (mg/kg bw)**	**Study Details**	**Comments**
100	0.7	A 6-month rat dietary study, based on reduced haemoglobin concentrations and increased reticulocytes at the higher dose.	The NOEL for the rat study was 0.7 mg/kg bw/day.
		Study Citation	**Comments Citation**
		Schmidt WM & Karbe E (1986a). Diuron: Toxicological study with Wistar rats paying special attention to effects on the blood (Administration in Diet for six months). Bayer AG Institute of Toxicology, Wuppertal, Friedrich-Ebert-Strasse 217-333, Western Germany. Report No: 14886 / Du Pont Report No: D/Tox 18.	
ARfD: 0.007 mg/kg bw			
SF	**NOEL (mg/kg bw)**	**Study Details**	**Comments**
100	0.7	A 6-month rat dietary study based on reduced haemoglobin concentrations and increased reticulocytes at the higher dose.	

	Study Citation	Comments Citation
	Schmidt WM & Karbe E (1986a). Diuron: Toxicological study with Wistar rats paying special attention to effects on the blood (Administration in Diet for six months). Bayer AG Institute of Toxicology, Wuppertal, Friedrich-Ebert-Strasse 217-333, Western Germany. Report No: 14886 / Du Pont Report No: D/Tox 18.	

8.6.2 Water Quality Guidelines

Health Values are intended for use by health authorities in managing the health risks associated with inadvertent exposure such as a spill or mis-use of a pesticide. The values are derived so as to limit intake from water alone to about 10% of the ADI, on the assumption that (based on current knowledge) there will be no significant risk to health for an adult weighing 70 kg at a daily water consumption of 2 L over a lifetime. Given that the ADI for diuron is 0.007 mg/kg bw/d, the Health Value may be calculated as:

$$\frac{0.007 \text{ mg/kg bw/d} \times 70 \text{ kg} \times 0.1}{2 \text{ L/d}}$$

$$= 0.0245 \text{ mg/L}$$

Hence, the current Health Value for diuron of 0.03 mg/L is supported.

8.6.3 Poisons Scheduling

Diuron is currently included in Appendix B of the Standard for the Uniform Scheduling of Drugs and Poisons (SUSDP), i.e. a substance considered not to require control by scheduling.

From the variety of acute toxicity studies submitted for this review, the acute oral LD50 of diuron was ranged from 3000 to 9087 mg/kg bw in an aqueous vehicle, while it was more toxic in an oil vehicle (LD50 1017 – 5000 mg/kg bw). However, since diuron active is in a physical state of white crystal, with a high melting point (158^{o}C) and a very low water solubility (42 ppm at 25^{o}C), the actual hazard caused by accidental ingestion will be low. Diuron also has low acute toxicity by the dermal or inhalation exposure route. It is neither a skin irritant nor a skin sensitiser, but is a slight eye irritant. Hence, the current scheduling classification is considered appropriate for diuron.

8.7 References

Agrawal RC, Kumar S & Mehrotra NK (1996). Micronucleus induction by diuron in mouse bone marrow. Toxicology Letters 89: 1-4.

Algate DR et al (1989). General pharmacological evaluation of DCMU. Lab: Huntingdon Research Centre Ltd, PO Box 2, Huntingdon, Cambridgeshire, PE18 6ES, England. Report No: 51579.

Arce GT (1984). Mutagenicity Evaluation of diuron in Salmonella Typhimurium. Lab: E I du Pont de Nemours and Company, Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware, 19714 USA. Report No: 52015.

Arce GT (1985). Assessment of diuron in the in vitro unscheduled DNA synthesis assay in primary rat hepatocytes. Lab: EI du Pont de Nemours and Company, Inc., Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware 19714. Report No: 51553.

Arce GT (1987a). Mutagenicity Evaluation of diuron in Salmonella Typhimurium (Supplement 1). Lab: E I du Pont de Nemours and Company, Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware, 19714 USA. Report No: 51559

Arce GT (1987b). Mutagenicity Evaluation of diuron in Salmonella Typhimurium (revised). Lab: E I du Pont de Nemours and Company, Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware, 19714 USA. Report No: 51558.

Arce GT (2001). Diuron: cancer classification and mechanism of action. Grrifin LLC, 2509 Rocky Ford Road, Valdosta GA 31601. Report No: 52119.

Bakili RA (2000). Primary dermal irritation study of diuron technical 97% in rabbits. Lab: Department of Toxicology, JAI Research Foundation, Valvada – 396 108 Dist. Valsad, Gujarat India.

Bakili RA (2000). Primary eye irritation study of diuron technical 97% in rabbits. Lab: Department of Toxicology, JAI Research Foundation, Valvada – 396 108 Dist. Valsad, Gujarat India.

Bakili RA (1999). Dermal sensitisation study of diuron technical 97% in guinea pigs [Buehler test). Lab: Department of Toxicology, JAI Research Foundation, Valvada – 396 108 Dist. Valsad, Gujarat India.

Beres E (1986a). Acute inhalation toxicity test of diuron technical active ingredient on Wistar rat. NEVIKI Research Institute for Heavy Chemical Industries. Veszprem.

Beres E (1986b). Investigation of oral cumulative toxicity of diuron technical active substance on both sex Wistar rat. NEVIKI Research Institute for Heavy Chemical Industries. Veszprem.

Beres E (1986c). 90 days feeding study of diuron technical active ingredient on Wistar rat. NEVIKI Research Institute for Heavy Chemical Industries. Veszprem.

Boven MV, Laruelle L & Daenens P (1990). HPLC analysis of diuron and metabolites in blood and urine. J Analytical Toxicology 14: 231-234.

Boyd D & Krupa V (1970). Protein-deficient diet and diuron toxicity. J Agr Food Chem. 18:1104-7.

Cook, JC (1990). Reproductive and fertility effects with diuron (IN 14740): Multigeneration reproduction study in rats. Lab: E I du Pont de Nemours and Company, Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware 19714, USA. Report no: 51525 & 51526.

Cox LR (1985). In vivo assay of diuron for chromosome aberrations in rat bone marrow cells. Lab: EI du Pont de Nemours and Company, Inc., Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware 19714. Report No: 51554.

Cox LR (1997a). In vivo assay of diuron for chromosome aberrations in rat bone marrow cells (Revised report). Lab: EI du Pont de Nemours and Company, Inc., Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware 19714. Report No: 51555.

Cox LR (1997b). In vivo assay of diuron for chromosome aberrations in rat bone marrow cells (Revision No 2). Lab: EI du Pont de Nemours and Company, Inc., Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware 19714. Report No: 51556.

Dearlove GE (1986a) Developmental toxicity study of H-16035 administered by gavage to rats. Lab: Argus Research Laboratories, Inc, Horsham, Pennsylvania 19044 USA. Report No: 51545.

Dearlove GE (1987a) Developmental toxicity study of H-16035 administered by gavage to rats (Supplement 1). Lab: Argus Research Laboratories, Inc, Horsham, Pennsylvania 19044 USA. Report No: 51546.

Dearlove GE (1986b). Developmenal toxicity study of H-16035 administered by gavage to New Zealand White rabbits. Lab: Argus research laboratories, Inc., 935 Horsham Road, Horsham, Pennsylvania 19044 USA. Report No. 51547.

Dearlove GE (1987b). Developmenal toxicity study of H-16035 administered by gavage to New Zealand White rabbits (Supplement 1). Lab: Argus research laboratories, Inc., 935 Horsham Road, Horsham, Pennsylvania 19044 USA. Report No. 51548.

Dunsire JP, Johnston AM & Jack L (1994). The metabolism and distribution of [Phenyl(U)-^{14}C] diuron in laying hens (Revision No 1). Lab: Inveresk Research International Tranent, EH33 2NE, Scotland. Sponser: EI DuPond de Nemours and Company, Agricultural Products Department, Experimental Station, Wilmington, Delaware 19880-0402. Report no: AMR 2171-91.

Eiben R (1988). Chronic toxicity study on NMRI mice-supplemental study to investigate haemotoxic effects (administration in the feed for 6 months – Part 1 of 3. Lab: Bayer AG, Institute for Toxicology, Wupprtal , Friedrich-Eblert-Strasse 217-233, West Germany. Report No: 17373.

Eiben R, Laliner G, Karbe E, Suberg H (1990). Diuron: Chronic toxicity and carcinogenicity with NMRI mice (administration in diet for 24 months) Volumes 1-3. Lab: Bayer AG, Institute for Toxicology, Wuppertal, Friedrich-Ebert-Strasse 271-233, West Germany. Report No: 51492, 51493 & 51494.

Eiben R, Laliner G, Karbe E, Suberg H (1994). Volume I of supplementary data supporting the diuron 2-year feeding study in NMRI mice. Lab: EI du Pont de Nemours and Company, Inc., Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware 19714. Report No: 51519.

Faul J (1980). Diuron-evidence of chloracne. Bayer AG, Institute for Toxicology, Medical Department, Dormagen, Germany & Bayer AG, Institute for Toxicology, Wuppertal-Elberfeld, Germany.

Faul J (1982). Statement to Pkt IV/1.2.2 of the BBA application form "Details of effects on man, internal company experience. Bayer AG, Institute for Toxicology, Medical Department, Dormagen, Germany & Bayer AG, Institute for Toxicology, Wuppertal-Elberfeld, Germany.

Geldmacher M, Mallinckrodt V&Schussler F (1971). Zu Stoffwechsel und toxizitat von 1-(3,4-dichlorphenyl)-3,3-dimethylharnstoff (diuron) beim menschen. Arch. Toxikol 27:187-192. Lab: Institut fur Rechtsmedizin der Universitat Erlangen-Nurnberg. Report no: not stated.

Heimann KG (1981). Diuron determination of acute toxicity (LD50). Lab: Bayer AG Institute for Toxicology, Wuppertal-Elberfeld, Germany. Report No: not stated.

Heimann KG (2001). Diuron: assessment of reversibility of urinary bladder effects after chronic oral application to rats. Lab: Bayer AG, Business Group Crop Protection, Development / Registration, D-51368 Leverkusen, Germany.

Heimann KG & Thyssen J (1983). Diuron active ingredient studies on acute toxicity. Lab: Bayer AG Institute for Toxicology, Wuppertal-Elberfeld, Germany. Report No: 11710.

Henry JE (1987). Dermal sensitisation study with IN-14,740-146 in guinea pigs. Lab: EI du Pont de Nemours and Company, Inc., Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware 19714. Report No: 51444.

Herbold B (1984a). Diuron: Salmonella / microsome test to evaluate for potential point mutation. Lab: Bayer AG, Institute of Toxicology, Wuppertal-Elberfeld, Report No: 49237.

Herbold B (1984b). POL test on E Coli to Evaluate for potential DNA damage. Lab: Bayer AG Institute of Toxicology, Wuppertal-Elberfeld. Report No: 49239.

Herbold BA (1983). Micronucleus test on the mouse to evaluate for mutagenic effect. Lab: Bayer A, Indtitute of Toxicology, Wuppertal FRG. Report No: 49238.

Herbold BA (1998a). Diuron: Micronucleus test on the mouse. Lab: Bayer A, Indtitute of Toxicology, Wuppertal FRG. Report No: 49244.

Herbold BA (1998b). On the relevance of the data presented by Agrawal et al. in toxicological letters 89, 1996, 1-4. Entitiled "Microculeus induction by diuron in mouse bone marrow" (Internal memo). Bayer AG, PH-PD Toxicology, Carcinogenicity and Genotoxicity.

Herbold BA (1989). In vitro cytogenetic study with human lymphocytes for the detection of induced clastogenic effects. Lab: Bayer AG, Indtitute of Toxicology, Wuppertal FRG. Report No: 49246.

Herbold B (1985). Diuron: Dominant lethal test on the male mouse to evaluate for mutagenic effect. Lab: Bayer AG, Institute of Toxicology. Study No: 49245

Hodge HC (1964). Short-term and chronic feeding studies with diuron in rats and dogs – An interpretive summary. Department of Pharmacology, University of Rochester, School of Medicine and Dentistry. Report No: 51491.

Hodge H C & Downs W L (1964). Chronic feeding studies of diuron in rats. Department of Pharmacology, University of Rochester School of Medicine and Dentistry, Rochester, New York, USA. Report No: 51486.

Hodge HC & Downs WL (1964). Chronic feeding studies of diuron in dogs. Department of Pharmacology, University of Rochester School of Medicine and Dentistry, Rochester, New York, USA. Report No. 51485.

Hoffmann K & Schilde B (1985). Diuron-chronic toxicity to dogs after oral administration (12-month feeding study). Bayer Ag, Institute for Toxicology, Wuppertal-Elberfedl, Germany. Report No: 51521.

Joshi G (2000). Acute inhalation toxicity study of diuron technical 97% in rats. Lab: Department of Toxicology, JAI Research Foundation, Valvada – 396 108 Dist. Valsad, Gujarat India.

Kamath HG (1998). Genetic toxicology: Salmonella typhimurium reverse mutation assay with Sanachem Diuron Technical. Lab: Toxicology Department, Rallis Research Centre, Rallis India Limited, Peenya II Phase, Bangalore 560 058 India. Sponsor: Sanachem (Pty) Limited, Old Mill Site Canelanda 4341, Durban 400, South Africa. Report No: 48720.

Kalra SK & Chahal KS (1979). Degradation of diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea in cows. Ecotoxicology Environmental Safety 3: 362-368. Report No: 51568

Kaplan AM (1975). Oral LD50 test. Lot No: M-989. Lab: E I du Pont de Nemours and Company Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware, USA. Lab Report No: 51374.

Kasa Z (1986). Study on the acute toxicity of diuron technical active ingredient Vol I. (Acute oral toxicity in rat, acute percutaneous toxicity in rat, acute intra-peritoneal toxicity in rat, acute eye irritant effect in rabbit, acute dermal irritant effect in rabbit). NEVIKI Research Institute for Heavy Chemical Industries. Veszprem.

Kasa Z (1986). Study on the acute toxicity of diuron technical active ingredient Vol II (Acute oral toxicity in mice). NEVIKI Research Institute for Heavy Chemical Industries.

Kasa Z (1986). Acute skin irritation and sensitisation testing of diuron technical active ingredient on guinea pigs. NEVIKI Research Institute for Heavy Chemical Industries. Veszprem.

Kinney LA (1987). Acute inhalation toxicity study with diuron in rats. Code: IN-14740-146. Lab/Sponsor: E I du Pont de Nemours and Company, Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware / Du Pont Agricultural Products, Wilmington, Delaware. Report No: 51468.

Kiss I (1986). Mutagenicity studies on diuron technical active substance. (Ames test, Micronucleus test, test of DNA damage by Sister Chromatid Exchange (SCE) test in CHO-KI cells. Lab: NEVIKI Research Institute for Heavy Chemical Industries. Veszprem.

Klein W (1986). Induction of and effect on UDS by test substance diuron. Lab: Austrian Research Center, Seibersdorf, Ges m b H A-2444, Seibersdorf. Report No: 49240.

Kurinnyi AI (1977). The mutagenicity of certain pesticides – derivatives of urea, carbamic and thiocarbamic acids. Cytology and Genetics 11: 62-64.

Madison WA (1983) Acute dermal toxicity – Method, summary, pathology. Primary dermal irritation – Method, summary. Primary eye irritation – Method, summary. Lot: 306202. Lab/Sponsor: Hazleton Raltech, Inc. Madison WI 53707. Report No: 11845.

Malek DE (1997). Volume 2 of Supplementary data supporting the diuron 2-year feeding study in rats. Lab: EI du Pont de Nemours and Compan, DuPont Agricultural Products, Barley Mill Plaza, Wilmington DE 19880-0038, USA. Report No: 51484.

Malek DE (1997). Cancer hazard characterization of diuron. EI du Pont de Nemours and Company, DuPont Agricultural Products, Barley Mill Plaza, Wilmington, Delaware 19880-0038 USA. Report No: 51520.

McKenzie SA (1992). Repeated dose dermal toxicity: 21-day study with DPX-14740-166 (diuron) in rabbits (revised No 1). Lab: Du Pont Agricultural Products, E I du Pont de Nemours and Company, Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware 19714. Report No: 51541.

Mihail D-BF & Schilde B (1984). Diuron subacute dermal toxicity study on rabbits. Lab: Institute of Toxicology, Bayer AG, Woppertal-Elberfeld.. Report-no. 12360. Study No: T3016060. Study Duration: June – July 1983.

Morrow RW (1976). Acute skin absorption on rabbits – ALD. Lot No: M-989. Lab: E I du Pont de Nemours and Company Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware, USA. Report No: 51381.

Morrow RW (1976). Skin acnegenesis (Dow method). Lab: E I du Pont de Nemours and Company, Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware, USA. Report No: 51437.

Needour C (1988). Response to CDFA's review of the diuron chronic rat study (Position paper). Report No: 51480.

Oellrich W (2001). Diuron – Summary of the toxicological and metabolism studies on the active substance. Lab: Bayer AG, Agrochemical Centre Monheim, D-51368 Leverkusen & Griffin (Europe) SA, Minervatstraat 8, B-1930 Zaventem.

Pauluhn J (1986). Diuron: Study for subacute inhalation toxicity to the rat (aerosol exposure 15 x 6 hours). Lab: Bayer AG, Institute for Toxicology, Wuppertal, Friedrich-Ebert-Strasse 217-233, West Germany.

Pauluhn J (1986b). Diuron: Study for subacute inhalation toxicity to the rat (aerosol exposure for 4 and 8 weeks). Lab: Bayer AG, Institute for Toxicology, Wuppertal-Elbertfelf. Report No: 14603.

Pauluhn J & Eben D-C A (1986). The concentration of diuron and its representative metabolites in the urine of male and female rats during a subacute inhalation study over eight weeks. Lab: Bayer AG, Fachbereich Toxikologie. Report No. 14754.

Rajwani LS (1999). Salmonella typhimurium reverse mutation assay of diuron technical. Lab: Microbiology Section, Department of Toxicology, JAI Research Foundation, Valvada – 396 108, Dist. Valsad Gujarat India. Sponsor: Ancom Crop Care Sdn. Bhd., 102 Block A, Phileo Damansara 1, Jalan 16/11, 46350 Petaling Jaya, Selangor Darul Ehsan, Malaysia.

Rana MD (1999). Acute dermal toxicity study of diuron technical 97% in rats. Lab: Department of Toxicology, JAI Research Foundation, Valvada – 396 108 Dist. Valsad, Gujarat India.

Rana MD (1999). Acute oral toxicity study of diuron technical 97% in rats. Lab: Department of Toxicology, JAI Research Foundation, Valvada – 396 108 Dist. Valsad, Gujarat India.

Reynolds VL (1992a). Mutagenicity testing of IN-15926-6 in the Salmonella Typhimurium plate assay. Lab: E I du Pont de Nemours and Company, Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware, 19714 USA. Report No: 51561.

Reynolds VL (1992b). Mutagenicity testing of DPX-12,402-46 in the Salmonella typhimurium plate assay. Lab: E I du Pont de Nemours and Company, Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware, 19714 USA. Report No: 51561.

Reynolds VL (1992c). Mutagenicity testing of IN-12894-5 in the Salmonella typhimurium plate incorporation assay. Lab: E I du Pont de Nemours and Company, Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware, 19714 USA. Report No: 51563.

Rossberg WM (1995). Volume 1 of Supplementary data supporting the diuron 2-year feeding study in rats. Lab: Bayer AG Institute of Toxicology, Wuppertal, Friedrich-Ebert-Strasse 217-333, West Germany. Report No: 51481.

Rossberg WM & Wirnitzer U (1994). Diuron: Study for chronic toxicity and cancerogenicity with Wistar rats (Administration in diet for up to two years, Addendum to Bayer-report no. 13962). Lab: Bayer AG Institute of Toxicology, Wuppertal, Friedrich-Ebert-Strasse 217-333, West Germany. Report No: 6548.

Rossberg WM & Wirnitzer U (1994). Diuron: Study for chronic toxicity and cancerogenicity with Wistar rats (Administration in diet for up to two years, Second addendum to Bayer-report no. 13962 dated October 10, 1985). Lab: Bayer AG Institute of Toxicology, Wuppertal, Friedrich-Ebert-Strasse 217-333, West Germany. Report No: 6548.

Rossberg WM & Wirnitzer U (1995). Study for chronic toxicity and cancerogenicity with Wistar rats (Addendum 1). Lab: Bayer AG Institute of Toxicology, Wuppertal, Friedrich-Ebert-Strasse 217-333, West Germany. Report No: 51482.

Rossberg WM & Eiben R (1997). Diuron: Study for chronic toxicity and cancerogenity with Wistar rats (Administration in diet for up to two years – Second amendment). Lab: Bayer AG Institute of Toxicology, Wuppertal, Friedrich-Ebert-Strasse 217-333, West Germany. Report No: 51483.

Sarver JW (1992). Approximate lethal dose (ALD) of IN-12894-5 in rats. Medical Research No: 4581-951. Lab/Sponsor: E I du Pont de Nemours and Company, Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware / Du Pont Agricultural Products, Wilmington, Delaware. Report No: 51375.

Sarver JW (1992). Approximate lethal dose (ALD) of IN-12894-6 in rats. Medical Research No: 4581-952. Lab/Sponsor: E I du Pont de Nemours and Company, Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware / Du Pont Agricultural Products, Wilmington, Delaware. Report No: 51376.

Scarisbrick DA & Martin JW (1981). Biochemical changes associated with chloracne in workers exposed to tetrachlorazobenzene and tetrachlorazoxybenzene. J Soc Occup Med 31: 158-163.

Schmidt WM (1985). Diuron: Study for chronic toxicity and carcinogenicity with Wistar rats (Administration in diet for up to two years). Lab: Bayer AG Institute of Toxicology, Wuppertal, Friedrich-Ebert-Strasse 217-333, West Germany. Report No: 51470 & 51471.

Schmidt WM & Karbe E (1986). Diuron: Toxicological study with Wistar rats paying special attention to effects on the blood (Administration in Diet for six months). Lab: Bayer AG Institute of Toxicology, Wuppertal, Friedrich-Dbert-Strasse 217-333, Western Germany. Report No: 51536 & 51540.

Schmidt WM & Karbe E (1986b). Study for toxicity to Wistar rats with special attention to urothelial alterations (Administration in Diet for 2, 4, 12 and 26 weeks with recovery). Lab: Institute of Toxicology, Bayer AG, Wuppertal, Friedrich-Dbert-Strasse 217-333, Western Germany. Report No: 51524.

Schneider PW (1984). "Karmex" toxicity summary. Report No: 51574.

Seiler JP (1978). Herbicidal phenylalkylureas as possible mutagens. I. Mutagenicity tests with some urea herbicides. Mutation Research 58: 353-359.

Sharp VW (1997a). Acute eye irritation/corrosion test with Sanachem diuron technical in rabbits. Lab: Biocon Research (Pty) Ltd, Pretoria 0001, South Africa. GLP/QA: yes. Guideline: OECD 405. Report No: 48714.

Sharp VW (1997b) Acute dermal irritation/corrosion test with Sanachem diuron technical in rabbits. Lab: Biocon Research (Pty) Ltd, Pretoria 0001, South Africa. Report No: 48713.

Sharp VW (1997c). Contact hypersensitivity to Sanachem Diuron Technical in albino guinea pigs (Magnusson Kligman Maximization Test). Lab: Biocon Research (Pty) Ltd, Pretoria 0001, South Africa. Report No: 48712.

Sherman H (1962). Ninety-day feeding study with 3-(3,4-dichlorophenyl)-1,1-dimethyl urea (diuron). Griffin L.L.C., 2509 Rocky Ford Road, Valdosta, GA 31601, USA. Medical Research Project Nos: MR-631 & MR-10. Report-no.97-62. Griffin Cooperation, P.O. Box 1847, and Rocky Ford Road, Valdosta, GA 31603-1847, USA. Report No: 51533.

Shivaram S (1998). Genetic toxicology: in vitro mammalian cell gene mutation test with Smachem Diuron Technical. Lab: Toxicology Department, Rallis Research Centre, Rallis India Limited, Peenya II Phase, Bangalore 560 058 India. Sponsor: Sanachem (Pty) Limited, Old Mill Site Canelanda 4341, Durban 400, South Africa. GLP/QA: yes. Report No: 48719.

Shivaram S (1999). Genetic toxicology: in vitro mammalian cytogenetic test with Smachem Diuron Technical. Lab: Toxicology Department, Rallis Research Centre, Rallis India Limited, Peenya II Phase, Bangalore 560 058 India. Sponsor: Sanachem (Pty) Limited, Old Mill Site Canelanda 4341, Durban 400, South Africa. Report No: 48721.

Torrington KG (1983). Letters to the Editor. J Occupational Medicine 25: 354-356.

Trochimowicz (1976). Two-week inhalation toxicity study on TCAB. Lab: E I du Pont de Nemours and Company, Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware, USA. Report No: 51438.

Trochimowicz HJ (1976). Approximate lethal concentration (ALC). Lab: E I du Pont de Nemours and Company, Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware, USA. Report No: 51467.

Tronnier H (1983). Diuron: Expertise by consultant dermatologist on testing for phototoxicity in test subjects. Report No: R 2543.

Ullman DV & Choy WN (1985). Mutagenicity evaluation of diuron in the CHO/HPRT assay. Lab: EI du Pont de Nemours and Company, Inc., Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware 19714. Report No: 51557.

Ullman DV (1985). In vivo assay of diuron for chromosome aberrations in rat bone marrow cells. Lab: EI du Pont de Nemours and Company, Inc., Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware 19714. Report No: 51554.

Van Pelt CS & Hoffman K (1993). Supplement to diuron chronic toxicity to dogs after oral administration (12-month feeding study). Lab: Bayer Ag, Institute for Toxicology, Wuppertal-Elberfeld, Germany. Report No: 51522.

Verheij ER et al (1989). Identification of diuron and four of its metabolites in human post-mortem plasma and urine by LC/MS with a moving-belt interface. J Anal Toxi 13: 8-12.

Volkner W (1987a). Chromosome aberration test in bone marrow cells of the Chinese hamster with diuron. Lab: CCR Cytotest Cell Research GmbH & Co. KG, Nieder-Ramstadter Stra□e 146. D-6100 Darmstadt GRG. Report No: 49241.

Volkner W (1987a). Sister chromatid exchange assay in bone marrow cells of the Chinese hamster with diuron. Lab: CCR Cytotest Cell Research GmbH & Co. KG, Nieder-Ramstadter Stra□e 146. D-6100 Darmstadt GRG. Report No: 49242.

Volkner W (1988). Mouse germ-cell cytogenetic assay with diuron. Lab: CCR Cytotest Cell Research GmbH & Co. KG, Nieder-Ramstadter Stra□e 146. D-6100 Darmstadt GRG. Report No: 49243.

Vos JG, Krajnc EI, Beekhof PK and van Logten MJ (1983). Methods for testing immune effects of toxic chemicals: Evaluation of the immunotoxicity of various pesticides in the rats. In Pestic Chem: Human Welfare Environment, Proc. Int. Congr. Pestic Chem., 5th, 3: 497-504.

Wandrag S (1993). Oral and Dermal limit test with Sanachem Sanuron (Diuron technical) in rats. Batch: 292-03-93. Report No: 1. Lab/Sponsor: Roodeplaat Research Laboratories (Pty) / Sanachem (Pty) Ltd. Ltd. Report No: 48715.

Wandrag S (1996a). Subchronic oral toxicity – rodent: 90-day study with Sanachem diuron technical in rats. Lab: Biocon Research (Pty) Ltd, Pretoria, South Africa. Sponsor: Sanachem (Pty) Ltd, Durban, South Africa. Report No: 48716.

Wandrag S (1996b). Subchronic dermal toxicity – rodent: 90-day study with Sanachem diuron technical in rats. Lab: Biocom Research (Pty) Ltd, Pretoria, South Africa. Sponsor: Sanachem (Pty) Ltd, Durban, South Africa. Report No: 48717.

Weber H & Abbink J (1988). [Phenyl-UL-^{14}C]-diuron: Investigation of the biokinetic behaviour in the rat. Lab: Institute for Metabolism Research, Metabolism Animal, PF-Zentrum Monheim, Building 6670, 5090 Leverkusen-Bayerwerk. Report No: 51571.

Wu D (1996). Absorption, distribution, metabolism and elimination of [^{14}C]-diuron in rats. Lab: XenoBiotic Laboratories, Inc. Plainsvoro NJ 08536 & EI du Pont de Nemours and Company Experimental Station, Wilmington DE 19880-0402. DuPont Report No: AMR 3145-94.

Xavier R & Pereira G (2001). Medical surveillance from manufacturing site of diuron. Bayer AG, Agrochemical Centre Monheim, PF-E/REG, Gebaude 6100, D-51368 Leverkusen & Griffin (Europe) SA, Minervatstraat 8, B-1930 Zaventem.

Zapp Jr (1970). Skin primary irritation and sensitisation test in guinea pigs. Lab: E I du Pont de Nemours and Company, Haskell Laboratory for Toxicology and Industrial Medicine, Newark, Delaware, USA. Report No: 51443.

8.8 Toxicological Abbreviations

Time		Weight	
d	Day	**bw**	Body weight
h	Hour	**g**	Gram
min	Minute	**kg**	Kilogram
mo	Month	**µg**	Microgram
wk	Week	**mg**	Milligram
s	Second	**ng**	Nanogram
yr	Year	**wt**	Weight

Length		Dosing	
cm	Centimetre	**id**	Intradermal
m	Metre	**im**	Intramuscular
µm	Micrometre	**inh**	Inhalation
mm	Millimetre	**ip**	Intraperitoneal
nm	Nanometre	**iv**	Intravenous
		po	Oral
		sc	Subcutaneous
		mg/kg bw/d	mg/kg bodyweight/day

Volume		Concentration	
L	Litre	**M**	Molar
mL	Millilitre	**ppb**	Parts per billion
µL	Microlitre	**ppm**	Parts per million

Clinical chemistry, haematology

A/G	Albumin/globulin ratio
ALT	Alanine aminotransferase (SGPT)
AP	Alkaline phosphatase
AST	Aspartate aminotransferase (SGOT)
BUN	Blood urea nitrogen
ChE	Cholinesterase
CPK	Creatine phosphatase (phosphokinase)
GGT	Gamma-glutamyl transferase
Hb	Haemoglobin
Hct	Haematocrit
LDH	Lactate dehydrogenase
LH	Luteinising hormone
MCH	Mean corpuscular haemoglobin
MCHC	Mean corpuscular haemoglobin concentration
MCV	Mean corpuscular volume
NTE	Neurotoxic target esterase
PCV	Packed cell volume (Haematocrit)
PT	Prothrombin time
RBC	Red blood cell/erythrocyte
T_3	Triiodothyroxine

T_4	Thyroxine
TSH	Thyroid stimulating hormone (thyrotropin)
WBC	White blood cell/leucocyte
WBC-DC	White blood cells – differential count

Anatomy

CNS	Central nervous system
GIT	Gastro-intestinal tract

Chemistry

DMSO	Dimethyl sulfoxide
GC	Gas chromatography
GLC	Gas liquid chromatography
HPLC	High pressure liquid chromatography
MS	Mass spectrometry
RIA	Radioimmunoassay
TLC	Thin layer chromatography

Terminology

ADI	Acceptable Daily Intake
ARfD	Acute Reference Dose
GLP	Good Laboratory Practice
LOEL	Lowest Observed Effect Level
MRL	Maximum Residue Limit or Level
NOEL	No Observed Effect Level
NOAEL	No Observed Adverse Effect Level
OP	Organophosphorus pesticide

Organisations & publications

ACPH	Advisory Committee on Pesticides and Health
APVMA	Australian Pesticides and Veterinary Medicines Authority
CAC	Codex Alimentarius Commission
ECETOC	European Chemical Industry Ecology and Toxicology Centre
FAO	Food and Agriculture Organisation of the UN
FAISD	First Aid Instructions & Safety Directions
IARC	International Agency for Research on Cancer
IPCS	International Programme on Chemical Safety
JECFA	FAO/WHO Joint Expert Committee on Food Additives
JMPR	Joint Meeting on Pesticide Residues
NCI	National Cancer Institute
NDPSC	National Drugs and Poisons Scheduling Committee
NHMRC	National Health and Medical Research Council
NOHSC	National Occupational Health & Safety Commission
NRA	National Registration Authority for Agricultural and Veterinary Chemicals
NTP	National Toxicology Program
US EPA	United States Environmental Protection Agency
WHO	World Health Organisation

9. ENVIRONMENTAL ASSESSMENT

9.1 Introduction

Diuron is a selective herbicide for broad leaf 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/drains and in non-agricultural areas (right-of-way, commercial and industrial areas) and often is used in combination with other herbicides such as bromacil and hexazinone.

Diuron is also used in antifouling 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 deregistered.

Environmental chemistry, fate and ecotoxicity data form the basis of the evaluation of diuron conducted by the Department of the Environment and Heritage (DEH). Additional material was obtained from other registrants, international reviews, Internet searches and other available literature sources.

9.1.1 Scope of Review

The review is to examine the following environmental effects:

- 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 sea grass;
- the potential role of diuron as a cause of die back in mangroves; and
- 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.

Crops where runoff could affect the GBRL are those grown on the Eastern side of the Great Dividing Range, in particular sugar cane but also bananas, pawpaw and pineapples, which are applied at the same rate range. Higher usage rates on rights-of-way, commercial and industrial areas will also be considered for impact on the GBRL. These are also the situation where effects on sea grasses and mangroves are most likely to be affected or have been reported.

The review is also to consider possible off-target damage to farmlands. While this could potentially involve all uses on the labels, those uses with high applications rates are likely to be of highest concern and especially use in irrigation channels and drainage ditches. Crops where runoff could cause off-target damage to farmlands included those previously give for the GBRL but also orchards application (apples, pear, citrus etc), grapes and grass seed crops where up to 3.6 kg ac/ha may be applied. Rights-of-way, commercial and industrial areas again will also be considered for off-target damage.

9.1.2 Labelling

Current Environmental Protection Statements

There are label warnings to avoid spraydrift 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 need for the environment to prevent contamination of nearby streams etc.

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 mm 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 carried the statement that undiluted chemicals were not to be disposed of on-site.

9.1.3 Environmental Exposure

9.1.3.1 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.

9.1.3.2 Environmental Release

Diuron is currently 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, sugar cane, vineyards and rights-of-way. Information indicates that the major use situations are sugar cane, cereals, irrigation channels and cotton. It is applied both pre- and post-emergent.

There are a number of products on the market where diuron is present in combination with other herbicides. These include hexazinone (in the main), bromacil, thidiazuron and glyphosate. In these combination products diuron is used at lower rates.

Antifouling Use
The use of diuron on vessels <25 metres in length has been revoked in the UK, Demark and the east coast of Sweden (Kevin, McHugh and Waldock, 2002). In Australia, there are approximately 20 marine antifouling paints that contain diuron. Depending on the other actives in these paints, the concentration of diuron ranges from 5 g/L to 80 g/L. Copper 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 sheather 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 are targeted for yachts (several for racing yachts) and other pleasure craft from their label directions 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 handymen (do-it-yourself, DIY). The DIY users will typically apply the paint by brush or roller to the boat hull, although pressure spray applications are also likely, with 2 coats applied over generally a two-day period, once per annum. Professional applicators (eg at marina facilities) would be likely to use airless spray application. Users will 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 antifouling 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 antifouling coatings may also be available from State environmental agencies (eg NSW EPA 1999; Vic EPA 1998).

The coverage of the hulls is some what variable, with some labels (those from International) stating 2 coats for hull and 3 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 21 clearly indicates that the majority of applications are likely to occur annually, indicating an expected lifetime of one year, although 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 with the variability reflecting the concentration of diuron used in the paint formulation, which in turn reflects other actives, types of hulls and there intended use, i.e. racing, offshore, deep water etc.

Table 21: 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
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[1] 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 [2]	28	12-20
Hempel's Seatech antifouling	42-52	3-4 (roller) 2-3 (spray)_	0.2 [3]	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)	0.2[3]	15	Not given

*Also contains chlorothalonil. [1]Assuming 75 μm dry equal to 150 μm wet. [2]Labels gives 200 μm per coat with 2 coats. [3]Labels gives 100 μm dry as minimum total film dry, assumed to equal 200 μm wet paint.

The release rate of diuron from these antifouling 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.

There was between 18-20 tonnes of diuron used in antifouling paints in Australia during 2003.

9.1.3.3 Frequency of Application

Most of the directions on the agricultural labels imply one or 2 applications per year/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/year.

9.1.3.4 Methods of Application

The majority of agricultural applications are expected to be done with boom-sprayers or other ground-rigs. The 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, sugar cane) and as directions are to avoid spray contact with the crop, aerial application is unlikely. Applications to irrigation ditches, drains etc is done using boom-sprayers or other ground-rigs as is application to rights-of-ways, commercial and industrial areas (railway tanker sprayer is considered a ground-rigs)

9.1.3.5 Amount Used

The total amount of diuron used in Australia is over 2000 tones per annum. Based on information the major uses are for sugarcane (~350 tonnes), cereals (~500 tonnes) and 400 tonnes on cotton, mainly used in the cotton regions both as a pre-plant spray and on irrigation channels. In addition, there are uses on several other broad acre crops (lucerne, lupins, peas and summer fallow) totalling approximately 100 tonnes of diuron used. It has been estimated in 1996 that Queensland sugar cane uses 197 tonnes per annum of diuron (Hamilton and Haydon, 1996) but based on recent information this would appear to have increased considerably. There is no breakdown of the amount used on irrigation channels, apart from that for cotton channels, or on rights-of-way usage.

9.1.4 Location and industry practices

9.1.4.1 Sugar Cane

Sugarcane is grown on coastal plains and river valleys in non-contiguous pockets along a 2,400 km stretch of the Australian east coast, from Mossman in North Queensland to near Grafton in NSW. The land used for sugar cane growing is generally within 100 km of the coast and mainly in areas of high rainfall and on river systems. In 2001, over 420,000 ha were harvested each year (http://www.canegrowers.com.au/overview.htm).

Soils in the growing areas range from coastal sands, volcanic soils and riverine silts and clays (nearly all are acid soils). Yearly rainfall can range from 4,400 mm in North Queensland to 940 mm in Grafton. Extensive drainage systems are used in the high rainfall areas. These consist of mainly open field drains connected to natural watercourses. Forty percent of the crop is supplementary irrigated at some stage during its growth cycle (Ham, 1994). There is no set planting time for sugarcane as this is tied in with the growing period of the crop in the various climatic zones in which it is grown. Ratooning takes place during the harvest period between June and December.

The entire cane crop is grown in tropical or sub-tropical areas that are prone to heavy rainfall events, where run-off from farms will generally be to natural waterways. Some natural creek systems have been restructured to allow for better water flow, and fields may be laser levelled to assist in movement of irrigation water and to facilitate run-off in cane fields after heavy rain. Sugarcane can be grown as near as 500 m to the coastline and very close to creeks or major rivers such as the Clarence River in NSW. As such, exposure to sensitive estuarine environments may result, such as mangroves, coastal embayments or lagoons, where sensitive species such as seagrasses occur[1].

The Ord river irrigation area of Western Australia is being expanded and a consortium plans to produce 400,000 tonnes of sugar per year, which would need a yearly planting of around 28,000 ha of sugarcane. Soils in this area range from riverine clays to loamy sands. This crop would be supplementary irrigated during early growth.

Sugar cane is reported as grown by mechanically planting setts (cuttings from mature cane stalks), which produce new shoots from the nodes of the setts with as many as 12 stalks growing from one sett[2]. The cane is then said to be allowed to grow for 12 to 16 months when it is harvested in the latter half of the year [June and December] (*ibid.*). By leaving

[1] Hhttp://www.canegrowers.com.au/industry/industry.htmH
[2] Hhttp://www.rochedaless.qld.edu.au/sugar.htmH

leftover cuttings after harvesting of the green cane, a moisture retaining, soil erosion preventing mulch is retained which also can help reduce weed growth; currently used in approximately 80% of the sugar cane regions in Queensland. Alternatively, the cane can be burnt before harvesting, mainly used in the Burdekin Irrigation Area. In either case the harvester can move along the rows of sugar cane, cutting the stalks off at ground level and chopping the cane into smaller lengths (billets), which are then delivered to mills for processing. In this process, the leafy tops of the stalks can be left on the ground as a mulch (*ibid*.).

Whether the cane is burnt or green at harvest there is a stubble of plants (stools) left in the soil. These grow new shoots [or ratoon crops] with each original sugarcane plant usually growing three or four ratoon crops[3]. When the final ratoon crop is harvested, the remaining shoots are reported as being ploughed out and the ground allowed to lie fallow for a year with legumes often planted on the fallow ground for soil rejuvenation (*ibid*.).

9.1.4.2 Irrigation and Drainage Channels

The use of diuron in irrigation and drainage channels potentially represents a potential route of high environmental exposure. One of the labels (from ChemAg Pty Ltd) also includes bore drains to control Prickly Acacia and Mimosa Bush and is for Queensland only. It is assumed this is for uncapped bores in Western Queensland and due to the dryness of this region, these bore drains are unlikely to link to existing river systems, except during floods. The use of diuron in the cotton regions is, as one registrant states, predominantly for use as a channel spray and one registrant indicates that this is approximately 60% of sales in cotton (sales in the cotton regions are approximately 400 tonnes per annum).

There are extensive irrigation channels throughout Australian with majority in the Eastern Sates. The major irrigation areas are in NSW, Queensland, South Australia and Victoria. There are small areas in Western Australia (Gascoyne and Ord Rivers). Cotton and rice are the a major irrigated crops, orchards are also grown using water from large irrigation schemes as is sugar cane, particularly in the Burdekin south of Townsville.

Drainage channels occur throughout the agricultural areas. In particular they are found in the irrigated areas and high rainfall regions, which include the sugar growing areas. The drains treated could include tail drains on irrigated farms, tile drains, drainage ditches and other such areas where water is drained from fields.

9.2 Fate And Behaviour In Water And Soil

The Department of the Environment and Heritage's 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.

[3] Hhttp://www.marysug.com.au/process.htmH

9.2.1 Hydrolysis

9.2.1.1 Aqueous hydrolysis

Study 1
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 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 radiolabeled 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 not 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 identifed 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 mantained.

Study 2
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 radiolabeled 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.

Summary

In a study conducted according to US EPA and EU Guidelines, there was no observable degradation at 25°C in the 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.

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 are considered reliable. At pH 7, there was insufficient degradation for determination of a half-life. There were 2 degradation products noted in the HPLC, only one of which was >10% of applied radioactivity (AR) and was identifed as 3,4-dichloroaniline (DCA) by co-chromatography.

In a second study conducted according to US EPA Guidelines, there was only limited degradation of 1-2% at all pH values (5, 7 and 9) and it was concluded that the half-life was greater than 500 days. There were 2 degradates identified as N'-(3,4-dichlorophenyl)-N-methyl urea (DCPMU) and 3,4-dichloroaniline (DCA).

9.2.2 Photolysis

9.2.2.1 Aqueous photolysis

Buffered and distilled water
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 22 for the latitudes relevant for Australia.

Table 22: 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 Department of the Environment and Heritage). 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 gas traps were 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 – the Department of the Environment and Heritage agrees.

Aqueous photolysis – Study 2

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, Kirkpatrick Shaw and Mobbs, 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.

Aqueous photolysis – Study 3

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 ECOTOC 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 DEH). The results of these calculations are given in Table 23.

Table 23: 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

9.2.2.2 Soil Photolysis

The photo-degradation of diuron on soil, uniformly ^{14}C-labelled in the phenyl ring, was studied according to the 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.

9.2.2.3 Summary

Aqueous Photolysis
The photolysis of diuron in buffered water was conducted according to US EPA Guidelines and to satisfy EU 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 to 6.7 to 22.4 days. 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. Two minor peaks in the HPLC were identified, one as 3-(4-chlorophenyl)-1,1-dimethyl urea or 3,4-dichlorophenyl urea and another as 3,4-dichloroaniline.

In a second study conducted according to US EPA guidelines, the photolysis of diuron was again first order and the half-life was determined as 9.0 days, 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 >10% of applied and were not identified.

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

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% 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 N'-(3,4-dichlorophenyl)-N-methyl urea (DCPMU).

9.2.3 Metabolism

9.2.3.1 Aerobic soil metabolism

Study 1
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, Kirkpatrick, Shaw and Chan, 1990). The soil used, a silt loam (Keyport soil) from Newark, Delaware, was treated with diuron at 19.5 µg/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 µg/g soil (dry weight). The sterile soil remained sterile throughout the study. Table 24 gives the characteristics of the soil.

Table 24: 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	84.2[1]	5.7[1]	10.1[1]	1.36*	7.3
Falkenberg, Sweden	Sand	90.9[1]	7.8[1]	2.1[1]	1.64*	5.8
Mogenstrupvej, Denmark	Sandy loam	58.2[1]	24.1[1]	17.7[1]	2.24*	6.0
Speyer 2.1, Germany	Sand	88.4[1]	9.8[1]	1.9[1]	1.08*	5.9

[1]From European data: sand =63-2000 µm; silt 2-63 µm clay <2 µm. * 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 25.

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. The degradation pathway is outlined in Figure 1.

Figure 1. Proposed metabolic pathway for diuron in aerobic soil.

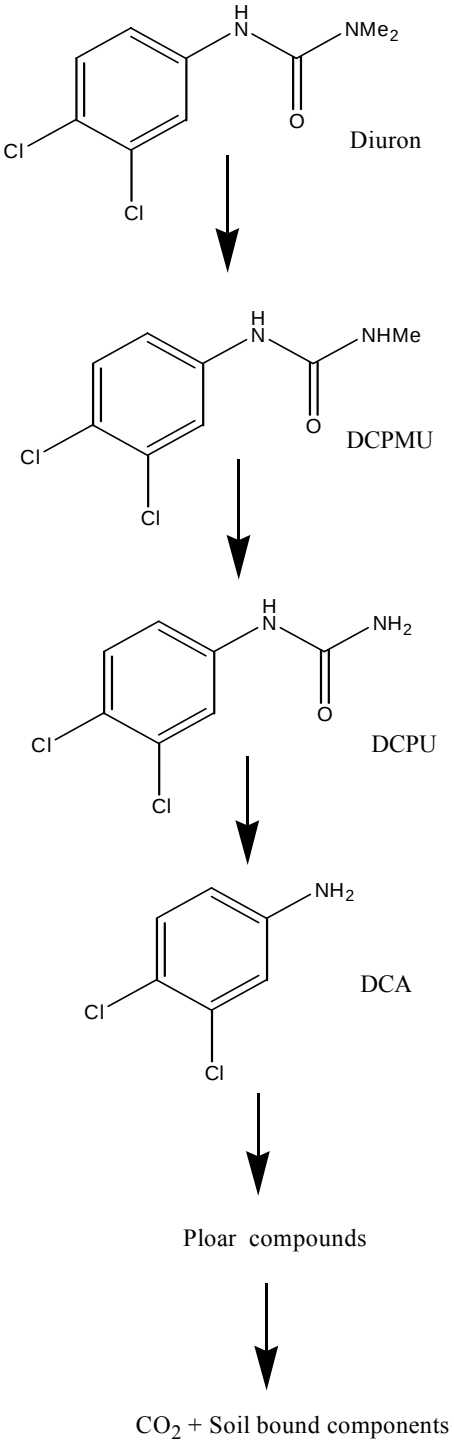


Table 25: Recoveries of radioactivity to various fractions as total of applied from Newark silt loam soil.

Fraction	Time of sample, Days after treatment (DAT)									
	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.

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

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 24. (The Swedish soils from Nantuna and Langaveka were also used for the lysimeters study.) The soils were dosed with the diuron at 3.52 μg/g 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 26. 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.

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. Figure 1 gives the degradation pathway.

Table 26: 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 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 26) 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. The Department of the Environment and Heritage 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 (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

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 24. The soil was pre-incubated for 22 days under aerobic conditions before being dosed with the ^{14}C-diuron at 8 μg/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[4] approximately field moisture capacity). The soil was analysed at various times by TLC analysis. The degradation half-life

[4] 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).

was derived using the Timme model (Timme *et al*, 1986).

The mass balance of the experiments ranged from 90.7% to 99.8%. There was a small amount of CO_2 evolved until 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.

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 tons/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.

9.2.3.2 Aerobic Aquatic Metabolism

Study 1

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 27.

Table 27: Characteristics of the sediments and water used (German classifications and soil textures).

	Water pH	**Sediment pH ($CaCl_2$)**	**Sediment Texture**	**Sand 63-2000 μm**	**Silt 2-63 μm**	**Clay <2 μm**	**% 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 preincubated for *ca*. 14 days to allow an

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[5]) with dissolved oxygen ranging from 41-94% of saturation and redox of 220-266 mV. The Erft sediment was mainly were 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 28 for Erft River and Table 29 for Hönniger Weiher. Almost all of the 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 28: Recovered radioactivity for River Erft in water and sediment as a percentage of applied radioactivity identified metabolites. Average of duplicate samples

Time	Total	Water		Sediment			
days	CO_2	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.

[5] 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.

Table 29: Recovered radioactivity for Hönniger Weiher in water and sediment as a percentage of applied radioactivity identified metabolites. Results are the average of duplicate samples.

Time days	Total CO_2	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.
m-CPDMU = 3-(meta-chlorophenyl)-1,1-dimethylurea

The DT50 and DT90 were calculated on first order kinetics except for the water dissipation used a first order multi compartment model (FOCM) as shown in Table 30. The results for the total system for Hönniger is not a statistically significant fit and therefore the half-life is not reliable.

Table 30: Half lives of dissipation of diuron in 2 sediment/water systems.

System	DT50 days	DT90 days	r^2
Erft River (water only)	8.8	29.3	0.981
Erft River (total system)	48	159	0.926
Hönniger Weiher (water only)*	4.2	182	0.999
Hönniger Weiher (total system)	232	>1 year	0.639

* first order multi compartment model (FOCM)

Diuron moved fairly rapidly to the sediment where it was degraded. In the Erft sediment, which was essentially aerobic, degradation was quicker than in the Hönniger sediment which was anaerobic in the early part of the study. It should also be noted that the microbes in the Erft River were probably conditioned for the degradation of diuron.

The Department of the Environment and Heritage 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 (under these anaerobic conditions) 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
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 agained - a

weakness of the study as it is not known if aerobic conditions were maintained. The labeled 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 = 0.9669). 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.

Literature

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 either 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 (10^4 colony forming units cf 10^7). No half-lives were determined. This report clearly shows that diuron can be degraded in aerobic conditions used pre-conditioned sediments. The Department of the Environment and Heritage 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 with current guidelines.

9.2.3.3 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 24) 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 31 gives the results.

Table 31: Recoveries of radioactivity to various fractions as total of applied from Keyport silt loam soil. All results as percentage of applied radioactivity.

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[1]	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

The amount of diuron is the sum from all extractions. * After 30 days conditions were changed to anaerobic by passing nitrogen through the system. [1] DCPMU = N'-(3,4-dichlorophenyl)-N-methyl urea

There was no volatiles trapped with the total of all trapped radioactivity <0.1% of applied. 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)

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 31). The half-life for the anaerobic phase was calculated as 1000 days with an r^2 of 0.32 (calculated by the Department of the Environment and Heritage), i.e. 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.

9.2.3.4 Anaerobic aquatic metabolism

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 cannel and were the same as used in the previous aerobic aquatic metabolism study. 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 labeled 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 = 0.7866, 4 data points). There was one main metabolite, m-CPDMU, that reached 81% of AR after 7 days, remained at that level till 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.)

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, Camper and Paynter, 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 appear in approximately stoichiometric amounts. The Department of the Environment and Heritage 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 with current guidelines.

Summary

Table 32: Summary of all half-lives and main metabolites.

Metabolism	Soil used, pH	Conditions	Half life, days	Major metabolite(s) identified
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
	Sandy loam	35% MWHC, 20°C	27	DCPMU, DCPU
	Sand	20°C, pF 2.5	112	DCPMU, DCPU
Aerobic Aquatic	Silty loam (Erft River)	20°C	48	DCPMU
	Sandy loamy silt (Hönniger)	20°C	232	DCPMU, m-CPDMU
	Clay loam	25°C	33	DCPMU, m-CPDMU
Anaerobic soil	Silt loam	25°C, 75% field moisture. 30 d aerobic then anaerobic	No degradation during anaerobic phase	-
Anaerobic aquatic	Clay loam	25°C, anaerobic	1.2 days	m-CPDMU. PDMU, m-CPMU

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% of AR with 14.9% remaining in the soils and 3.36% as CO_2 (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, DCPMU and DCPU were identified.

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% 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% of MWHC) reduced the half-life to just 27 days. The TLC analysis identified 3 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 CO_2 free air for 101 days at 20°C and at field capacity (pF 2.5). 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 2-comparement model to give a half-life of 112 days and a DT50 for DCPMU of 35 days. The analysis identified 2 metabolites by comparison with authentic samples: DCPMU and DCPU.

Aerobic aquatic metabolism

The aerobic aquatic metabolism of diuron was conducted according to EC SETAC-Europe Procedures using two sediment-water systems collected from two locations in the Germany; River Erft, a river following 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 with the Erft sediment also mainly aerobic. The Hönniger sediment was essentially anaerobic at first (28 days) then became aerobic. Diuron moved fairly rapidly to the sediments where it was degraded quicker in the Erft system (half-life = 48 days) than in the Hönniger system (232 days). 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 the 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 the 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 2 main metabolites, m-CPDMU and DCPMU. The degradation pathway proposed is the same at for the previous aerobic aquatic metabolism study and involves two pathways, one demethylation while the other proceeds via 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.

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 and then the soil was 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 only be recovered 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.

Anaerobic aquatic metabolism

The anaerobic aquatic metabolism of ^{14}C-diuron was studied under according to US EPA Guideline using a clay loam sediment (used for the aerobic aquatic metabolism study). The diuron was applied and then incubated in a dark under nitrogen at 25°C to give a degradation half-life of 1.2 days using first order kinetics. The main metabolite was 3-(3-chlorophenyl)-1,1-dimethyl urea (m-CPDMU) that reached 81% after 7 days, remained at that level till day 98, then declined to 15% of AR at the end of the study. Other metabolites detected were phenyl dimethyl urea (PDMU or fenuron - another herbicide, maximum 13% of applied), and 3-(3-chlorophenyl)-1-dimethyl urea (m-CPMU, maximum 18% 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 m-CPMU. In a

supplemental report it is noted by the author that the reductive dechlorination is fast and explains the relatively short half-lives of diuron in this study.

Conclusion

From the metabolism studies there appears to be two metabolic pathways for the degradation of diuron, one under aerobic conditions and other for anaerobic conditions. The aerobic pathway involves demethylation of the urea to give the metabolites DCPMU and DCPU while the anaerobic pathway is quicker and involves dechlorination of the phenyl ring, a typical anaerobic degradation, to give m-CPDMU and PDMU.

The aerobic degradation rates (half-lives) in soil range from 20 to 119 days at 20°C, excluding one outlier at 372 days, and degradation is slower in cooler conditions, 143 days, at 10°C. The half-lives were similar in the aerobic aquatic degradation studies at 33 and 48 days, with one exception at 232 days but this system became anaerobic during the incubation period. It should be noted that in the study with the shortest half-life (33 days) conditions were marginally aerobic at the start and the anaerobic degradate m-CPDMU was the principal degradate, suggesting that conditions be came more anaerobic. The only other system that became anaerobic was the anaerobic soil degradation study but there was no degradation during the anaerobic period. Under the continuous aquatic anaerobic conditions, the degradation is faster with a half-life of 1.2 days. This could be due to stronger anaerobic conditions but this is not clear from this report as only the redox range during the test was reported which indicated that conditions were reducing to strongly reducing.

9.2.4 Mobility in Soils

9.2.4.1 Adsorption/desorption potential

Adsorption/desorption - 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). Fenuron and m-CPDMU are both significant anaerobic metabolites of diuron. 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 33 gives the soils characteristics and Table 34 the results.

Table 33: Characteristics of test soils.

Origin	Soil Name	Soil Type	Organic matter	pH	% Sand	% Silt	% Clay	Koc [1]
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 34: The adsorption coefficients for diuron, m-CPDMU and fenuron.

Soil Name	K_f, µg/g soil	Koc	1/n	Koc_{des}	K_f, µg/g soil	Koc	1/n	K_f, µg/g soil	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

Nd = not determined.

The Kocs 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 Kocs (not given in Table 34) 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 - Adsorption/desorption of 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 Koc_{des} 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 35.

Table 35: Characteristics of test soils and adsorption coefficients.

Origin	Soil Type	om	pH	% Sand/Silt/Clay	K_f, µg/g	Koc *	1/n	Koc_{des} *
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 the Department of the Environment and Heritage from Kom using Koc = Kom X 1.74.

The Kocs 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 Koc_{des} in Table 35. However, these need to be considered as unreliable 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.

Adsorption/desorption - 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, Konig and Sommer, 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 36 gives the soils characteristics and Table 37 the results.

Table 36: Characteristics of test soils.

Origin	Soil Name	Soil Type	Organic carbon	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 'im Tal'	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 37: The adsorption coefficients for DCPMU.

Soil Name	K_f, µg/g soil	Koc	r^2	1/n	Koc_{des}
BBA 2.1	3.49	4989	1.000	0.7629	786
Borstel	9.37	1358	0.999	0.7561	2030
Höfchen 'im Tal'	15.63	651	0.999	0.7565	929
Tonboden	4.76	744	1.000	0.7390	1205

Nd = not determined.

The Kocs 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.

Adsorption/desorption - 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 38 gives the soils characteristics and Table 39 the results.

Table 38: Characteristics of test soils.

Soil Name	Soil Type	Organic carbon	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 im Tal	Silt	2.11	6.7	8.2	81.5	10.3
BBA S6	Clay	1.89	6.9	21.7	35.4	42.9

Table39: The adsorption coefficients for DCPU.

Soil Name	K_f, µg/g soil	Koc	r^2	1/n	Koc_{des}
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 im Tal	11.12	527	0.999	0.757	659
BBA S6	12.02	636	0.998	0.787	792

Nd = not determined.

The Kocs 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.

9.2.4.2 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 under taken in Sweden (Bergström, Bramble, Aronsson, Brücher and Norwood, 1996).

Two sandy soils (Nantuna and Langaveka, details in Table 40) 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.

Table 40: Soil characteristics in the soils used for lysimeters.

Soil		Soil Type	Organic matter	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 µg/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 Department of the Environment and Heritage 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 daytime 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 Australian. However, the drier Australian conditions that occur inland would also reduce the microbial activity and hence the degradation of diuron and therefore diuron could be expected to leach, especially in the first periods of rainfall after a dry spell (i.e. in the first flush). The Australian field data clearly shows that diuron is detected in surface water and in sediment.

9.2.4.3 Summary

Adsorption/desorption

The adsorption/desorption of diuron was performed by batch equilibrium studies to meet US EPA Guidelines using 4 soils agricultural soils. The Kocs ranged from 418 to 574 and indicate that diuron is moderately adsorbed to the soils tested. It is rated as being of low to medium mobility. The narrow range indicates the organic matter is the major determinate of adsorption. The desorption data shows that there was considerable loss of diuron from one soil, 40% of the initially adsorbed diuron was lost after 5 cycles of desorption, compared to 7-17 % for the other 3 soils.

The adsorption/desorption of diuron, fenuron and m-CPDMU in 5 soils was performed to meet US EPA Guidelines. Fenuron and m-CPDMU are both anaerobic metabolites of diuron. In the preliminary studies two soils showed <10% adsorption and as this was not sufficient for isotherm testing the rest of the study was conducted using the three soils only. The Kocs from the screening were from 366 to 1750 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 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, in contrast to that from the previous study. For the metabolite m-CPDMU the Kocs from the screening data ranged from 40 to 323 and is rated as being 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 fenuron, the screening results show Koc from 33 to 138 (high to very high mobility) and similar for the isotherm data. In all cases the metabolites were more mobile than the parent compound diuron.

The adsorption/desorption of DCPMU, a major aerobic metabolite of diuron, was performed in 4 soils to meet US EPA Guidelines. The Kocs 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).

The adsorption/desorption of DCPU, a major aerobic metabolite of diuron, was performed in 5 soils to meet US EPA Guidelines. The Kocs 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).

Field Lysimeters

To evaluate the leachability of diuron under field conditions two field lysimeters were set up in Sweden using 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). The leachates and soils sections were analysed for total radioactivity, diuron and metabolites.

At 2 kg ac/ha, there were 6 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 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 diuron and 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% 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 ($CO_3^{=}$) 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.

It is concluded by Department of the Environment and Heritage that the study shows limited leaching at the lower rate but also indicates that at higher rates the leaching is proportionately higher.

9.2.5 Field Studies

9.2.5.1 Terrestrial Field Studies

Application to bare ground - Study 1 (interim report)
A terrestrial field dissipation study was conducted according to US EPA Guideline 164-1 (Bramble, Behmke, Frizzell and Norwood, 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 41 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 Figure 1) was detected. The limit of quantification was 20 μg/kg soil and results below this figure should be considered to be estimates only. Table 42 is a summary of soil residues found in upper most section of soil (0-15 cm), averaged from 3 plots at each site.

Table41: 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	Sand	Sand	Silt loam	Silt loam	Silt loam	Silty clay loam	Silty clay loam	Silty clay loam

Table42: 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).

	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. Table 42 gives the concentration of diuron and DCPMU in the first 0-15 cm depth to the end of the interim report. 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 diuron or its first metabolite is 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 43. Also included are the results of first order analysis, which show statistically acceptable results.

Table 43: The half-lives (days) and statistical factors for degradation of diuron in field studies.

Test site	**DT50 days**	**DT90 days**	**r^2**	**Transition time**	**First order (calculated by DEH)**	
					DT50 days	**r^2**
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 44. The additional results increased the calculated half-lives (cf first order analysis in Table 43) and these are also given in Table 44.

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.

Table44: 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 r^2	73; 0.8245			141; 0.7978		135; 0.8689			

Terrestrial Field Study 2

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 45 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.

Table45: Soil characteristics in the soils for field studies conducted in Delaware and California.

Soil		Soil Type	Organic matter	pH	% Sand	% Silt	% Clay
Newark, Delaware	0-30	Silty clay loam	0.8	5.7	8.0	64.4	27.6
	30-60	Silty clay loam	0.2	5.2	6.0	66.4	27.6
Madera, California	0-30	Sandy loam	1.1	7.6	54.0	28.4	17.6
	30-60	Loam	0.7	8.3	46.0	36.4	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 46 is a summary of soil residues found in upper most section of soil (0-15 cm). At the sites either one, 2 or 3 plots were sampled at each sample, the result in Table 46 are averaged from 2 or 3 plots at each sites or from the plot sampled at that date.

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 46 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.

Table 46: 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[3]	7[2]	14[2]	30[1]	61[1]	90[3]	124[3]	149[2]	181[2]	210[2]	243[2]	299[2]	359[2]	418[2]
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[1]	7[1]	15[2]	29[1]	59[1]	89[1]	112[2]	152[2]	179[2]	219[1]	239[1]	300[2]	358[2]	415[2]
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

[1] Single plot sampled; [2] average of 2 plots; [3] average of 3 plots. bld = below detection

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 102 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 the Department of the Environment and Heritage) 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 DEH), 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 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 or a problem with preparation of the spray etc. 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.

Terrestrial Field Study 3 - 6 German sites

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 47 gives the details of the soils and the calculated half-lives.

Table47: Terrestrial degradation of diuron at 6 sites in Germany.

Site	Sand/silt/clay	pH	oc	Soil type	DT50 days	r^{2*}
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 Department of the Environment and Heritage.

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.

Terrestrial Field Dissipation Study 4 - 4 Australian sites

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 48 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 of cultivation, irrigation etc. 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.

Table48: 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 Kocs 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 DEH). 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. The Department of the Environment and Heritage can only agree.

9.2.5.2 Field Dissipation and Transport

Field Dissipation and Transport - Study 1

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. The Department of the Environment and Heritage 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 nonlinear 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 mg/L) were in the treatment area and for 2 and 4 DAT only (maximum of 0.013 mg/L). There were no other detections of diuron or its metabolites in any other water sample.

The Department of the Environment and Heritage 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 to soil or dissolved in the water.

Field Dissipation and Transport - Study 2

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 DEH 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 49 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 nonlinear 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 49: 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, see Table 49) showed positive results in the treatment area at time zero and was considered by the authors to be due to spraydrift. 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 50. There were no metabolites detected in any water sample. The majority of positive detections (greater than the LOQ of 0.01 mg/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.

Table50: 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	-	10[1]	blq	
Plot a	-	blq	28	38	10 [1]	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 DEH 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, i.e. 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 bound to soil from erosion, where it either is mobilised or degrades. The study gives some tantalising 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.

9.2.5.3 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, Neus, Bulcke, Cools, Eelen

and Dekkers, 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 = 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.

9.2.5.4 Summary

Application to bare ground - 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% of target rate. All sites received natural rainfall plus additional irrigation to ensure monthly total were above the historical (baseline 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 cm) after 238-301 days was 3-19% of the initially applied. The calculated half-lives (first order analysis) were calculated as 73, 141 and 135 days. The half–life of the metabolite DCPMU at the 3 sites was also calculated as 182, 231, 112 days.

There were occasional detections of diuron in the 15-30 cm 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 cm above the limit of quantification (LOQ = 0.020 mg/kg) at 0.023 mg/kg. DCPMU was mainly detected in the first 0-15 cm of the soil with only occasional detections lower down (15-30 cm with the highest at 0.028 mg/kg).

Terrestrial 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. Over the test, the Newark site received mainly natural rainfall amounting to 1659 mm while the California site was irrigated for the first 3 months and received 1 to 4 hours of irrigation per day.

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

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. At California 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% of the target rate, for some samples only one plot was analysed and with the normal high variability between plots, this is unsatisfactory.

Terrestrial Field Study 3

A terrestrial field study was conducted at 6 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 DAT. 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 is 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 cm soil sections only on 3 occasions. There were 3 additional detections deeper than 20 cm on day 0 but these are likely to be due to contamination during sampling.

Terrestrial Field Study 4

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. 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 of cultivation, irrigation etc but had bare soil and were not trash covered, as is normal practice. The effect of trash cover was examined separately.

The results of this study show that the Kocs 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 >250 days using a second order equation but these can be misleading as the DT90s were not reported.

The runoff of diuron and its leaching was also examined at these test sites. Runoff of diuron was monitored and <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 between 0.37-10.6 μg/L. Diuron was detected in a groundwater at a maximum concentration of ~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% 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 <15% of application rate (estimated graphically by DEH).

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.

Terrestrial Field Study 5

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 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 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 for 159 days when 19.6 mm (0.77 inches) fell.

The results of the soil analysis on the slope and berm showed that diuron dissipated with a DT50 of 142 days, calculated using a nonlinear 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 mm). There were no other detections of diuron or its metabolites in any other water sample.

The Department of the Environment and Heritage 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.

Terrestrial Field Study 6

A field dissipation and transport study was conducted as above according to US EPA Guidelines in Arkansas. The soil on the side of the ditch was a silt loam soil while the sediment in the irrigation channel was not classified. The weather at the site over sampling period (November-May) of the study was typical, with ~860 mm of rainfall.

The results of the soil analysis showed that diuron dissipated from the soil with a DT50 of 105 days calculated using a nonlinear regression analysis (first order analysis gives an average of 104 days). The metabolite DCPMU was detected in these soil samples, initially from 0 DAT 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 spraydrift. The concentration of diuron in the sediment near the treatment area shows a reasonably consistent level of around 0.5 mg/kg except for the 179 DAT with the highest value of 1.61 mg/kg. Only one metabolite was detected, that being DCPMU, with maximum concentration of 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 majority of positive detections from the scheduled water samples occurred 9 to 34 DAT, which appears to show limited aquatic exposure. However, the raw data for 48 DAT show levels of diuron only slightly below the limit of quantification. If this is a general situation, then the information tends to show 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 one 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 DAT) had most concentrations of diuron below the limit

of quantification except for 152 DAT (event 10, first sample) when one of 2 duplicate analyses gave a reading of 10 μg/L.

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

Terrestrial Field Study 7

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.

The Department of the Environment and Heritage 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 in Belgium, diuron was applied at 3 kg ac/ha to 2 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 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 = 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.

Conclusion

The overseas terrestrial field studies (12 sites) gave soil DT50s ranging from 67 to 231 days with one site having limited degradation. At 11 overseas sites there was no evidence of vertical movement but in one Californian study, there was evidence that diuron had moved

vertically to lower soil profiles (45-60 cm). When diuron was used on the sides of irrigation channels (2 sites), the concentration of diuron in the channel water reached 130 µg/L and was >10 µg/L for a 3 week period at one site. This was related to rainfall at this site. At the other site diuron was not detected in the channel water but there was no rain and therefore no runoff into the channel but when it did rain (256 DAT), analysis of sediment showed that diuron had moved from the sides of the channel. When diuron was used on the sides of highways for weed control the concentration of diuron in runoff following simulate rain ranged from 144-1770 µg/L. Total mass of herbicide leaving the plots in runoff reached 5.4% of the applied diuron. Concentrations of diuron in natural rain runoff were from 46-2849 µg/L and up to 8.4% of the applied diuron ran off in one 28-hr period.

Australian field studies were conducted at sugarcane farms (3 sites) over 3 years in the Bundaberg region. The DT50 for diuron ranged from 6.5 to 20 days at 2 sites with one site having limited degradation every year and the DT50 was given as >250 days. Again there was no evidence of vertical movement at any of these sites. The concentration in diuron in runoff water was 0.37-120 µg/L and in groundwater the maximum was 6.5 µg/L.

9.2.6 Measured Field Concentrations

9.2.6.1 Australia

Sugar cane Areas - Estuaries

Following an episode of severe dieback of mangroves in the Pioneer River estuary (Mackay in Queensland), diuron was detected in sediment at four sampled sites in a study by Duke et al (2001). 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 confirm that transport of diuron has occurred from farms into drains and thence into the estuary. The authors concluded from this and other evidence that of 12 possible causes of mangrove dieback that they had considered, the chief suspect was pesticide usage by the sugarcane industry, in particular the use of diuron (present at up to 4 µg/kg dw in the same samples) but sediment burial, excessive nutrients and heavy metals could not be discounted.

The Pioneer River flows into the GBRMPA and has a significant area of the catchment (18.8%) under sugar cane with application of diuron amounting to 23435 kg/year (http://www.gbrmpa.gov.au/corp_site/key_issues/water_quality/action_plan). The Buscasia/Eimeo estuaries have minimum human impact in their catchments, are within the Mackay region, and therefore were use as ‘reference sites’.

The report of Duke was challenged by Kirkwood and Dowling (2002), who provided further observational, climatic and historic evidence and argued that burial or partial burial of mangrove pneumatophores was a more plausible explanation of the mangrove dieback in question. They concluded that herbicides are not the most likely cause of the current dieback of mangroves in the Pioneer River estuary because:

1. there are insufficient data available to demonstrate higher herbicide concentrations in dieback areas than non-dieback areas;
2. there is no evidence to indicate that the comparatively very low herbicide concentrations that were recorded were sufficient to kill mangroves, “although herbicides at the

concentrations recorded have been shown to affect seagrasses physiologically, the biological differences between seagrasses and mangroves are so great that it seems unreasonable to expect mangroves to exhibit the same physiological responses as seagrasses to herbicides".

Duke et al (2003) have now published a report of further work 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 (see Table 51). 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 2002 (Barnes Creek, sites M1 and M2, see Table 51), the concentrations of diuron were similar in both years, possibly indication that the level of diuron being 'recharged' in the sediment.

Other possible causative agents that were considered in the second Duke report 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 pneumatophore burial (measured as height from cable root to surface) and the presence of dieback. There was a strong 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, declining levels of chlorophyll in mature leaves and decreasing numbers of healthy seedlings in the surveyed plots. The plot surveys also showed that while *A. marina* was the only species to be suffering from wide spread dieback, *Aegiceras corniculatum* (river mangrove) was also affected with dead branches and yellowing leaves in some plots in the Pioneer River area and *Ceriops australis* (yellow mangrove) showed significant dieback in some plots but not in all. Transects showed that *A. marina* increased in health the further towards the landward areas of the mangroves range and away from the creeks/rivers.

Table51: Measured concentrations of diuron in sediment. Samples taken from creeks/estuaries in sugar cane growing areas of Queensland as report by Duke et al, 2001 and 2003, see Appendix 1 for maps of sites and collection points.

Diuron detected in sediment (µg/kg dw)							
Mackay area				**South and north of Cairns**			
Site	**Code**	**2000**	**2002**	**Site**	**Code**	**2000**	**2002**
		-	1.7	Johnstone R	MP1	-	1
		-	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	-				

The investigators again conclude that there is strong correlative and some causative evidence implicating herbicides, particularly diuron, as a primary agent causing serious dieback of mangroves in the Mackay region. The report notes herbicides also act as stress agents, and that along with other stress factors, the plants are eventually terminally stressed.

Pioneer River – Concentration of Diuron during Flow.

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 take 4 sites across the catchment. At two sites several samples were taken these were Dumbleton Weir gauging station, located at the bottom of the catchment (drainage area of 1485 km^2, ~95% of catchment), and Finch Hatton creek, a small largely unimpacted creek within the catchment. 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. Table 52 gives timing of samples and concentration of diuron found, while Figure 2 gives the hydrograph at Dumbleton Weir (second sample was not analysed for diuron).

Table 52: Timing of samples and concentration of diuron found.

Site	Time of sample[1]	Diuron, µg/L
Dumbleton Weir	0815	8.5
	1500	2.5
	2325	1.1
	0900(15/02)	0.90
Finch Hatton Creek	0730	NDR
	1030	NDR
Mia Mia Bridge, Pioneer River	1030	0.40
Cattle Creek	1055	1.00

[1]All samples taken on 14/02 except last sample at Dumbleton taken on 15/02. NDR = No detectable residue, limit of reporting set at 0.3 µg/L

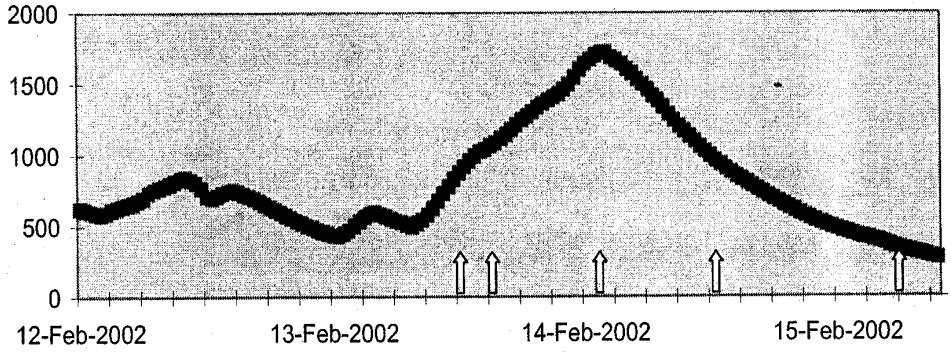
The pesticide loads at Dumbleton was determined using simple interpolation and integration over the flow event with extrapolation to get a point concentration at the very start and end of the hydrograph. Total diuron load was estimated at 470 kg, which given the previously estimated diuron usage in this catchment of 23.5 tonnes per annum (Hamilton and Haydon, 1996), gives runoff of diuron as 2% of applied.

Considering that last usage of diuron would have been earlier during canopy closure (December/January) and that degradation in the field and adsorption should have occurred, the amount of diuron in the runoff is significant. However, it must be noted that there was larger area than normal being planted as setts (~30% of cane production rather than the normal 15-20%) due to an old cultivar becoming susceptible to fungal problems. This may

have resulted in more diuron being used on the replanted cane than is typical for the area. Nevertheless, even a 50% increase in diuron usage to 35 tonnes would imply 1.3% of the applied diuron ran-off and the amount of diuron in the runoff water remains significant.

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).

Figure 2. The hydrograph at Dumbleton Weir on the Pioneer River showing sampling times and volume of flow (cubic metres of water per second, cumecs). Note that pesticides were not analysed in the second sample.



Sugar cane Areas - offshore

In a recent report the concentrations of diuron in sediment and seagrass from 16 intertidal sites (<1 m deep; 3 samples per site pooled), located from Cape York to Moreton Bay at important dugong habitats, together with 24 subtidal sites (<5 m deep, in duplicate 3 random grab samples, 500-1000 m apart) located near major estuaries have been determined (Haynes, Müller and Carter, 2000) (See Appendix 1 for locations). In the intertidal 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 matrixes. 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 subtidal sites, diuron was detected at 9 of the 24 subtidal sites at concentrations ranging from 0.2 to 10.1 μg/kg dw (see Table 53). The positive detections were mainly near rivers draining the sugar growing areas.

Table 53: Levels of diuron found in subtidal sediments in rivers, area under sugarcane in nearby river catchments and amount of diuron used in catchment.

River[1]	DR	BR	RR	JR	TR	C	HR	L
Concentration μg/kg dw	0.2[2]	0.35	1.1	10.0	1.4[2]	0.8	2.0	1.6[3]
Area under sugarcane[4], km[2]	48	76	232	394	247	58[5]	691	691[6]
Diuron used in catchment[4] kg	2378	835	4700	17353	2768	1250[5]	16600	16600[6]

[1]Abrevations 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 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 54). The highest levels of diuron from the sugar cane 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 54: Results for diuron from a study examining pesticide residues in Queensland irrigation channels and drains. See appendix 1 for location of sites.

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

Channels are irrigation supply water; drains collect excess water from the fields.

Cotton Growing Areas

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 55 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 55: 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 (from 230)	33 (from 230)	35 (from 255)	28 (from 209)	14 (from 280)	27 (from 300)	56 (from 300)

[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 24 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.

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 monthly 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).

In conclusion, this 5-year monitoring study in the South West of NSW shows that diuron is a low level contaminant of water from farms where diuron has been used. Concentrations reached approximately 20 μg/L in surface flows from treated areas (4.5 kg ac/ha) and 30 μg/L in sub-surface tile drains. In creeks draining large irrigation areas (Mirrool and Little Mirrool), levels reached a maximum of 7.5 μg/L.

Hervey Bay, Queensland

Low concentrations of diuron, together with other herbicides, were detected in surface waters and sediments in inter-tidal seagrass meadows of *Zostera capricorni* in Hervey Bay, Queensland (McMahon, Bengston-Nash, Eagleham, Müller, Duke and Winderlich, 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 sugar cane 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 sugar cane area covering 2.7% of the catchment (8500 ha, 3.3 tonnes of diuron used, Hamilton and Haydon 1997). The sugar cane 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 sugar cane is based on 1994 data, which could be out of date.

Surface waters together with 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 surface water at the seagrass meadows ranged from <5 (detectable but below limit of quantification) to 25 ng/L and in the sediments at not detectable to 0.2 ng/kg dw. The highest value occurred 1 km from the mouth of Big Tuan Creek, a small creek, and 5 km from the mouth of the Mary River. 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.

9.2.6.2 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 56 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 sq km, with most less than 1000 sq km) 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 sq km) 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 sq km) 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 56: 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, i.e. atrazine, simazine.

UK

The Environment Agency (UK) conducts routine monitoring of pesticides in freshwater and their results for diuron in 1996 and 1997 have been summarized (Pesticides Safety Directorate, 2002). The summary table in this report is reproduced below as Table 57.

Table 57: Level of diuron in freshwater in the UK by regions for 1996 and 1997, from Pesticides Safety Directorate, 2002.

Region	No. of samples		Percent above MRV		MRV ng/L		Average ng/L		Maximum, 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

MRV = minimum reporting value

As can be seen in Table 57, 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, (*ibid)*. 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 58.

Table 58: Measured concentrations in marine waters at 3 coastal areas of the UK during 1998.

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 58, 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 etc,), 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.

9.2.6.3 Summary

Monitoring Studies: Sugar cane

Diuron was been detected in sediment at 4, 0.8 and 3 μg/kg dw in samples taken from areas affected by mangrove dieback in the Pioneer River estuary and 0.2 μg/kg dw in one sample taken in an area of relatively normal mangroves. The authors concluded from this and other evidence that the chief suspect of mangrove dieback was pesticide usage by the sugarcane industry, in particular the use of diuron. This report was challenged and it was argued that there was insufficient data to demonstrate higher herbicide concentrations in dieback areas than non-dieback areas and there was no evidence to indicate that the low herbicide concentrations were sufficient to kill mangroves.

In a subsequent report of further work investigating the cause of the mangrove dieback in the Mackay district diuron was found in all sediment samples at 0.1-8.2 μg/kg. It was also found in core water samples and in water column samples. Other possible causative agents were considered in the second report including heavy metal contamination, excessive nutrients, sediment burial and accessory factors. There was a strong correlation with the concentration of diuron in the sediments and the overall health of the mangrove but no correlation with other possible causative agents such as toxic heavy metals, excessive nutrients or burial. The investigators again concluded that there is strong correlative and some causative evidence implicating herbicides, particularly diuron, as a primary agent causing serious dieback of mangroves in the Mackay region.

The concentrations of diuron in sediment and seagrass located near important dugong habitats along the Queensland coast have also been determined. In the intertidal sediments, there were 3 detections from 16 sites tested (0.5, 1.7 and 0.6 μg/kg dw for Cairns, Cardwell and Moreton Bay respectively) and at the subtidal sites, diuron was detected at 9 of the 24 subtidal sites tested at concentrations up to 10.1 μg/kg dw. The highest detections were near river mouths draining the sugar growing areas. Diuron was also present in the seagrasses at 4 sites (0.6, 1.1, 0.8 and 1.7 μg/kg dw for Cairns, Cardwell, Pallarenda and Moreton Bay respectively). It is noted that the positive detections in the sediment also coincide with detections in the seagrasses and at comparable levels.

Low concentrations of diuron, together with other herbicides, were detected in surface waters and sediments in inter-tidal seagrass meadows in Hervey Bay, Queensland. Surface waters together with sediments were sampled in the seagrass meadows and the health of the seagrasses monitored as well. 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 and in the sediments at not detectable to 0.2 ng/kg dw. Sampling of the Mary River (major river flowing into Hervey Bay during the moderate flows) gave concentrations ranging from 15 to 105 ng/L but with the 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 seagrass at the sampling sites appeared healthy and there was positive growth and development during the study period. The authors conclude that with the low background levels herbicides in the water, predominantly diuron, there was no detectable impact on seagrass.

Monitoring Studies: Queensland

In a study that focused on pesticide contamination of sediments in irrigation channels and drains in various areas of Queensland diuron was detected in 72% of all samples, with the most frequent detections and highest concentrations of diuron generally occurring in drains from cotton crops. The range was from <0.36 to 340 μg/kg sediment dw.

Monitoring Studies: NSW

In a long-term study on pesticide contamination in rivers in the cotton regions of NSW, diuron was detected in all river basins near irrigated cotton and not necessarily associated with runoff events. Most detections were during the irrigation season and in the irrigation areas and the highest concentration of diuron was 24 μg/L from a runoff event. During this runoff event samples were taken in the Gwydir River during heavy rainfall and a maximum concentration of 24 μg/L occurred in the first runoff waters (first flush) then the concentration 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. Diuron was not reported from sediments in these rivers.

Monitoring in the southwestern irrigation areas of NSW over a 5-year period showed at times significant levels of diuron. The area is a major agricultural area comprising several irrigation schemes, and diuron is used for weed control in horticulture particularly citrus and in irrigation channels. Sampling of the main drains showed that in 41% of all samples taken diuron was detected and the maximum was 9.5 μg/L. Surface water was sampled monthly with diuron detected at least once per month at a maximum concentration of 5.4 μg/L. In one month 66% of the sampling sites gave positive detections of diuron. Approximately 40% of tile drains at 49 horticulture farms had detectable levels of diuron and the maximum concentration was 28 μg/L. Surface runoff following first irrigation at a citrus orchard had average of concentrations of diuron of 10.9 μg/L. Daily automatic monitoring of Mirrool Creek gave levels of between 0.05 and <1 μg/L and automatic monitoring of Little Mirrool Creek levels between 0.1 and 7.5 μg/L. It was concluded that this 5-year monitoring study shows that diuron is a contaminant of water from farms where diuron has been used.

Overseas monitoring studies

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

The Environment Agency (UK) conducts routine monitoring of pesticides in water and their results for diuron in 1996 and 1997 were summarized for fresh and marine waters. The level of diuron reported in the freshwater various considerable with the 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 3 sites in the UK and 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.

9.2.7 Summary of Fate and Behaviour

9.2.7.1 Hydrolysis

In a study conducted according to US EPA and EU Guidelines, there was no observable degradation at 25°C in the 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.

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 are considered reliable. At pH 7, there was insufficient degradation for determination of a half-life. There were 2 degradation products noted in the HPLC, only one of which was >10% of applied radioactivity (AR) and was identified as 3,4-dichloroaniline (DCA) by co-chromatography.

In a second study conducted according to US EPA Guidelines, there was only limited degradation of 1-2% at all pH values (5, 7 and 9) and it was concluded that the half-life was greater than 500 days. There were 2 degradates identified as N'-(3,4-dichlorophenyl)-N-methyl urea (DCPMU) and 3,4-dichloroaniline (DCA).

9.2.7.2 Photolysis

Aqueous Photolysis

The photolysis of diuron in buffered water was conducted according to US EPA Guidelines and to satisfy EU 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 to 6.7 to 22.4 days. 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. Two minor peaks in the HPLC were identified, one as 3-(4-chlorophenyl)-1,1-dimethyl urea or 3,4-dichlorophenyl urea and another as 3,4-dichloroaniline.

In a second study conducted according to US EPA guidelines, the photolysis of diuron was again first order and the half-life was determined as 9.0 days, 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 >10% of applied and were not identified.

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

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% 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 N'-(3,4-dichlorophenyl)-N-methyl urea (DCPMU).

9.2.7.3 Metabolism

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% of AR with 14.9% remaining in the soils and 3.36% as CO_2 (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, DCPMU and DCPU were identified.

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% 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% of MWHC) reduced the half-life to just 27 days. The TLC analysis identified 3 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 CO_2 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 2-compartment model to give a half-life of 112 days and a DT50 for DCPMU of 35 days. The analysis identified 2 metabolites by comparison with authentic samples: DCPMU and DCPU.

Aerobic aquatic metabolism
The aerobic aquatic metabolism of diuron was conducted according to EC SETAC-Europe Procedures using two sediment-water systems collected from two locations in the Germany, the River Erft, a river following 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 with the Erft sediment also mainly aerobic. The Hönniger sediment was essentially anaerobic at first (28 days) then became aerobic. Diuron moved fairly rapidly to the sediments where it was degraded quicker in the Erft system (half-life = 48 days) than in the Hönniger system (232 days). 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 the 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 the 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 2 main metabolites, m-CPDMU and DCPMU. The degradation pathway proposed is the same at for the previous aerobic aquatic metabolism study and involves two pathways, one demethylation while the other proceeds via 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.

Soil anaerobic 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 and then the soil was 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 only be recovered 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.

Anaerobic aquatic metabolism

The anaerobic aquatic metabolism of ^{14}C-diuron was studied under according to US EPA Guideline using a clay loam sediment (used for the aerobic aquatic metabolism study). The diuron was applied and then incubated in a dark under nitrogen at 25°C to give a degradation half-life of 1.2 days using first order kinetics. The main metabolite was 3-(3-chlorophenyl)-1,1-dimethyl urea (m-CPDMU) that reached 81% after 7 days, remained at that level till day 98 then declined to 15% of AR at the end of the study. Other metabolites detected were phenyl dimethyl urea (or fenuron - another herbicide, maximum 13% of applied), and 3-(3-chlorophenyl)-1-dimethyl urea (m-CPMU, maximum 18% 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 m-CPMU. In a supplemental report it is noted by the author that the reductive dechlorination is fast and explains the relatively short half-lives of diuron in this study.

Conclusions on metabolism

From the metabolism studies there appears to be two metabolic pathways for the degradation of diuron, one under aerobic conditions and other for anaerobic conditions. The aerobic pathway involves demethylation of the urea to give the metabolites DCPMU and DCPU, while the anaerobic pathway is quicker and involves dechlorination of the phenyl ring, a typical anaerobic degradation, to give m-CPDMU and PDMU.

The aerobic degradation rates (half-lives) in soil range from 20 to 119 days at 20°C, excluding one outlier at 372 days, and degradation is slower in cooler conditions, 143 days, at 10°C. The half-lives were similar in the aerobic aquatic degradation studies at 33 and 48 days, with one exception at 232 days but this system became anaerobic during the incubation period. It should be noted that in the study with the shortest half-life (33 days) conditions were marginally aerobic at the start and the anaerobic degradate m-CPDMU was the principal degradate, suggesting that conditions be came more anaerobic. The only other system that became anaerobic was the anaerobic soil degradation study but there was no degradation

during the anaerobic period. Under the continuous aquatic anaerobic conditions, the degradation is faster with a half-life of 1.2 days. This could be due to stronger anaerobic conditions but this is not clear from this report as only the redox range during the test was reported which indicated that conditions were reducing to strongly reducing.

9.2.7.4 Mobility in Soils

Adsorption/desorption

The adsorption/desorption of diuron was performed by batch equilibrium studies to meet US EPA Guideline using 4 soils agricultural soils. The Kocs 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 Kd values ranged from 261 to 661 but as these were generated from only one effective concentration and therefore may not reliable. The desorption data shows that there was considerable loss of diuron from one soil, 40% of the initially adsorbed diuron was lost after 5 cycles of desorption, compared to 7-17 % for the other 3 soil. It is noted that the Dover soil has the lowest amount of clay of the four soils studied.

The adsorption/desorption of diuron, m-CPDMU and PDMU (fenuron) in 5 soils was performed to meet US EPA Guidelines. Fenuron and m-CPDMU are both anaerobic metabolites of diuron. In the preliminary studies two soils showed <10% 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 Kocs 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 Kocs 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 Kocs ranged from 40 to 323 and is rated as being 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 fenuron, the screening results show Koc from 33 to 138 (high to very high mobility) and similar for the isotherm data. In all cases the metabolites were more mobile than the parent compound diuron.

The adsorption/desorption of DCPMU, a major aerobic metabolite of diuron, was performed in 4 soils to meet US EPA Guidelines. The Kocs 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 Kocs. The adsorption/desorption of DCPU, a major aerobic metabolite of diuron, was performed in 5 soils to meet US EPA Guidelines. The Kocs 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).

Field Lysimeters

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 2 kg ac/ha, there were 6 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 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 diuron and 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% 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 ($CO_3^{=}$) 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). For Nantuna, the diuron was in the 0-5 cm layer and for Langaveka more had moved into the 5-10 cm layer. The laboratory half-lives were 20 and 119 days for Nantuna and Langaveka soils respectively at 20°C, 70% MWHC.

It is concluded by Department of the Environment and Heritage that the study shows limited leaching at the lower rate but also indicates that at higher rates the leaching is proportionately higher.

9.2.7.5 Field Studies

Terrestrial 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% of target rate. All sites received natural rainfall plus additional irrigation to ensure monthly total 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 cm) after 238-301 days was 3-19% of the initially applied. The calculated half-lives (first order analysis) were calculated as 73, 141 and 135 days. The half–life of the metabolite DCPMU at the 3 sites was also calculated as 182, 231, 112 days.

There were occasional detections of diuron in the 15-30 cm 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 cm above the limit of quantification (LOQ = 0.020 mg/kg) at 0.023 mg/kg. DCPMU was mainly detected in the first 0-15 cm of the soil with only occasional detections lower down (15-30 cm with the highest at 0.028 mg/kg).

Terrestrial 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. Over the test, the Newark site received mainly natural rainfall amounting to 1659 mm while the California site was irrigated for the first 3 months and received 1 to 4 hours of irrigation per day.

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

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. At California 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% of the target rate, for some samples only one plot was analysed and with the normal high variability between plots, this is unsatisfactory.

Terrestrial Field Study 3

A terrestrial field study was conducted at 6 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 DAT. 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 is 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 cm soil sections only on 3 occasions. There were 3 additional detections deeper than 20 cm on day 0 but these are likely to be due to contamination during sampling.

Terrestrial Field Study 4

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. 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 of cultivation, irrigation etc but had bare soil and were not trash covered, as is normal practice. The effect of trash cover was examined separately.

The results of this study show that the Kocs 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 >250 days using a second order equation but these can be misleading as the DT90s were not reported.

The runoff of diuron and its leaching was also examined at these test sites. Runoff of diuron was monitored and <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 between 0.37-2.9 μg/L. Diuron was detected in a groundwater at a maximum concentration of ~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% 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 <15% of application rate (estimated graphically by DEH).

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.

Terrestrial Field Study 5

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 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 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 for 159 days when 19.6 mm (0.77 inches) fell.

The results of the soil analysis on the slope and berm showed that diuron dissipated with a DT50 of 142 days, calculated using a nonlinear 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 mm). There were no other detections of diuron or its metabolites in any other water sample.

The Department of the Environment and Heritage 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.

Terrestrial Field Study 6

A field dissipation and transport study was conducted as above 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 ~860 mm of rainfall.

The results of the soil analysis showed that diuron dissipated from the soil with a DT50 of 105 days calculated using a nonlinear regression analysis (first order analysis gives an average of 104 days). The metabolite DCPMU was detected in these soil samples, initially from 0 DAT 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 spraydrift. The concentration of diuron in the sediment near the treatment area shows a reasonably consistent level of around 0.5 mg/kg except for the 179 DAT with the highest value of 1.61 mg/kg. Only one metabolite was detected, that being DCPMU, with maximum concentration of 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 majority of positive detections from the scheduled water samples occurred 9 to 34 DAT, which appears to show limited aquatic exposure. However, the raw data for 48 DAT show levels of diuron only slightly below the limit of quantification. If this is a general situation, then the information tends to show 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 DAT) had most concentrations of diuron below the limit of quantification except for 152 DAT (event 10, first sample) when one of 2 duplicate analyses gave a reading of 10 μg/L.

It is concluded that while the study does show 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 tantalising hints as to the likely fate of diuron but due to the relatively insensitive limit of quantification used, further conclusions are speculative.

Terrestrial Field Study 7

A study was conducted in California 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 simulated runoff ranged from 144 to 1770 μg/L. Total mass of herbicide leaving the plots in runoff accounted for up to 5.4% 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% of the diuron in one 28-hr period.

Literature

In an existing tree orchard on a loam soil in Belgium, diuron was applied at 3 kg ac/ha to 2 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 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 ($r = 0.9984$) 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.

Conclusion on Field Studies

The overseas terrestrial field studies (12 sites) gave soil DT50s ranging from 67 to 231 days with one site having limited degradation. At 11 overseas sites there was no evidence of vertical movement but in one Californian study, there was evidence that diuron had moved vertically to lower soil profiles (45-60 cm). When diuron was used on the sides of irrigation channels (2 sites), the concentration of diuron in the channel water reached 130 μg/L and was >10 μg/L for a 3 week period at one site. This was related to rainfall at this site. At the other site diuron was not detected in the channel water but there was no rain and therefore no runoff into the channel but when it did rain (256 DAT), analysis of sediment showed that diuron had moved from the sides of the channel. When diuron was used on the sides of highways for weed control the concentration of diuron in runoff following simulate rain ranged from 144-1770 μg/L. Total mass of herbicide leaving the plots in runoff reached 5.4% of the applied diuron. Concentrations of diuron in natural rain runoff were from 46-2849 μg/L and up to 8.4% of the applied diuron ran off in one 28-hr period.

Australian field studies were conducted at sugarcane farms (3 sites) over 3 years in the Bundaberg region. The DT50 for diuron ranged from 6.5 to 20 days at 2 sites with one site having limited degradation every year and the DT50 was given as >250 days. Again there was no evidence of vertical movement at any of these sites. The concentration in diuron in runoff water was 0.37-120 μg/L and in groundwater the maximum was 6.5 μg/L.

9.2.7.6 Measured Field Concentrations

Monitoring Studies: Sugar cane

Diuron was been detected in sediment at 4, 0.8 and 3 μg/kg dw in samples taken from areas affected by mangrove dieback in the Pioneer River estuary and 0.2 μg/kg dw in one sample taken in an area of relatively normal mangroves. The authors concluded from this and other evidence that the chief suspect of mangrove dieback was pesticide usage by the sugarcane industry, in particular the use of diuron. This report was challenged and it was argued that there was insufficient data to demonstrate higher herbicide concentrations in dieback areas than non-dieback areas and there was no evidence to indicate that the low herbicide concentrations were sufficient to kill mangroves.

In a subsequent report on the cause of the mangrove dieback in the Mackay district, diuron was found in all sediment samples at 0.1-8.2 μg/kg. It was also found in core water samples and in water column samples. Other possible causative agents were considered in the second report including heavy metal contamination, excessive nutrients, sediment burial and accessory factors. There was a strong correlation with the concentration of diuron in the sediments and the overall health of the mangroves but no correlation with other possible causative agents examined such as toxic heavy metals, excessive nutrients or burial. The investigators again concluded that there is strong correlative and some causative evidence implicating herbicides, particularly diuron, as a primary agent causing serious dieback of mangroves in the Mackay region.

The concentrations of diuron in sediment and seagrass located near important dugong habitats along the Queensland coast have also been determined. In the intertidal sediments, there were 3 detections from 16 sites tested (0.5, 1.7 and 0.6 μg/kg dw for Cairns, Cardwell and Moreton Bay respectively) and at the subtidal sites, diuron was detected at 9 of the 24 subtidal sites tested at concentrations up to 10.1 μg/kg dw. The highest detections where near river mouths draining the sugar growing areas. Diuron was also present in the seagrasses at 4 sites (0.6, 1.1, 0.8 and 1.7 μg/kg dw for Cairns, Cardwell, Pallarenda and Moreton Bay respectively). It

is noted that the positive detections in the sediment also coincide with detections in the seagrasses at comparable levels.

Low concentrations of diuron, together with other herbicides, were detected in surface waters and sediments in inter-tidal seagrass meadows in Hervey Bay, Queensland. Surface waters together with sediments were sampled in the seagrass meadows and the health of the seagrasses monitored as well. 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 and in the sediments at not detectable to 0.2 ng/kg dw. Sampling of the Mary River (major river flowing into Hervey Bay during the moderate flows) gave concentrations ranging from 15 to 105 ng/L but with the 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 seagrass at the sampling sites appeared healthy and there was positive growth and development during the study period. The authors conclude that with the low background levels herbicides in the water, predominantly diuron, there was no detectable impact on seagrass.

Monitoring Studies: Queensland

In a study that focused on pesticide contamination of sediments in irrigation channels and drains in various areas of Queensland diuron was detected in 72% of all samples, with the most frequent detections and highest concentrations of diuron generally occurring in drains from cotton crops. The range was from <0.36 to 340 μg/kg sediment dw.

Monitoring Studies: NSW

In a long-term study on pesticide contamination in rivers in the cotton regions of NSW, diuron was detected in all river basins near irrigated cotton and not necessarily associated with runoff events. Most detections were during the irrigation season and in the irrigation areas and the highest concentration of diuron was 24 μg/L from a runoff event. During this runoff event samples were taken in the Gwydir River during heavy rainfall and a maximum concentration of 24 μg/L occurred in the first runoff waters (first flush) then the concentration 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. Diuron was not reported from sediments in these rivers.

Monitoring in the southwestern irrigation areas of NSW over a 5-year period showed at times significant levels of diuron. The area is a major agricultural area comprising several irrigation schemes, and diuron is used for weed control in horticulture particularly citrus and in irrigation channels. Sampling of the main drains showed that in 41% of all samples taken diuron was detected and the maximum was 9.5 μg/L. Surface water was sampled monthly with diuron detected at least once per month at a maximum concentration of 5.4 μg/L. In one month 66% of the sampling sites gave positive detections of diuron. Approximately 40% of tile drains at 49 horticulture farms had detectable levels of diuron and the maximum concentration was 28 μg/L. Surface runoff following first irrigation at a citrus orchard had average of concentrations of diuron of 10.9 μg/L. Daily automatic monitoring of Mirrool Creek gave levels of between 0.05 and <1 μg/L and automatic monitoring of Little Mirrool Creek levels between 0.1 and 7.5 μg/L. It was concluded that this 5-year monitoring study shows that diuron is a contaminant of water from farms where diuron has been used.

Overseas monitoring studies

The United States Geological Survey (USGS) conducted a large water quality program in 20 hydrologic basins. 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 seems to indicate that diuron is not a significant leacher but it does enter surface waters. The maximum concentration occurred in surface drainage from agricultural area (14 μg/L) but surface water from urban areas also had high levels (8.04 μg/L). Sampling in larger river and streams gave lower levels with maximum of just 1.2 μg/L.

The Environment Agency (UK) conducts routine monitoring of pesticides in freshwater and their results for diuron in 1996 and 1997 were summarized for fresh and marine waters. The level of diuron reported in the freshwater varied considerably with the 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 3 sites in the UK and 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.

9.3 Ecotoxicity

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" (i.e. 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 Department of the Environment and Heritage 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).

There are numerous additional reports in the open scientific literature or in the US EPA ECOTOX database[6] – in general, these have not been consulted for this assessment except those specifically designed for reef organisms and plants where there is a high level of concern and are key to the scope of this review.

9.3.1 Toxicity to Aquatic Organisms

9.3.1.1 Algae

As might be expected, given that diuron is a herbicide, algae were much more sensitive to diuron than fish or aquatic invertebrates. Only one study was submitted by an applicant.

[6] The US EPA ECOTOX database is publicly available on the US EPA website (http://www.epa.gov/ecotox/) - it is largely based on various types of studies published in the scientific literature in regard to industrial chemicals as well as pesticides, but may also include unpublished GLP studies to standard guidelines.

Green alga

The effect of diuron (technical) 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 EC_{50} for growth was determined as 11 (CI 7.3-16.3) µg/L (probits) and the NOEC was <1.0 µg/L.

Pesticide EcoToxicity Database

Available data from Pesticide Ecotoxicity database and US EPA RED (US EPA 2003) indicate that diuron can generally be classified as very highly toxic to aquatic plants, including algae and diatoms (Table 59). The EC50s for green algae (Chlorophyceae) ranged from 2.4 to 37 µg ac/L making these algae the most sensitive but the brown and red algae species tested fell into this range.

Table 59: 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)				
Porphyridium 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 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, see Table 59. The EC50 value for the prolonged 10-day data shown in Table 59 is also within a similar range of 10-20 µg/L, i.e. the durations more commonly used in algal toxicity tests. Consideration of these results does not

indicate whether diuron is algistatic or algicidal, although it is likely that at lower concentrations diuron will be algistatic, i.e. after a brief exposure the algae will grow normally when returned to a clean medium.

9.3.1.2 Corals

Toxicity of Photosystem II Herbicides to Corals

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 dinoflagellates (unicellular algae) that live symbiotically in the gastrodermis of the coral organisms[7]. Pulse-Amplitude Modulated (PAM) chlorophyll fluorescence techniques were used to examine changes in the maximum effective quantum yield ($\Delta F/F'_m$) of symbiotic dinoflagellates within the host tissues of the coral[8].

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 $\Delta F/F'_m$ and 24 h for F_v/F_m). The EC50 for $\Delta F/F'_m$ 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 $\Delta F/F'_m$ 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 (see Table 59 above). 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:

- $\Delta F/Fm'$ was reduced within minutes by exposure to diuron but recovered quickly on return to fresh running seawater; after 5 hours, $\Delta F/Fm'$ recovered to within 5% of control value.
- the effects of diuron (3 µg/L for up to 8 h) on $\Delta F/F'_m$ 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 $\Delta F/F'_m$ between different temperatures.

There were repeated exposures to pulses of cybutryne – a triazine herbicide but not using diuron. These pulsed exposures (daily 2 h exposure to 30 µg/L over 4 d) using cybutryne resulted in a 30% decrease in the density of symbiotic dinoflagellates in the tissues of *Seriatopora hystrix*. Whether similar effects may be expected from pulse exposure to diuron is unknown, although it would be reasonable to assume that such effects could occur at some

[7] 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. Hhttp://ag.arizona.edu/azaqua/algaeclass/symbios.htmH; Hhttp://www.wfu.edu/users/braukm0/coralsymbiosis.htmlH; Levy et al (2003) and Salih, Hoegh-Guldberg and Cox (1998).

[8] See footnote 2

concentration (cybutryne was more toxic than diuron to *Seriatopora hystrix* in the short-term study - EC50 = 0.7 µg/L).

Toxicity of Diuron and Atrazine to 4 Coral Species

Another paper by the same principal researcher (Jones, Müller, Haynes and Schreiber 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 (*ΔF/Fm*) 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 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 *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 $\Delta F/F'_m$ 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 $\Delta F/F'_m$ and F_v/F_m, 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. If sufficient concentrations and duration of exposure to diuron were to occur it is likely that coral bleaching may also occur.

The $\Delta F/F'_m$ 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* (in host; in the coral tissue) was 3.7 µg/L.

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.

Impact of Diuron on the Metabolism of the coral Porites cylindrical

The effect of diuron (and 2,4-D) on the hermatypic coral *Porites cylindrical* was investigated (Råberg, Nyström, Erös and Plantman, 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 ($\Delta F/F'_m$) and non-photochemical quenching[9]) 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 ($\Delta F/F'_m$) and non-photochemical quenching but no effects (p = 0.05) on maximum quantum yield and respiration compared to control values.

[9] The non-photochemical quenching is measured from (Fm-F'm)/(Fm-Fs) which shows the light energy dissipation via heat.

Impact of reduced photosynthetic yields on coral reproduction

Coral colonies of *Acropora tenuis* were exposed to diuron concentrations of 1 µg/L and 10 µg/L for 52 days and compared to control colonies on the reef (Cantin, 2004). Exposure was concluded when the first adult colony visibly set to spawn, then gametes from the reef control and 10 µg/L colonies were collected for larval metamorphosis trials. The larvae from corals exposed to 1 µg/L of diuron showed visible bleaching and reduced photosynthetic yields (Fv/Fm) while larvae from the 10 µg/L exposures lack zooxanthellae and were almost completely bleached. Larval settlement and metamorphosis of larvae that lacked zooxanthellae was not reduced by constant 10 µg/L diuron exposure during gamete development compared to larvae from control colonies on the reef. However, after settlement, the corals from larvae that were exposed to 10 µg/L of diuron remained pale and even those exposed to just 1 µg/L were paler than the controls, i.e. less zooxanthellae than controls (Andrew Negri, personal communication).

These results indicate that while coral colonies may be under high photosynthetic stress due to diuron exposure, they are capable of acquiring sufficient energy for reproduction in order to produce viable gametes, but there could be effects on the larvae themselves.

Conclusion

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* EC50 for $\Delta F/F'_m$ (reduction in quantum yield, a measure of the change in photosystem II fluorescence) of 2.3 µg/L, NOEC < 0.3 µg/L and LOEC = 0.3 µg/L. The other corals gave an EC50 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.

Another paper reported studies with diuron and four species of coral (those above, *Seriatopora hystrix* and *Acropora formosa*, plus *Montipora digitata* and *Porites cylindrica*), again using chlorophyll fluorescence techniques. The measured EC50s based on $\Delta F/F'_m$ ((maximum effective quantum yield:10 hours exposures, 100 µmol 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 the EC50 from 3.7 µg/L at 'normal' light levels to 2.9 µg/L at 75% shading. The effect of reduced salinity was also examined (35 to 27 part per thousand) but there was no significant interaction between diuron and the reduced salinity levels. Exposure 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 cylindrical* has been reported. The corals were exposed to 3 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 control. 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.

In a report on the effects of diuron on coral reproduction, coral colonies of *Acropora tenuis* were exposed to diuron at concentrations of 1 µg/L and 10 µg/L for 52 days and the coral spawning compared to control coral colonies on the reef. The larvae from corals exposed to 1 µg/L of diuron showed signs of visible bleaching and had reduced photosynthetic yields (measured by Fv/Fm: maximum potential quantum yield) while larvae from the 10 µg/L exposures lack zooxanthellae and were almost completely bleached. Larval settlement and metamorphosis was not affected compared to the reef controls although the larvae and new corals remained paler and bleached compared to controls. These results indicate that while coral colonies may be under high photosynthetic stress due to diuron exposure, reproduction is not affected and they produce viable gametes.

9.3.1.3 Aquatic and semi-aquatic plants

Duckweeds

There are no duckweeds studies in the US EPA Ecotoxicity database and reported in the US EPA RED (US EPA 2003), but there are 3 reports listed for diuron on the US EPA ECOTOX database (see footnote 6, page 101) 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* (large duckweed):[10] 7 d EC50 = 41 µg/L.

From the plant descriptions below (Footnote 10), *Lemna perpusilla* appears to be similar to the standard test species *Lemna gibba* and *Lemna minor*, whereas *Spirodela polyrhiza* (*Lemna major*) is a larger plant with more roots per frond. These literature studies are reviewed below.

Effects of herbicides on 2 Lemna species

The purpose of the study was to identify the toxicity to aquatic non-target species of a range of herbicides including diuron (Liu and Cedeno-Maldanado, 1974). 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 (fluometron, ametryn and prometryn as well as diuron), under controlled laboratory conditions from cultures maintained in exponential growth. The test species were *Lemna major* (*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

[10] Both species are noted in Annex 1 of draft OECD Guideline 221 (*Lemna* sp. Growth Inhibition Test) as duckweed species that have been used for toxicity testing. However, despite prior use of other species, *Lemna gibba* and *Lemna minor* are the only species recommended under the 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. Reasons for not using the other species may include their relative occurrence in the environment, ease of culture and maintenance in a vegetative state, and relative size and sensitivity to toxicants. NPWRC (undated) indicates that *Lemna perpusilla* flowers and fruits more freely than other duckweeds (a potential disadvantage for use as a standard test species) and from the descriptions provided appears to have slightly smaller fronds (1-3.3 mm long) than *Lemna gibba* and *Lemna minor* (2-5 mm and 2-4 mm, respectively), whereas *Lemna major* appears to have slightly larger fronds (3-6 mm long) with 4-9 roots per frond and other differences leading it to be now classed as a different genus.

from plots of increase in frond number as a % of the control against concentration (data for the four replicates are not available, hence DEH has not recalculated these according to standard methods). The resulting estimates for *L. major* and *L. perusilla* were 1.75 X 10^{-7} M (41 μg/L) and 6.4 X 10^{-8} M (15 μg/L), respectively.

Phototoxicity of Diuron to Lemma minor
The purpose of the study was to compare the toxicity of diuron alone and in combination with two other toxicants, copper and folpet to duckweed (*L. minor*) (Teisseire, Couderchet and Vernet, 1999). 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.

Effect of Diuron and its Metabolites on Lemna gibba.
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, Marchand, Eullaffroy and Popovic, 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, 2, 25 and 100 μg/L and then the PSII operational quantum yield[11] 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). 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. The level of reduction was 5.6, 27, 79 and 93% compared to control for diuron, DCPMU, DCPU and DCA respectively, at concentrations of 50 μg/L for both diuron and DCPMU and 100 μg/L for DCPU and DCA.

It is concluded that both DCPU and DCA are unlikely to have significant herbicidal activity but that the metabolite DCPMU is herbicidal and its activity is approximately 75% of that of diuron in this test using duckweed.

Seagrasses
The effect of diuron on three species of seagrasses has been studied using PAM fluorometer (Haynes, Ralph, Pranges and Dennison, 2000). The seagrasses were wild collected together with sediment (Moreton Bay, Australia) and were identified as *Halophila ovalis*, *Cymodocea*

[11] 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."

serrulata and *Zostera capricorni.* The authors note 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. 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. The results were expressed as effective quantum yield.

Analysis of the water column for diuron gave initial values of 0.1/0.1, 0.9/0.8, 8.1/8.4 and 86/100 μg/L for each duplicate and after 5 days the levels of diuron were similar. Average concentrations for each test concentration were 0.1, 0.9, 7.8 and 85 μg/L.

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* and *Z. capricorni* were depressed for all test concentrations (30 and 10% of control respectively at 0.1 μg/L), with *H. ovalis* showing the most effects at all test concentrations. 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 μg/L) for all seagrass species (Dunnet's Test).

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 0.1 μg/L in the water column. The authors note that with measured concentrations of diuron in sediment at up to 10 μg/kg, partitioning models indicate that the overlaying concentration could reach 1 μg/L which is within range to inhibit photosynthesis in seagrasses. The Department of Environment and Heritage notes that while photosynthesis could be affected, this on its own would not lead to mortality of seagrasses unless additional environmental stressors were involved, eg storm damage, sedimentation, grazing etc. 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.

Mangroves

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 60.

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. The Department of the Environment and Heritage 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 60: Concentration of diuron (µg/kg dw) in the upper 1 cm layer of sediment from the mangrove study. Samples pooled from 6 pots.

Initial dosage µg/kg dw of sediment	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 leave 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.

While atrazine showed the quickest and highest phototoxicity as measured by the PAM method after 14 days, by 71 days the atrazine treated plants had recovered to be similar to control. This was considered to be due to atrazine degrading in the sediments.

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. Based on 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.

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 Study
Duke *et al* (2003) also 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. 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, although the data set is very limited.

Attachment 2 gives the measured concentrations of diuron in sediment (vertical) against the upstream distribution of *A. marina* from the mouth (reading from right to left) in 5 estuaries, 3 with dieback of the mangrove species *A. marina* and 2 showing no effects. 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 were conducted through the mangroves and these 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.

While the field studies in the Duke report are not absolute proof, they do show that with

diuron concentrations in sediment >2 μg/kg effect on the sensitive mangrove species *Avicennia marina* (the common mangrove) could be expected and at higher levels of diuron in sediments other mangrove species may also show symptoms. This is in contrast to the preliminary laboratory trial where effects were only noted at 4000 μg/kg. One possible interpretation is that under field conditions there are additional stressors not taken into account by the laboratory trial.

Conclusion

Duckweed
There are currently no studies with diuron conducted to a current internationally accepted guideline using duckweed. There is an old scientific literature report showing EC50 values of 41 μg/L for *Lemma 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 *Lemma gibba*, the standard test organisms. A more modern literature report gives the IC50 (inhibition of growth) for *Lemma 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.

Seagrasses
The effect of diuron on three species of seagrasses, collected from the wild and were 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 only depressed at the two highest test concentrations. 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 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. The authors note that with measured concentration of diuron in sediment at up to 10 μg/kg, partitioning models indicate that overlaying concentration could reach 1 μg/L, which is within the range to inhibit photosynthesis in seagrasses.

It was 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 0.1 μg/L in the water column.

Mangroves
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") has been reported. 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 dw of sediment), using herbicide dissolved in water to which "commercially bought" clay was then added and mixed to simulate natural run-off conditions.

A potentially confounding effect on the rate treatments in this preliminary study was that for

each replicate all four treatments were contained within the same tank, receiving the same simulated tidal water. However, the concentrations of diuron in sediment (top 1 cm), taken at intervals up to 71 days after dosing, show a gradual decline except for the lowest test concentration where there was a slight increase.

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 significant compared to 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 ~340 μg/kg leaf (dry weight) and *A. corniculatum* was the second highest with ~230 μg/kg.

The research suggested that the salt-excreting mangrove species were more vulnerable to diuron and other herbicides than salt-excluding ones. Based on 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 Study
In areas where there was dieback of mangroves there were measurable concentrations of diuron in the sediments (0-2 cm), ranging from 1.2 to 8.2 μg/kg. However, where there was no dieback the concentrations of diuron measured were <1.2 μg/kg in the sediments (0-2 cm). 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 2 small areas, this was not wide spread and considered due to localised effects. While the field studies are not absolute proof, they do show that with diuron concentrations in sediment >2 μg/kg effect sensitive mangrove species.

9.3.1.4 Aquatic and benthic organisms

Crustose Coralline Algae
The effect of diuron on crustose coralline algae from the Great Barrier Reef area has also been examined (Harrington, Fabricius, Eaglesham and Negri, 2004). Crustose coralline algae 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 crustose coralline algae). Consequently changes in crustose coralline algae abundance can result in changes in the structure, function and abundance of corals in reef ecosystems. The paper looked at the effect of diuron, several 'clean' sediments and diuron with sediment using Pulse-Amplitude Modulated (PAM) chlorophyll fluorescence techniques to examine changes in the maximum effective quantum yield ($\Delta F/F'_m$) in the algae tissues[12] on 4 species of crustose coralline algae.

[12] cf. in plants (Marwood et al 2001): "Stimulation of fluorescence from chlorophyll-*a* in photosystem II (PSII) reaction centres under different light conditions produces several parameters, each describing the efficiency of a photochemical reaction or process within the photosynthetic apparatus. The variable fluorescence ratio F_v/F_m, which describes the maximum efficiency of PSII photochemistry, is calculated from the minimum fluorescence (F_o) in the dark and the maximum fluorescence (Fm) on application of a saturating light to the dark-adapted

For diuron only exposures the crustose coralline algae species *Porolithon onkodes* and *Titanoderma prototypum* were exposed to diuron in clean seawater for 72 hours. The dose-response curve was flat and all tested concentrations (0.1 to 30 µg/L) gave similar responses for maximum effective quantum yield ($\Delta F/F'_m$ 65-45% of control value). The LOEC was 0.1 µg/L of diuron. This effect was considered to be reversible. Visible effects were noted at 30 µg/L of diuron with patchy loss of pigment in both species and there was no mortality.

In the tests using 4 different sediments [fine estuarine silt (<63 µm), medium estuarine sand (63-250 µm), fine offshore sediments (<63 µm) and calcareous sediment (sawdust from dried corals, <63 µm)], field collected and not dosed with diuron, the fine estuarine silt and offshore sediment inhibited the $\Delta F/F'_m$ more than the other sediments. The sediments were mixed with the tank water to ensure uniform distribution and were applied at approximately 100 mg/cm^2. *Neogoniolithon fosliei* and *P. onkodes* were more sensitive than *Hydrolithon reinboldii* (the most abundant crustose coralline algae species on the inshore reefs in the GBR). After exposure for 105 hours, the sediment was gently removed from the crustose coralline algae and these were then transferred to clean seawater. All species exposed to the 4 different sediments had fully recovered their photosynthetic capacity to be comparable with controls within 4 days except *P. onkodes* that was exposed to the fine estuarine silt which only recovered to be 80% of control and showed loss of pigmentation. [It should be noted that the fine estuarine silt used was contaminated by diuron at 0.28 mg/kg.]

The authors also note that the morphology of *H. reinboldii*, with pits and crevices, differs from the other two species used that were flat and smooth. In the test it was observed that the sediment did not settle evenly on *H. reinboldii* and much of the surface remained uncovered, which could have affected the measurements of the photosynthetic yields (the tip of the probe measures the fluorescence from an area 5.5 mm in diameter).

In the final experiments, diuron and fine estuarine silt sediment were tested independently as well as in combination using *P. onkodes* for 105 hours (exposure period), then 9 days in clean seawater (recovery period). For the diuron only exposures the concentrations used were 1.0, 3.0, 10 and 30 µg/L. The sediments were applied as previous. There was an initial drop in $\Delta F/F'_m$ for all treatments but the lower treatments reverted to control and only 30 µg/L remained lower than control during the exposure period. Visible bleaching occurred but only following exposure to highest level of diuron (30 µg/L). There was complete recovery of the $\Delta F/F'_m$ back to control levels after 3.5 days in clean seawater for all the diuron alone treatments. For sediment alone the $\Delta F/F'_m$ decreased steadily and was <20% of control by the end of the exposure period. Recovery was slow and only reached 80% of control after 9 days.

For the combination test, diuron was added to fine estuarine sediments suspended in seawater for 24 hours (at 1.0, 3.0, 10 and 30 µg/L nominal of final test volume) before the contaminated wet sediments were distributed over the crustose coralline algae for 105 hours. The $\Delta F/F'_m$ was <30% of control for all treatments after 35 hours and recovery was slow and remained only 60% of control after 9 days in uncontaminated seawater. Some fragments died (17%), with 59% showing bleached portions.

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plant. The minimum (F_s) and maximum ($F'm$) fluorescence levels in the light-adapted plant are used to calculate $\Delta F/F'm$, the quantum yield of photochemistry in functional PSII reaction centres during steady-state photosynthesis. This parameter represents the efficiency with which excitation energy captured by the chlorophyll antenna is used in electron transport."

The combination test used the sensitive species *P. onkodes* rather than the less sensitive inshore species *H. reinboldii*. Note that *P. onkodes* is dominant on mid and offshore reefs and the second most common crustal algae on non-impacted inshore reefs but rare on impacted inshore reefs, while *H. reinboldii* remains common on inshore reefs, included those that are impacted by anthropogenic activities (Andrew Negri, personal communication).

Conclusion
Diuron is rated as highly toxicity to algae according to the US EPA classification. From the US EPA RED, the acute toxic of diuron to algae (LC50s) ranges from 2.4 to 95 μg ac/L.

Marine crustose coral algae are very sensitive to the effects of diuron with a LOEC of 0.1 μg/L for diuron alone in clean water. For sediment alone there was a significant effect on photosynthesis and recovery was slow. However, when the diuron was adsorbed to the sediment beforehand, simulating a runoff event, photosynthesis was reduced the quickest and more significantly than the other two tests using diuron or sediment alone. Recovery was also the slowest of the 3 treatments and there was mortality of the algae (17%), not noted in the other treatments, together with significant bleaching (59%) at 1 μg/L and above.

Other Invertebrates

Only one study was submitted.

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.

Pesticide EcoToxicity Database
While there are only two studies reported in the Pesticide Ecotoxicity database and US EPA RED (US EPA 2003) on chronic exposure to diuron, there are a number of studies on acute toxicity, see Table 61. The most sensitive acute result was LC50 of 0.16 mg/L for scud and for chronic toxicity was LOEC of 0.2 mg/L and NOEC of <0.2 mg/L for *Daphnia magna*. Diuron is rated as moderately to highly toxic to aquatic invertebrates.

Table 61: Summary of aquatic toxicity studies with diuron – aquatic invertebrates, acute and chronic exposure.

US EPA Guideline	Comments	Toxicity (95% confidence limits)	Year reported[1]	US EPA category[2]
Water flea (*Daphnia magna*)				
72-2b – acute exposure	Active constituent (80%); Static conditions	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 conditions	28 d LOEC = 0.2 mg/L NOEC = not determined (assumed to be <0.2 mg/L)	1979	Supplemental
Water flea (*Daphnia pulex*)				
72-2a – acute exposure	Active constituent (80%) – 1st instar; Static conditions	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 conditions	48 h EC50 = 2.0 (1.4-2.8) mg/L; NOEC = NR	1980	Core
Mysid shrimp (*Mysidopsis bahia*)				
72-3a – acute exposure	Active constituent (99%) static conditions	96 h LC50 = 1.1 (0.97-1.3) mg/L; NOEC = 0.6 mg/L	1987	Supplemental
72-3a – acute exposure	Active constituent (99%) static conditions	96 h LC50 = 1.2 (1.0-1.6) mg/L; NOEC = 0.6 mg/L	1987	Supplemental
72-4b	Active constituent (96.8%) early life stage; Static conditions	28 d LOEC = 0.56 mg/L NOEC = 0.27 mg/L	1992	Core
Scud (*Gammarus*)				
72-2a – acute exposure	Active constituent (95%) – embryo/larvae, static conditions	96 h LC50 = 0.16 (0.13-0.19) mg/L; NOEC = NR	1980	Core
Brown shrimp (*Penaeus aztecus*)				
72-3 – acute exposure	Active constituent (95%) Flow-through conditions	48 h LC50 = 1.0 mg/L NOEC = NR	1986	Supplemental
Eastern oyster (*Crassostrum virginica*)				
72-3 – acute exposure	Active constituent (96.8%) Flow-through conditions	96 h EC50 = 4.8 mg/L NOEC = 2.4 mg/L	1991	Core
72-3b – acute exposure	Active constituent (96.8%) Flow-through conditions	96 h EC50 = 1.8 mg/L NOEC = NR	1986	Core

[1] Only the year when study was done as reported in Pesticide EcoToxicity Database,;
[2] Category as listed on the US EPA Ecological Effects Branch Pesticide EcoToxicity Database. NR = Not reported

Conclusion
According to the US EPA classification, diuron is rated as slightly toxic to *D. magna*. From the US EPA RED (US EPA 2003), the acute toxicity of diuron to aquatic invertebrates (LC50s) ranges from 0.16 to 6.7 mg ac/L, corresponding to a rating of moderately to highly toxic. Chronic data from the database is limited to 2 studies with the most sensitive LOEC of 0.2 mg ac/L for *D. magna* and NOEC of <0.2 mg ac/L and the other for mysid shrimp gives 28 day LOEC and NOEC of 0.56 and 0.26 mg ac/L respectively and a MATC of 0.39 mg ac/L.

9.3.1.5 Fish

Acute
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 LC_{50} 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.

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 LC_{50} 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 62). 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.

Hepatotoxicity of Diuron to Australian Marine fish
The toxicity of diuron to pink snapper (*Pagrus aratus*) was measured by its affect 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 μg/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 μg/L compared to control ($p < 0.0380$) and there was an increase at 5 μg/L that was not significantly different (Tukey's Test).
The Department of Environment and Heritage 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 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.

Table 62: Summary of aquatic toxicity studies with diuron – fish, acute and chronic exposure.

US EPA Guideline	Comments	Toxicity, LC50 mg/L test substance (95% CL)	Year reported[1]	US EPA category[2]
Bluegill sunfish (*Lepomis macrochirus*)				
72-1 96 h	Active constituent (28%); static conditions	84.0 (68.3-103.3)	1975	Core
	Active constituent (95%); static conditions	3.2 (2.53-4.05)	1976	Core
	Active constituent (95%); static conditions	2.8 (2.3-3.3)	1986	Core
	Active constituent (80%); static conditions	>300 (NR)	1991	Core
Rainbow trout (*Oncorhynchus mykiss*)				
72-1 96 h	Active constituent (28%); static conditions	23.8 (20-28.3)	1975	Core
	Active constituent (95%); static conditions	1.95 (1.5-2.54)	1976	Core
	Active constituent (80% WP); static conditions	16 (11-23)	1980	Supplementary
	Active constituent (80%); static conditions	19.6 (NR)	1991	Core
Fathead minnow (*Pimephales promelas*)				
`72-1	Active constituent (98.6%); static conditions	14.2 (13.4-15.0)	1975	Supplementary
Cutthroat trout (*Oncorhynchus clarki*)				
72-1 96 h	Active constituent (95%) static conditions	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 conditions	2.4 (NR)	1986	Supplementary
Lake trout (*Salvelinus namaycush*)				
72-1 96 h	Active constituent (95%) static conditions	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 conditions	6.3 (NR)	1986	Supplementary
Sheepshead minnow (*Cyprinodon variegates*)				
72-3, 96 h	Active constituent (99%) static conditions	6.7 (NR) NOEC = 3.6	1986	Core

[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

Chronic

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. The Department of the Environment and Heritage 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.

Pesticide EcoToxicity Database
There are two studies reported in the Pesticide Ecotoxicity database and US EPA RED (US EPA 2003) on chronic exposure of fish to diuron, see Table 63. The most sensitive result was LOEC of 61.8 µg/L and NOEC of 26.4 µg/L for fathead minnow. From the acute toxic results in the database fathead minnow are not the most sensitive test species for diuron.

Table 63; 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 reported[1]	US EPA category[2]
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 MATC = 40.4 µg/L	1975	Core
Sheepshead minnow (*Cyprinodon variegates*)				
72-4a early life stage study (38 days total)	Active constituent (96.8%) – flow through conditions	LOEC = 440 µg/L NOEC = NR	1992	Supplementary

1 Only the year when study was done as reported in US EPA Pesticide EcoToxicity Database; [2] Category listed on the US EPA Pesticide EcoToxicity Database

Conclusion
Diuron is rated as slightly toxic to rainbow trout for acute exposure, according to the US EPA classification, and for prolonged toxicity the LC50 (14 days) was 8.8 (CI 7.9-9.8) mg/L with a NOEC of 5 mg/L. From the US EPA Pesticide EcoToxicity Database, the range of acute LC50s for diuron is from 0.67 to 23.5 mg ac/L, excluding one entry of 240 mg ac/L, corresponding to a rating of slightly to highly toxic. Diuron affects the livers of pink snapper (*Pagrus aratus*), measured using sorbitol dehydrogenase (SDH) 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 while diuron is only moderately toxic to fish, diuron is causing hepatocellular toxicity at considerably lower levels.

Chronic data from the database is limited to 2 studies with the most sensitive LOEC of 61.8 µg ac/L and NOEC of 26.4 µg ac/L (MATC = 40.4 µg ac/L).

9.3.2 Toxicity to Terrestrial Organisms

9.3.2.1 Invertebrates

From the US EPA RED (US EPA, 2003), diuron can be classified as virtually non-toxic to honeybees (>100 µg ac/bee, see Table 64), and is rated as non-toxic to bees (Tomlin, 2003). Diuron is considered as non-toxic to earthworms,
(see http://pubs.cas.psu.edu/freepubs/pdfs/uc182.pdf).

Table 64: Summary of bee toxicity studies with diuron.

US EPA Guideline	Source	Comments	Toxicity	Year reported
Honey Bee (*Apis mellifera*)				
141-1 –	US EPA RED	Tech. 48 hr; contact exposure	EC50 = 145 µg/bee	1975

9.3.2.2 Birds

The applicants provided no data. From the Pesticide EcoToxicity Database and the US EPA RED (US EPA 2003), the 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. There was no chronic exposure/reproductive NOEL and LOEL reported. These results are summarised in Table 65.

Table 65: 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	Reference or year reported[1]	US EPA category[2]
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
71-2a – sub-acute dietary exposure	Active constituent (>95%) - 9 days old, 8 day study duration	LC50 = 1730 (1482-2035) ppm; NOEL = NR	1975	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
71-2b – sub-acute dietary exposure	Active constituent (>95%) – 10 day old ducklings, 8 day study duration	LC50 = >5000 ppm; NOEL = NR	1975	Core
Ring neck pheasant (Phasianus spp)				
71-2 – sub-acute dietary exposure	Active constituent (>95%) – 15 day old chicks, 8 day study duration	LC50 = >5000 ppm; NOEL = NR	1975	Core
Japanese quail (Coturnix japonica)				
71-2 – sub-acute dietary exposure	Active constituent (>95%) – 12 day old chicks, 8 day study duration	LC50 = >5000 ppm; NOEL = NR	1975	Core

[1] Reference cited where it has been provided - where the summary has been obtained from the US EPA Pesticide EcoToxicity Database, only the year has been cited;
[2] Category listed on the US EPA Pesticide EcoToxicity Database. NR = not recorded

9.3.2.3 Mammals

The data in Table 66 are from Tomlin (2003) and the Department of the Environment and Heritage has not seen the full reports. These show that diuron has low acute toxicity to rats and that its chronic toxicity to rats and dogs is low.

Table 66: Summary of toxicity to mammals.

Test	Species	Result
Acute oral	Rat	LD_{50} > 3000 mg/kg
Chronic toxicity	Rat 2 years	NOEL = 250 mg/kg in diet.
	Dog, 2 years	NOAEL = 125 mg/kg in diet.

9.3.2.4 Terrestrial Plants

Table 67 summarises toxicity studies from the US EPA RED (US EPA 2003) for the effects of diuron applied to soil on seedling emergence or applied to young seedlings on seedling growth, according to US EPA guideline 123-1 (Tier 2 studies, conducted in 1999). As expected, diuron is phytotoxic at very low rates, ranging from 0.44 to 0.0022 kg/ha based on EC25 data for vegetative vigour, but species clearly differ widely in their susceptibility to diuron.

Table 67: Summary of terrestrial plant toxicity studies with diuron. All studies used technical, 96.8 to 97.3% active.

Species		EC25 (kg/ha)	EC05 (kg/ha)	Effect	US EPA category[1]
Common name	Taxonomic name				
US EPA Guideline 123-1a – seedling emergence					
Corn	*Zea mays*	6.4	0.84	Shoot height	Core
Sorghum	*Sorghum bicolor*	0.91	0.84	Shoot height	Core
Onion	*Allium cepa*	0.11	0.10	Shoot dry weight	Core
Wheat	*Triticum aestivum*	1.18	0.43	Shoot dry weight	Core
Pea	*Pisum sativum*	>13.4	13.4	Shoot height	Core
Soybean	*Glycine max*	<13.4	13.4	Shoot height	Core
Cucumber	*Cucumis sativus*	0.38	0.21	Shoot dry weight	Core
Rape	*Brassica napus*	0.11	0.053	Shoot dry weight	Core
Sugar beet	*Beta vulgaris*	0.10	0.053	Shoot dry weight	Core
Tomato	*Lycopersicon esculentum*	0.09	0.053	Shoot dry weight	Core
US EPA Guideline 123-1b – plants vegetative vigour					
Corn	*Zea mays*	0.44	0.21	Shoot dry weight	Core
Sorghum	*Sorghum bicolor*	0.084	0.013	Shoot dry weight	Core
Onion	*Allium cepa*	0.17	0.11	Shoot dry weight	Core
Wheat	*Triticum aestivum*	0.013	0.0022	Shoot dry weight	Core
Pea	*Pisum sativum*	0.016	0.0034	Shoot dry weight	Core
Soybean	*Glycine max*	0.013	0.0022	Shoot dry weight	Core
Cucumber	*Cucumis sativus*	0.006	0.006	Shoot dry weight	Core
Rape	*Brassica napus*	0.037	0.013	Shoot dry weight	Core
Sugar beet	*Beta vulgaris*	0.01	0.006	Shoot dry weight	Core
Tomato	*Lycopersicon esculentum*	0.0022	0.0011	Shoot dry weight	Core

[1] Category listed on the US EPA Ecological Effects Branch Pesticide EcoToxicity Database.

9.3.3 Conclusions

9.3.3.1 Aquatic Organisms

Algae
Diuron is rated as highly toxicity to algae according to the US EPA classification. From the US EPA RED, the acute toxic of diuron to algae (LC50s) ranges from 2.4 to 95 µg ac/L.

Marine crustose coral algae are very sensitive to the effects of diuron with a LOEC of 0.1 µg/L for diuron alone in clean water. For sediment alone there was a significant effect on photosynthesis and recovery was slow. However, when the diuron was adsorbed to the sediment beforehand, simulating a runoff event, photosynthesis was reduced the quickest and more significantly than the other two tests using diuron or sediment alone. Recovery was also the slowest of the 3 treatments and there was mortality of the algae (17%), not noted in the other treatments, together with significant bleaching (59%) at 1 µg/L and above.

Corals
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* EC50 for $\Delta F/F'_m$ (measure of the change in photosystem II fluorescence) of 2.3 µg/L, NOEC < 0.3 µg/L and LOEC = 0.3 µg/L. The other corals gave an EC50 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.

Another paper reported studies with diuron and four species of coral (those above, *Seriatopora hystrix* and *Acropora formosa*, plus *Montipora digitata* and *Porites cylindrica*), again using chlorophyll fluorescence techniques. The measured EC50s based on $\Delta F/F'_m$, (maximum effective quantum yield: 10 hours exposures, 100 µmol 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 the EC50 from 3.7 µg/L at 'normal' light levels to 2.9 µg/L at 75% 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 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 cylindrical* has been reported. The corals were exposed to 3 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 control. 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.

In a report on the effects of diuron on coral reproduction, coral colonies of *Acropora tenuis* were exposed to diuron at concentrations of 1 μg/L and 10 μg/L for 52 days and the coral spawning compared to control coral colonies on the reef. The larvae from corals exposed to 1 μg/L of diuron showed signs of visible bleaching and had reduced photosynthetic yields (Fv/Fm: maximum potential quantum yield) while larvae from the 10 μg/L exposures lack zooxanthellae and were almost completely bleached. Larval settlement and metamorphosis was not affected compared to the reef controls although the larvae and new corals remained paler and bleached compared to controls. These results indicate that while coral colonies may be under high photosynthetic stress due to diuron exposure, reproduction is not affected and they produce viable gametes.

Aquatic and Semi-aquatic Plants

Duckweed

There are currently no studies with diuron conducted to a current internationally accepted guideline using duckweed. There is an old scientific literature report showing EC50 values of 41 μg/L for *Lemma 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 *Lemma gibba*, the standard test organisms. A more modern literature report gives the IC50 (inhibition of growth) for *Lemma 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.

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 only depressed at the two highest test concentrations. 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 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. The authors note that with measured concentration of diuron in sediment at up to 10 μg/kg, partitioning models indicate that overlaying concentration could reach 1 μg/L, which is within the range to inhibit photosynthesis in seagrasses.

It was concluded that the study shows that there is a significant effect on the quantum yield of *H ovalis* and *Z. capricorni* with exposure to diuron at 0.1 μg/L in the water column.

Mangroves

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") has been reported. 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 dw of sediment), using herbicide dissolved in water to which "commercially bought" clay was then added and mixed to simulate natural run-off conditions.

A potentially confounding effect on the rate treatments in this preliminary study was that for each replicate all four treatments were contained within the same tank, receiving the same simulated tidal water. However, the concentrations of diuron in sediment (top 1 cm), taken at intervals up to 71 days after dosing, show a gradual decline except for the lowest test concentration where there was a slight increase.

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 significant compared to 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 ~340 μg/kg leaf (dry weight) and *A. corniculatum* was the second highest with ~230 μg/kg.

The research suggested that the salt-excreting mangrove species were more vulnerable to diuron and other herbicides than salt-excluding ones. Based on 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 Study
In areas where there was dieback of mangroves, there were measurable concentrations of diuron in the sediments (0-2 cm), ranging from 1.2 to 8.2 μg/kg. However, where there was no dieback the concentrations of diuron measured were <1.2 μg/kg in the sediments (0-2 cm). 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 2 small areas, this was not wide spread and considered due to localised effects. While the field studies are not absolute proof, they do show that with diuron concentrations in sediment >2 μg/kg effect sensitive mangrove species.

Aquatic and Benthic Invertebrates
According to the US EPA classification, diuron is rated as slightly toxic to *D. magna*. From the US EPA Pesticide EcoToxicity Database available from the US EPA RED (US EPA 2003), the acute toxicity of diuron to aquatic invertebrates (LC50s) ranges from 0.16 to 6.7 mg ac/L, corresponding to a rating of moderately to highly toxic. Chronic data from the database is limited to 2 studies with the most sensitive LOEC of 0.2 mg ac/L for *D. magna* and NOEC of <0.2 mg ac/L and the other for mysid shrimp gives 28 day LOEC and NOEC of 0.56 and 0.26 mg ac/L respectively and a MATC of 0.39 mg ac/L.

Fish
Diuron is rated as slightly toxic to rainbow trout for acute exposure, according to the US EPA classification, and for prolonged toxicity the LC50 (14 days) was 8.8 (CI 7.9-9.8) mg/L with a NOEC of 5 mg/L. From the US EPA Pesticide EcoToxicity Database available in the US EPA RED (US EPA 2003), the range of acute LC50s for diuron is from 0.67 to 23.5 mg ac/L, excluding one entry of 240 mg ac/L, corresponding to a rating of slightly to highly toxic. Diuron affects the livers of pink snapper (*Pagrus aratus*), measured using sorbitol

dehydrogenase (SDH) 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 while diuron is only moderately toxic to fish, diuron is causing hepatocellular toxicity at considerably lower levels. Chronic data from the database is limited to 2 studies with the most sensitive LOEC of 61.8 μg ac/L and NOEC of 26.4 μg ac/L (MATC = 40.4 μg ac/L).

9.3.3.2 Terrestrial Organisms

Terrestrial invertebrates
Diuron is rated as non-toxic to bees and earthworms.

Avian
From the US EPA RED, the toxicity of diuron to bobwhite quail, the most sensitive species, is rated as slightly toxic in both the acute oral and dietary tests. It was rated as practically non-toxic to the other 3 species tested.

Mammals
Diuron has low acute toxicity to rats and low chronic toxicity to rats and dogs.

Terrestrial Plants
Diuron is very toxic to non-target plants, as would be expected. It is most toxic to plants after emergence and the most sensitive crop test was tomatoes with an EC25 of 2.2 g/ha for seedlings and an EC25 of 90 g/ha for seeds.

9.4 Environmental Risk Assessment

This review is focused on several key environmental impacts surrounding the use of diuron, as indicated in the scope of the review (see page 39) and these will be the major focus of this risk assessment. The scope of the review is limited to runoff from sugarcane; its effects on the Great Barrier Reef Lagoon, seagrasses and mangroves; and the impact of runoff from other uses. Spraydrift has also been considered as it can be a significant route of environmental exposure; it contributes to the overall loading in natural water systems and therefore contributes to the apparent level of runoff and impact on non-target organisms. In addition, the risk to avian and terrestrial non-target organisms will also be briefly examined.

Diuron is currently 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, sugar cane, vineyards and rights-of-way. It is applied both pre- and post-emergent.

The following evaluations generally follow the US EPA approach (Urban and Cook 1986) to establish a risk quotient value (Q) from the ratio of the Estimated Environmental Concentration (EEC) and the lowest effects concentration, such as an LC50 or EC50. The Department of the Environment and Heritage generally considers the following as an appropriate guide for the establishment of risk:

- $Q > 0.5$: risk is unacceptable,
- $0.1 \leq Q \leq 0.5$: risk may be able to be mitigated by some form of risk management, such as label restraints for a specific use and an identified hazard arising from that use, and

- Q < 0.1: risk is considered low (and may or may not require some form of risk management, such as general label restraints).

For chronic exposure (eg repeated sprays and/or relatively persistent substances), it is considered that the risk is acceptable if the EEC estimated for prolonged exposure is less than the NOEC for the aquatic species most sensitive to chronic exposure, and the situation will be considered further if the chronic EEC exceeds the NOEC.

9.4.1 Estimated Environmental Concentrations

Table 68 gives the minimum/maximum estimated environmental concentrations (EEC) of diuron in treated soil at 5 cm deep assuming complete mixing. The EEC for direct overspray for a single application rate application to water 15 cm deep is also included.

Table 68: The EECs for various applications of diuron to soil and from direct overspray into water 15 cm deep.

Agricultural situation	Min-max rates kg/ha	EEC in soil min/max. mg/kg [1]	EEC in water min/max mg/L [2]
Orchards	1.8-3.6	2.67-5.33	1.2-2.4
Broadacre	0.45-1.8	0.667-2.67	0.3-1.2
Rights-of-way, commercial and industrial areas	Initially 4-36 retreatment at 3.1-16	5.92-53.3	2.67-24
Irrigation and drainage channels	10-75	14.8-111	6.67-50
Sugarcane	1.8-3.6	2.67-5.33	1.2-2.4

EEC = estimated environmental concentration. [1]Soil is 5 cm deep and assumes uniform mixing. [2]Water is 15 cm deep

9.4.2 Risk to Aquatic Organisms

To determine the risk to aquatic organisms, the Department of the Environment and Heritage normal approach is to use the most sensitive endpoints. Thus the LC/EC50 used would be:

LC50 for fish = 0.71 mg/L
EC50 for invertebrates = 0.16 mg/L
EC50 for duckweed = 15 μg/L
EC50 for algae = 2.4 μg/L.

However, with a larger data set an alternative approach is to use the distribution of all data and determine a probabilistic value for the toxicity. This approach uses all the data rather than a single sensitive endpoint and ensures protection for the majority of organisms.

9.2.4.1 Australian Water Quality Guidelines

In the Australian water quality guidelines derived by ANZECC, there is no guideline value for diuron due to insufficient chronic data to establish one[13]. Instead, a low reliability trigger value was calculated using a limited chronic data set. For freshwater, the low reliability trigger value of 0.2 μg/L was set using an assessment factor of 200 while for marine water the

[13] http://www.deh.gov.au/water/quality/nwqms/pubs/wqg-ch3.pdf

trigger value was 1.8 μg/L using an assessment factor of 1000[14]. The data set used to determine these values is different from that used in this review and the data set comprised:

15 species freshwater fish, LC50 500-63,000; 1 chronic study, NOEC of 33.4 μg/L
6 species of freshwater crustaceans, LC50 160-15,500 μg/L
2 species of freshwater insects, LC50 1200-3600 μg/L
no data for freshwater algae
1 marine fish LC50 6300 μg/L
1 marine mollusc EC50 1800 μg/L

Note the lack of data for algae, the most sensitive species. Therefore rather than use the low reliability trigger values, Department of the Environment and Heritage used all the acute data for algae (18 species freshwater and marine), aquatic invertebrate (7 species) and fish (8 species) from Tables 58, 59 and 60 and the ANZECC/ARMCANZ BurrliOZ software program (Campbell, Palmer, Shao and Wilson, 2000). The program fits the data set to the Burr Type 3 distribution. .

As NOEC values were not available for most test species, a default conversion value of 0.1 for the transformation of EC50 data to NOEC was used. Using this methodology, the Department of the Environment and Heritage estimates that the water quality guideline would be 0.2 μg/L, which is the same as the current interim guideline for freshwater. Note this used all the data and did not differentiate between freshwater and marine species. The Department of the Environment and Heritage's normal approach for aquatic risk assessment is to use the most sensitive LC/EC50 (fish, invertebrates and algae) with a 10-fold safety factor (used as quotient of 0.1). Both the alternative water quality guideline and DEH's normal (algae EC50/10 = 0.24 μg/L) approaches give similar endpoints.

The Australian water quality guidelines uses the 99th percentile based on NOEL for all species for highly protection and lower percentiles for less protection. In order to determine the level of protection needed for areas of different ecological importance, the trigger values for 99, 95, 90 and 80% protection were determined using the BurrilOZ software and the results are given in Table 69.

Table 69: Trigger values for all species.

Level of protection (% species)	99	95	90	80
Guideline Value μg/L	0.22	0.6	1.0	2.0

9.4.2.2 Runoff

Runoff of diuron from treated areas is a key environmental route of exposure and is the most important aspect of the review, as detailed in the scope (see 0). This will be considered in some detail.

Runoff is highly dependent on several factors, some of which are location specific and others event specific. The most important are rainfall and its intensity, infiltration of soil (in turn related to moisture content of soil), the slope, type of soil type of drainage, crops type, amount of trash on soil and cultivation (Mensink, de Greef and Linders, 1996). In addition, water erosion of soil removes soil particles, mainly the fine silts enriched with organic matter, and

[14] http://www.deh.gov.au/water/quality/nwqms/pubs/volume2-8-3b.pdf

therefore chemicals adsorbed to organic matter in soil may be disproportionately transported via erosion.

In order to simplify the runoff and have some estimates of values, simplistic models are used. The Department of the Environment and Heritage uses, as a first tier or filter, the following model: a 1 ha field is treated then a 100 mm of rainfall event occurs with 10% of the rainfall, carrying 10% of the treatment, runoffs into a 1 ha water body 15 cm deep. This assumes the dilution results from the 15 cm deep water, 100 mm of rain and 10 mm of runoff water, total depth of 26 cm. Table 70 gives the results using this very simplistic model.

Table 70: The EEC from runoff using the Department of the Environment and Heritage's simple model (a 1 ha field; 100 mm of rainfall, 10% runoff into 15 cm deep pond where 10% of applied runs off).

Agricultural situation	Min-max rates kg/ha	EEC µg/L		Quotient[1]					
				fish		invert		algae	
		min	max	min	max	min	max	min	max
Orchards	1.8-3.6	69.2	138	0.10	0.19	0.43	0.86	28.83	57.50
Broadacre	0.45-1.8	17.3	69.2	0.02	0.10	0.11	0.43	7.21	28.83
Rights-of-way, commercial and industrial areas	Initially 4-36 retreatment at 3.1-16	153	1384	0.22	1.95	0.96	8.65	63.75	576.67
Irrigation and drainage channels	10-75	384	2884	0.54	4.06	2.40	18.03	160.00	1201.67
Sugarcane	1.8-3.6	69.2	138	0.10	0.19	0.43	0.86	28.83	57.50

[1] for fish 0.71 mg/L, invertebrates 0.16 mg/L and algae 2.4 µg/L.
Dark shading Q > 0.5. Light shading 0.5 > Q >0.1.

Table 70 clearly shows that there is unlikely to be a risk to fish and only a slight risk to aquatic invertebrates at rates of <1.8 kg ac/ha, i.e. broadacre use, but there is a high risk to algae. For rates between 1.8-3.6 kg ac/ha (orchards and sugar cane), there is a slight risk to fish, a slight to moderate risk to invertebrates and again a very high risk to algae (and duckweed, data not shown). The very high label rates, particularly from use in rights-of-way, commercial areas and irrigation/drainage channels, show moderate to high risk to fish and invertebrates and a very high risk to algae. However, this is a first tier (or screening level) assessment and further refinement is required.

The model used is very simple and does not include effects for adsorption, larger land areas, interception by vegetation, degradation etc. However, as a screening model the results are comparable with that from the US EPA GENEEC model (US EPA 2004b), also a screening level model, eg at 3.6 kg ac/ha, GENEEC gives maximum concentration of 116 µg/L compared to 138 µg/L in Table 70. GENEEC also includes a spraydrift component, uses a larger land area (10 ha) and a deeper pond (2.0 metres). Note that the GENEEC was used with a large spraydrift buffer – used to minimise the effect of spraydrift (see Attachment 4).

The level of runoff in the model used Table 70 can readily refined by decreasing the amount of chemical that runs off, say to 1%, in which case the quotients are all reduced by a tenth. Then fish and aquatic invertebrates are considered as low risk for cropping situations (orchards, broadacre and sugarcane) but algae remain at high risk. However, as the field data shows that in a 1 in 2-year rainfall event approximately 2% of applied diuron ran-off (see Section 9.2.7.6), assuming 1% would be below measured field results. Other factors that can be used include increased area treated, percentage of untreated land (and therefore uncontaminated runoff and increased dilution), and increased water depth.

To refine the simplistic Department of the Environment and Heritage model, it is assumed that 20% of the area in a small catchment (100 ha) is treated and a 100 mm rainfall event occurs with 30% of the rainfall running off, carrying 5% of the treatment to form a pond. Note that the treatment area (20%) reflects the total area of sugarcane in the Pioneer River catchment (worst-case) and that 80% of the rain forming the pond comes from untreated areas in the model. In addition, an allowance is made for one cycle of adsorption[15] with K_d (assumes $K_f = K_d$) of 2.9 (worst case) or an average of 12.1.

Table 71: The EEC from runoff using the Department of the Environment and Heritage's more realistic simple model of 20% of catchment treated; 100 mm of rainfall, 30% runoff carrying 5% of treatment with one cycle of adsorption (see footnote 15).

Rates, kg/ha	0.45	1.8	3.6	4	10	16	36	75
Kd = 2.91								
EEC, µg/L	3.85	15.4	30.8	34.2	85.5	137	308	641
Quotients	0.01	0.03	0.06	0.06	0.16	0.25	0.57	1.19
Fish	0.01	0.06	0.11	0.13	0.32	0.51	1.14	2.37
Invertebrates								
Algae	1.60	6.42	12.83	14.25	35.63	57.08	128.33	267.08
Kd = 12.12								
EEC, µg/L	1.15	4.58	9.16	10.2	25.4	40.7	91.6	191
Quotients	0.00	0.01	0.02	0.02	0.05	0.08	0.17	0.35
Fish	0.00	0.02	0.03	0.04	0.09	0.15	0.34	0.71
Invertebrates								
Algae	0.48	1.91	3.82	4.25	10.58	16.96	38.17	79.58

[1]Kd is the lowest value. [2] Kd is the average value. Dark shading Q > 0.5. light shading 0.5 > Q >0.1.

The results of this model show that there is a risk to fish and invertebrates at high application rates and at rates higher than 16 kg ac/ha the risk is unacceptable with the low soil adsorption (Kd) assumption. For algae the risk is high and unacceptable for all application rates with the low soil adsorption but with the average soil adsorption the risk is slight at the lowest rates but remains high at rates of 1.8 kg ac/ha and above. There is also at a high and unacceptable risk to duckweed with applications of 3.6 kg ac/ha and above using the EC50 of 15 µg/L. While not shown in Table 71, there is also at a high and unacceptable risk to duckweed with applications of 3.6 kg ac/ha and above using the EC50 of 15 µg/L.

For most situations the assumptions in the model are considered reasonable although in very wet situations the amount of runoff (30%) is probably to low. A separate situation is aerial application to wheat when the fields are to wet for ground equipment. Under these conditions, diuron is likely to be more mobile and runoff higher. Using the same mode but assuming that 60% of the rainfall runoff carrying 10% of the applied diuron (application rate of wheat is 280 g ac/ha), the quotient for algae are 1.0 and 0.31 for low and average Kd respectively. Thus, this application to wheat is acceptable based on this model despite the wet soils and resulting higher runoff.

The US EPA uses the model PRZM/EXAMS at their tier two model and is a refinement on the GENEEC model. The model uses actual soil and 30-year weather data for specific sites in

[15] The Kd is used according to equation concentration in water = total runoff x 1/(Kd + 1). Therefore for Kd = 2.9, 25.6% is in water phase and 74.4% adsorbed; for Kd = 12.1, 7.6% is in water phase. This simplistic calculation does not taken into account volumes of water or mass of soil or other factors such as slope, rainfall intensity etc

the US and therefore is not directly comparable to Australia. Nevertheless, their results in the RED for diuron (US EPA 2003) in apples (New York, 4 lb/ac [3.6 kg/ha]) gives a 90th percentile peak concentration of 53 μg/L and an annual mean (over 30 years) of 32 μg/L, which is reasonably comparable with that in Table 71 for 3.6 kg /ha. The other crops modelled are citrus in Florida and grapes in California, both at 9.6 lb/ac (8.6 kg/ha), with 90th percentile peak concentrations of 332 and 40 μg/L and the annual means of 52 and 17 μg/L, respectively. At 8.6 kg/ha, the Department of the Environment and Heritage's refined model gives 95.5 μg/L, higher than the Florida annual mean result (wet sub-tropical climate) but lower than their peak concentration and it is significantly higher than the peak 90th result for California. This most probably reflects the effect of the fine sandy loam at the Californian site (high infiltration) and low rainfall (dry Mediterranean climate).

The US EPA PRZM/EXAMS model using USA weather information gives results somewhat similar to the results in Table 71 and therefore this relatively simplistic model is seen as being realistic in its results. Also, the results at 3.6 kg ac/ha (= maximum rate for sugarcane) with the average Kd value are comparable with the peak measured concentrations of 8.5 μg/L in the Pioneer River (see Table 72).

However, as there is a considerable amount of measured field data available, these will be examined rather than relying on modelling.

Field Data

The information from field studies will be examined with respect to the major use pattern that contributed to the environmental measured levels.

Sugarcane

The use of diuron on sugarcane and its impact on downstream mangroves and offshore seagrasses, as well as the Great Barrier Reef, are key aspects of this review. Several field-monitoring studies were examined in Section 0 and the results from these will be considered here.

Concentration of diuron in the Pioneer River

The level of diuron in the Pioneer River was measured during a significant rainfall event (Simpson, 2002, see Section 9.2.6.1). Total rainfall over the two-day event averaged 233 mm and examinations of the rainfall records indicate that this was a 1 in 2 year occurrence. Average rainfall in the catchment for February is ~350 mm. The rainfall event is considered to have a realistic probability of occurring relatively frequently.

Samples taken at the Dumbleton Weir gauging station, located at the bottom of the catchment (drainage area of 1485 km^2, ~95% of catchment) gave measured concentrations of between 0.9 to 8.5 μg/L. The higher values occurred at the start of the runoff event and then tapered off. In the centre of the catchment (Mia Mia bridge and Cattle Creek), levels of diuron were lower. Table 72 gives the measured levels together with the quotients for algae, again using the most sensitive EC50 (2.4 μg/L) as the endpoint.

Table 72: Concentration of diuron at Dumbleton Weir gauging station on the Pioneer River during 24 hours intense rainfall and the quotient for algae.

Site	Time of sample[1]	Diuron, μg/L	Quotient, algae EC50 2.4 μg/L	Quotient duckweed
Dumbleton Weir	0815	8.5	3.54	0.57
	1500	2.5	1.04	0.17
	2325	1.1	0.46	0.07
	0900(15/02)	0.90	0.38	0.06
Mia Mia Bridge, Pioneer River	1030	0.40	0.17	0.03
Cattle Creek	1055	1.00	0.42	0.07

[1]All samples taken on 14/02 except last sample at Dumbleton taken on 15/02. NDR = No detectable residue, limit of reporting set at 0.3 μg/L. Dark shading Q > 0.5. light shading 0.5 > Q >0.1.

Table 72 clearly shows that during this one runoff event the peak levels of diuron were very toxic to algae, which then declined and approached a more acceptable level after 24 hours (Q ~0.4). For most of the flow during the runoff the risk to algae was high enough to be considered unacceptable. This is for one intense rainfall event (1 in 2 year event) that occurred approximately half way during the wet and some time after the last applications of diuron (it is expected the most sugarcane farmers in the Pioneer River catchment would have applied diuron during November to January prior to canopy closure). Had earlier runoff events been monitored, the measured concentrations of diuron could well have been higher. With this in mind, quotients of between 0.1 and 0.5 in Table 72 are considered to show a risk to algae.

The Department of the Environment and Heritage notes that all of the measured levels in Table 72 are above the interim water quality guideline for diuron of 0.2 μg/L. Also, the peak levels at the Weir could affect aquatic plants with Q > 0.1, although this is likely to be of short duration. In addition, the diuron will slowly adsorb to the sediments and build up there until it reaches equilibrium and it will be available for uptake by plants. The degradation rate in the sediment from the Pioneer River and its estuary is unknown but in the aerobic aquatic metabolism laboratory studies the half-lives ranged from 33 to 232 days.

A complicating factor in interpreting the measured levels of diuron is that there are two sources for diuron, one from application to the cane field themselves and the other from application to the drains running from the field to the creeks/rivers in the catchment. Due to the amount of diuron used in cane production, estimated at 197 tonnes in Queensland (Hamilton and Haydon, 1996), this is the major source of the diuron measured in the Pioneer River based upon reported sales of diuron (see Section 9.1.3.5, page 43).

It is concluded that the measured levels of diuron in the Pioneer River during flow events are higher than what is acceptable to protect aquatic organisms, mainly algae but could also include aquatic plants growing in the river sediments, including mangroves, and seagrasses offshore where these sediments deposit. Amounts of diuron used should be reduced so that expected peak levels are less than 2.4 μg/L (i.e. Q < 1.0), noting that algae have high fecundity and therefore are expected to recover from short exposures, provided there is time to recover. It is recommended that the current maximum rate is reduced by a quarter to 0.9 kg ac/ha, i.e. equal to broadacre rates, being mindful of the strong uptake of trash blank etc and how it has reduced the need for longer-term weed control and herbicide use in the sugarcane production systems.

Diuron in Sediment

The level of diuron in several sediments has been measured in areas associated with sugarcane. It has been found in irrigation channels and drains (Muller *et al* 2000, See Section 0), estuaries (Duke, 2001 and 2003, see Section 0) and in offshore sediment (Haynes, Müller and Carter, 2000, see Section 0; McMahon *et al* 2004, see 0). The major organisms exposed to diuron when bound to sediment are expected to be plants and algae growing in the sediment, organisms foraging in the sediments such as crabs and other invertebrates or organisms burrowing in the sediments eg worms.

In order to do a comparison between the measured levels of diuron in sediment and possible effects on non-target plants growing in these sediments, the experimentally derived EC25 for terrestrial plants (see 0) is used. The most sensitive plant for seedling emergence was tomatoes with an EC25 of 0.09 kg/ha. Only the seedling emergence data are used as the test chemical (diuron) was soil applied whereas in the plant vigour test the seedlings were directly oversprayed. As the seedling data was in kg/ha and the concentration of diuron expressed as µg/kg, the measured levels of diuron in sediment were expressed as rates per hectare in 5 cm of soil (soil density assumed at 1.5 g/mL).

Sediment from drains

Diuron has been found in the sediments in drains that provide the drainage from sugarcane farms (Müller et al 2000). The measured level in drains (irrigation drains) from the Mareeba-Dimbuah and Burdekin are given in Table 73 together with quotients for the most sensitive terrestrial plant in the study on seedlings (note that this compares leaf exposure from seedling vigour test (oversprayed) to root exposure). The EC25 of 2.2 g/ha is converted to concentration in sediment of 2.9 µg/kg assuming a soil density of 1.5 and depth of 5 cm. As the measured results are for the drains (irrigation drains), not considered to be part of the natural environment, a 1:4 factor is used to allow for 80% mixing of the contaminated sediment with uncontaminated sediment from non-treated areas (i.e. this assumes that 20% of catchment is treated with diuron as for the Pioneer River).

Table 73: Measured levels of diuron in sediment from sugarcane areas and quotient from most sensitive seedlings

Region	Sample	+ve samples/samples taken	Mean µg/kg	Range µg/kg	Quotient[1] (range)
Mareeba-Dimbulah	drains	5/10	9.1	<0.36-37	0.65 (0.02-25)
Burdekin	drains	20/21	25	<1-120	1.7 (0.07-82)

[1]Quotient is for tomato seedlings (EC25 = 2.2 g/ha), the most sensitive terrestrial seedling and includes a 1:4 mixing with uncontaminated sediments. [2] 1 sample only.

The results show that the level of diuron in sediment from drains draining sugarcane fields is potentially toxic to plants, including aquatic plants, noting that the endpoint used is derived from overspray. Many levels are above the estimated mangrove LOEC of 2 µg/kg (see below). The majority of the diuron in the drains is from either application to the cane fields or from treatment of the drains. Degradation in the sediment is unlikely to reduce the risk to an acceptable level given that the longest sediment half-life was 232 days (Department of the Environment and Heritage will use worst case, i.e. longest half-lives, as there was no information on degradation of diuron in Australian sediments). More diuron may also be expected to be deposited from subsequent water flows.

It is concluded that the measured levels of diuron in sediment of drains from sugarcane areas are high and likely to affect non-target plants including aquatic plants and mangroves growing

in sediments near to sugarcane fields. Therefore, it is recommended that the amount of diuron used in sugarcane production needs to be reduced or eliminated such that the levels in sediments in drains no longer pose an potential risk to non-target aquatic plants including mangroves. Note that there are two sources of diuron involved, direct application to the drains (very high rate) and application to sugarcane (high amounts of diuron used), and both would have to be reduced or eliminated.

Estuary Sediment

There is no laboratory information that shows the effects of diuron on mangroves, the major plant growing in estuary sediments. However, there are field observations that show one species of mangrove, *Avicennia marina,* has been affected near sugarcane with the hypothesis that diuron is the primary reason, based on current information (Duke *et al* 2003).

The field observations seem to indicate that the mangroves were affected when diuron was >2 µg/kg in sediment. At two sites, the Duke report showed that there was a dose response relationship between the percentage of *Avicennia marina* affected and concentration of diuron in sediments. Without additional studies being conducted, this is currently the strongest evidence that diuron is the most likely toxicant that is causing the dieback of *A. marina*. Therefore the value of 2 µg/kg of diuron in sediment is used as the LOEC for mangroves. Table 74 gives the measured levels of diuron in sediments from the Duke reports (Duke *et al* 2001 and 2003) and compares these to the seedling data (tomato vigour) and the LOEC for mangroves. Again, the Department of the Environment and Heritage notes that the seedling data used (EC25 = 2.2 g/ha) is for seedling vigour, where the seedlings were oversprayed, is being converted to concentration in soil and therefore care has to be taken in the interpretation of results.

Table 74: Measured concentrations of diuron in sediment. Samples taken from creeks/estuaries in sugar cane growing areas of Queensland as reported by Duke *et al*, 2001 and 2003.

Site	Con. Diuron µg/kg	Equivalent rate. g/ha	Potential effect on mangroves[1]	Quotient Seedling
Pioneer River	1.7	1.28	no	0.58
	6.0	4.50	yes	2.05
	1.2	0.90	no	0.41
Barnes Creek	5.1	3.83	yes	1.74
	1.0	0.75	no	0.34
	3.0	2.25	yes	1.02
	7.9	5.93	yes	2.70
	8.2	6.15	yes	2.80
Bakers Creek	2.4	1.80	yes	0.82
	4.3	3.23	yes	1.47
	4.3	3.23	yes	1.47
	6.2	4.65	yes	2.11
Johnson River	1	0.75	no	0.34
	0.4	0.30	no	0.14
	0.7	0.53	no	0.24
	2.6	1.95	yes	0.89
	2.6	1.95	yes	0.89
	5	3.75	yes	1.70
	5.2	3.90	yes	1.77
Daintree River	0.1	0.08	no	0.04
	1.1	0.83	no	0.38
	0.64	0.48	no	0.22

[1]Possible effect on mangroves determined using LOEC of 2 µg/kg of diuron in sediment. Dark shading Q > 0.5.

The results in Table 74 clearly show that sediment from several areas in the Pioneer River estuary is likely to impact on mangroves, which is unacceptable given the key role of mangroves in stabilising the estuary mud flats, thereby limiting movement of sediment to the Barrier Reef, and as nurseries to marine organisms. As the maximum concentration of diuron is approximately 8 µg/kg, four times the LOEC for mangroves, this level needs be reduced to less than the LOEC, i.e. reduced to less than a quarter of current levels. Again noting that there are two sources of diuron involved, direct application to the drains and application to sugarcane (higher amounts of diuron used), the need to reduce the environmental impact from application to drains will be considered below. It is recommended that the current maximum rate for application to sugarcane is reduced to a quarter of current rates, ie to 0.9 kg ac/ha and equal to broadacre rates, being mindful of the strong uptake of trash blanket and how it has reduced the need for longer-term weed control and herbicide use in the sugarcane production systems.

Offshore marine sediments

Diuron has been detected in sediments from intertidal sites (<1 m deep; 3 samples per site pooled, sampled during February and May 1997) and subtidal sites (<5 m deep, in duplicate 3 random grab samples, 500-1000 m apart, sampled between June and November) located from Cape York to Moreton Bay (Haynes, Müller and Carter, 2000). In the intertidal samples, diuron was detected at 3 of the 16 sites, with concentrations of 0.5, 0.6 and 1.7 µg/kg dw (Cairns, Moreton Bay West and Cardwell respectively)[16] and at the subtidal sites, diuron was detected at 9 of the 24 sites at concentrations ranging from 0.2 to 10.1 µg/kg dw. All these detections were at river mouths or near rivers draining the sugar growing areas. Table 75 gives these sites, the concentration of diuron detected (mean of 2 duplicate samples) and quotients for tomato seedlings, used as substitute for seagrasses as no dose response data was available for seagrasses.

Table 75: Measured levels of diuron in subtidal sediment (<5 m deep) in 1998 between June and November and quotient for tomato seedlings(vigour test).

River[1]	DR	BR	RR	JR	TR	C	HR	L	FR
Con. µg/kg dw	0.2[2]	0.35	1.1	10.0	1.4[2]	0.8	2.0	1.6[3]	0.9[2]
Q, tomatoes seedlings	0.07	0.12	0.38	3.41	0.48	0.27	0.68	0.55	0.31
Con. in overlaying water µg/L; Kd = 2.9	0.06	0.09	0.28	2.56	0.36	0.21	0.51	0.42	0.23
Con. in overlaying water µg/L; Kd = 12.1	0.02	0.03	0.08	0.76	0.11	0.06	0.15	0.12	0.07

[1]Abrevations used: DR Daintree River; BR Barron Rivers; RR Russell River; JR Johnson River; TR Tully River; C Cardwell; HR Herbert River, L Lucinda and FR Fitzory River. [2]Result from one replicate, other replicate was below detection limit (<0.1 µg/kg dw). [3]Not replicated

The quoatant in Table 75, based on tomato seedlings, show that effects on non-target plants growing in these sediments are possible. Similarly, the 3 positive samples from the intertidal sites would give quotients ranging from 0.17-0.58. Data on seagrasses (see 9.3.1.3) showed that diuron at a concentration of 0.1 µg/L affected chlorophyll fluorescence in two species of seagrasses (*Halophila ovalis* and *Zostera capricorni*) and this is therefore a LOEC for seagrass. Based on the observed sediment concentrations and using a Kd of 2.9 (worst case), the predicted chronic water column diuron concentrations near the mouths of these wet tropics rivers are likely to range from 0.05 to 2.6 µg/L (note that as tidal effects were not

[16] Cairns and Cardwell are in the tropics and sugarcane is grown nearby while Moreton Bay West is near Brisbane.

considered, it would be more appropriate to consider these as pore water concentrations). This is above the LOEC at 6 sites (all but Daintree and Barron Rivers) and therefore effects on seagrass are likely. Even with the average Kd value of 12.1, the concentration in the overlying water ranges from 0.02 to 0.76 μg/L and is above the LOEC at 4 sites (Johnson, Tully and Herbert Rivers and Lucinda). For the 3 intertidal sites and using the average Kd (12.1), slight effects on seagrasses were considered likely at only one site, Cardwell, with an estimated concentration in the overlying water of 0.13 μg/L.

While the effect measured, inhibition of chlorophyll fluorescence, does not directly relate to mortality, seagrasses that are already under 'natural stressors' such as sediment, low light levels etc, may be adversely by diuron inhibiting photosynthesis. In addition, concentrations are likely to be higher during monsoon rainfall periods that occur over the summer months (November to April) when the first rainfalls of the wet season flush diuron from the catchments, increasing the risk to seagrass. This is also the time when there is high sediment loads and the natural stressors are also high.

It is concluded that based on measured levels of diuron in offshore subtidal sediments and the LOEC of 0.1 μg/L for seagrass, diuron could adversely affect seagrass. Due to the key ecological importance of seagrasses to the endangered dugong and as nurseries to juvenile marine animals, the possible impact of diuron on seagrasses is of concern. Given that this is occurring in the Great Barrier Reef Marine Park, it is recommended that the amount of diuron reaching these sediment needs to be reduced and thus the amount of diuron used in sugarcane production should be reduced. Therefore, as previously, it is recommended the current maximum rate is reduced to a maximum of 0.9 kg ac/ha, i.e. equal to broadacre rates, with only a single application per annum. Also, if diuron is continued to be used to treat channels and drains, based on the seagrass consideration, this use should be restricted or reduced in the sugarcane areas in order to reduce the risk to seagrasses.

Effects on Corals

Runoff from the rivers draining sugarcane crops that flows into the Great Barrier Reef lagoon (GBRL) is likely to carry diuron as dissolved material and adsorbed to sediment. Thus diuron could affect the coral on the reef directly, especially those on inshore reefs. An indirect effect could occur when diuron affects crustose coralline algae. As a given species of coral larvae will preferentially settle on selected crustose coralline algae species, effects on the distribution of crustose coralline algae will indirectly affect the distribution of corals (see 9.3.1.4 for more information).

The Department of the Environment and Heritage uses a 1:10 dilution (Environment Australia, 2003) for industrial chemicals entering seawater (this may be generous for diuron considering that the freshwater plume will not dilute rapidly in protected inshore areas and also that the GBRL is high conservation area). Applying this dilution to the measured levels of diuron in the Pioneer River at Dumbleton Weir during the flood event (assumes no changes in the concentration of diuron in the river due to dilution or new sources of diuron), as given in Table 76, gives the EEC for comparison to the LOEC for crustose coralline algae and corals on inshore reefs.

The LOEC for diuron on crustose coralline algae, using the most sensitive species tested, is 0.1 μg/L (reduced photosynthesis) and a NOEC was not determined (Harrington, Fabricius, Eaglesham and Negri, 2004). When a solution at 1 μg/L was mixed with sediment there was 17% mortality in the crustose coralline algae. For corals the LOEC was 0.3 μg/L for effects on chlorophyll of the coral dinoflagellates (Jones and Kerswell, 2003) and bleaching of larval

stage was visible at 1 µg/L and these larvae remained paler than controls after settlement (Cantin, 2004). For the studies assessed in this review, there was no information on NOEC levels and therefore the LOEC will be used instead.

Table 76: Measured levels of diuron at Dumbleton Weir and the EEC in offshore marine waters allowing 1:10 dilution.

Measured concentrations µg/L	EEC in marine waters, µg/L	Quotient for CCA, LOEC = 0.1 µg/L	Quotient for Corals, LOEC = 0.3 µg/L
8.5	0.85	8.5	2.8
2.5	0.25	2.5	0.8
1.1	0.1	1	0.33
0.90	0.09	0.9	0.3

Dark shading Q > 0.5; CCA = crustose coralline algae

The results in Table 76 clearly show that sensitive crustose coralline algae species are likely to be affected by diuron dissolved in water from the Pioneer River draining the sugarcane fields within the catchment. Note that a quotient of 0.5 was arbitrarily used as the endpoint used was the LOEC, not the normal LC/EC50 or NOEC endpoints. Similarly, corals could be directly affected by the peak concentrations and indirectly due to impacts on crustose coralline algae.

Diuron will also be adsorbed to the suspended sediments and carried by river to the inshore reefs. Based on the observed sediment concentrations (see Table 75 above) and using a Kd of 2.9 (worst case), the predicted chronic concentrations near the mouths of these wet tropics rivers are likely to range from 0.05 to 2.6 µg/L and is above the LOEC for corals at 5 sites and above the LOEC for crustose coralline algae at 6 sites. Clearly there could be an impact on the inshore reef system of the GBRMP. Even with the average Kd value of 12.1, the concentration in the overlying water ranges from 0.02 to 0.76 µg/L and is above the LOEC for corals at one site and at 2 other sites the quotient is above 0.5 and therefore there could be risks to corals. Similarly for crustose coralline algae, the estimated concentrations for the worst case are above the LOEC at 5 sites and there could be risks at 6 sites. It is assumed that further dilution will reduce the concentrations of diuron to below the LOECs on the offshore reefs.

Due to the high conservation values within the GBRMP area, the level of diuron in inshore regions is unacceptable and measures should be taken to reduce the overall amount and peak concentrations reaching the GBR lagoon. As previously recommended, the current maximum rate for sugar cane should be reduced to 0.9 kg ac/ha, i.e. equal to the broadacre rates, with only a single application per annum. This is expected to reduce overall concentrations to about a quarter of current levels and while peak levels would be close to the LOEC for corals, levels in general would be significantly below. Also, based on the coral calculations, diuron should not be used to treat channels or drains in the sugarcane areas or other areas that drain into the GBRMP at the current label rates.

Cotton

The use of diuron in cotton relates to its use before sowing to treat weeds and for treatment of irrigation channels and drains within the cotton irrigation areas. Table 77 gives the maximum water concentrations of diuron in each season measured by the NSW Department of Land and Water Conservation program in Northern NSW. The 5 major rivers in the area all have cotton in their lower catchments and receive water from the cotton drains. The quotients are for algae based on the sensitive endpoint for green algae of 2.4 µg/L.

Table 77: Maximum measured levels in rivers in northern NSW from cotton irrigation areas. Quotients are for green algae using the EC50 of 2.4 µg/L.

NSW River		1991/92	1992/93	1993/94	1994/95	1995/96	1996/97	1997/98
Borders Rivers	Conc µg/L	5	3	2.5	0.4	1	2	0.9
	quotient	2.08	1.25	1.04	0.17	0.42	0.83	0.38
Gwydir River	Conc µg/L	5	4.2	1	5	23	5.4	10
	quotient	2.08	1.75	0.42	2.08	9.58	2.25	4.17
Namoi River	Conc µg/L	0.65	0.9	0.2	<0.05	0.2	0.2	2
	quotient	0.27	0.38	0.08	0.0	0.08	0.08	0.83
Macquarie River	Conc µg/L	0.2	0.3	<0.05	<0.05	<0.05	-	-
	quotient	0.08	0.13	0.0	0.0	0.0		
Darling River	Conc µg/L	-	<0.05	<0.05	<0.05	<0.05	0.1	-
	quotient		0.0	0.0	0.0	0.0	0.04	

Dark shading Q > 0.5. light shading 0.5 > Q >0.1.

Table 77 shows that the peak measured levels of diuron from weekly/fortnightly grab samples taken in rivers from NSW are above acceptable levels for three rivers. It should be noted that these are not the maximum levels likely in the rivers during runoff events, except for the Gwydir River of 23 µg/L. Monitoring the Gwydir River during heavy rainfall over 3 days gave maximum levels of diuron of 24 µg/L which then declined to 6 µg/L. To indicate the risk to the river, the quotients for algae are calculated to range from a peak of 10 to 2.5. This indicates that during the 3-day event the sensitive algae species in the river could have been affected, although the alga may have been able to recover from this one challenge after the levels dropped. However, if there were several runoff events, all resulting in the concentrations of diuron >1.2 µg/L (Q=0.5), considered to be possible given the levels of diuron in the grab samples, then algae populations are likely to be affected.

While there were no data on the levels of diuron in sediment in the drainage channels in NSW, the sediments from these rivers were not analysed for diuron, it is expected that the drains in NSW have similar levels of diuron as in Queensland. The level of diuron in sediments from drains draining cotton fields in Queensland is relatively high and approaches that obtained from sugarcane fields (see Table 78).

Table 78: Measured levels of diuron in sediment from drains in Queensland cotton areas and quotient from the most sensitive terrestrial seedlings.

Region	+ve samples/samples taken	Mean µg/kg	Range µg/kg	Quotient (range)
Emerald	25/26	17	<1-54	1.2 (0.07-3.7)
St George	7/12	6.3	<0.4-14	0.43 (0.03-0.95)
Dawson Valley	15/15	80	8.8-340	5.4 (0.6-23)

[1]Quotient is for tomato seedlings EC25 = 2.2 g/ha, the most sensitive terrestrial seedling and includes a 1:4 mixing with uncontaminated sediments.

It is concluded that used of diuron in cotton fields and to treat channels and drains in the cotton growing areas of Australia results in levels of diuron in the rivers that could cause environmental impacts on non-target plants, although the extent of any impacts is not known at this stage. Algae are at risk as well as aquatic plants or terrestrial non-target plants growing in the contaminated sediments from cotton applications or use of diuron to treat drain and

channels. Note that this is a significant use in cotton areas (see Section 9.1.3.5 and therefore the high rates used for channels and drains needs to be significantly reduced (see below). To reduce the environmental impact from application to cotton fields (assuming that approximately half of the observed diuron in the rivers is due to applications to cotton fields), it is recommended that the maximum application rate for diuron be reduced to 900 g ac/ha and that there be no more than 2 applications at this rate per season.

Citrus

Diuron is used for weed control in citrus at a rate of between 1.8-3.6 kg ac/ha, and in irrigation channels during winter. A major monitoring study in the southwestern irrigation areas of NSW (1990-1995) showed that at times there were significant levels of diuron in drains and creeks (see 9.2.6.1 for details; Bowmer *et al* 1998).

Sampling of the main drains over a 2 year period in the MIA (Murrumbidgee Irrigation Area) showed that 41% of all water samples taken contained detectable levels of diuron (limit of detection 0.1 μg/L), with a maximum of 9.5 μg/L. During one irrigation season, from September to May, monthly samples of surface water in the MIA gave a maximum concentration of 5.4 μg/L which occurred in October. These peak levels are above the EC50 for algae (Q is 2.25 and 4.0 for 5.4 and 9.5 μg/L respectively) and therefore indicate that there is a potential environmental risk during these periods. These maximum results both occurred in the October samples, close to when most of the diuron is used in spring, and thus they represent runoff from treated areas.

Samples taken of tile (sub-surface) drains at horticultural farms in the MIA in January, May and August showed that approximately 40% of farms had detectable levels (>0.05 μg/L) of diuron and the maximum concentration was 28 μg/L from the August sample. Examination of the raw data in the report shows that in January just 2 of 50 tile drains examined had levels >1 μg/L and the quotients for algae were 1.2 and 3.9. In May, 6 of the 50 tile drains had concentrations of >1 μg/L with maximum of 2.4 μg/L and Q ≤ 1.0. In August the same 6 tile drains had higher concentrations with a maximum of 27.8 μg/L (Q = 11.6). Given that these samples were taken from the tile drain pump-outs, there should be further dilution in the receiving waters. Nevertheless, as these samples were taken in just 3 months in the year, and not necessarily those where peak levels of diuron would be expected, these results would indicate that diuron is likely to pose a potential unacceptable environmental risk in this area. Further, as green algae are most sensitive, levels of >1 μg/L are considered to indicate a risk to algae.

The surface runoff from a citrus farm (normally grown on sandy soils or other soils with good drainage) following the first irrigation event (although runoff from a storm event had already occurred following herbicide application) after application of diuron at 4.5 kg ac/ha (above the current label rate of 3.6 kg ac/ha) had concentrations between 1.2 to 20 μg/L. The average concentration was 10.9 μg/L and the average quotient of 4.5 for algae (EC50 2.4 μg/L). Grab samples for Mirrool Creek just above Barren Box Swamp showed diuron was present most of the time but at low levels and below levels where there was a risk to algae (Q<0.1 for green algae). Daily automatic monitoring from 5 October to 30 November of Mirrool Creek gave low levels of diuron (0.05 and <1 μg/L) but similar monitoring of Little Mirrool Creek gave mean levels of 1.19 μg/L with range 0.1 and 7.5 μg/L. The resulting quotient for the mean levels in Little Mirrool Creek are unacceptable, Q > 0.5, and range from 0.04 to 3.1. As all samples from both creeks had diuron present above the detection limit (0.05 μg/L), there is chronic exposure.

It is concluded that the peak measured levels of diuron in the MIA are above acceptable levels and given that daily sampling of two major creeks in the area also showed high peak levels together with chronic exposures. Therefore, the amount of diuron entering the aquatic environment needs to reduce to more acceptable levels. Again, there are two sources of diuron involved, direct application to the drains and application to the crop (the risk from use in drains will be addressed below). It is recommended that maximum application rates in citrus be reduced to 0.9 kg ac/ha in order to reduce the maximum quotient in Little Mirrool Creek to <1.0 for algae, noting they are grown on sandy soil or other well draining soils. If two applications are to be made, these should be as a split rate with total annual application not exceeding 0.9 kg ac/ha.

Horticultural crops

From the runoff modelling there is likely to be unacceptable environmental impact from all applications equal or greater than 1.8 kg ac/ha, with the crops not already mentioned mainly being horticultural crops (apples, pears, bananas, pawpaw, coffee, grapes and pineapples). As many of these crops are grown and treated with diuron similar to citrus and citrus is considered to cause an unacceptable environmental risk, the use of diuron according to the current labels in these crops is also likely to result in an unacceptable environmental risk. Several of these crops are grown in the tropics (bananas, pawpaw, coffee, and pineapples) and therefore could affect the Great Barrier Reef Lagoon.

As for citrus, it is recommended that the maximum application rate for diuron in horticultural crops be reduced to 0.9 kg ac/ha, based on the runoff model and considering the measured levels in rivers from citrus applications. In addition, the tropical crops could impact on the GBR lagoon, as was shown for sugarcane, and therefore it is recommended that the rates in these crops is reduced to that recommended for sugarcane, i.e. maximum application of 0.9 kg ac/ha per year. If two applications are to be made, these should be as a split rate with total annual application not exceeding 0.9 kg ac/ha.

Irrigation Ditches

Field studies

Two field studies on the field dissipation and transport of diuron were presented where the sides and tops of drainage ditches were treated with diuron at 13.4 kg/ha (see Section 9.2.5.2, page 72). For the study conducted in California, there was limited rainfall that limited the movement of diuron from the treated slopes and berms. The more relevant study is from Arkansas, where there was significant rainfall and runoff. While the rainfall over the study period (256 days) is significantly higher (860 mm) than is typical for large areas of Australia, it somewhat typical of high rainfall areas on the Queensland coastal fringe during the wet (rainfall in sugarcane areas is >1000 mm/annum). The bottom of the ditch where the water flowed was not treated so the results were for runoff (excluding the day 0 results). Table 79 gives a summary of the grab sample data in water within the ditch and these figures were used to determine a quotient for algae, the most sensitive organisms.

Table 79: Summary of maximum concentration in water in a drainage ditch in Arkansas. Sides and top were treated at 13.4 kg ac/ha.

DAT	9	13	34	48	61	91
Maximum measured concentration µg/L	30	38	12	9.8	<10[1]	<10[1]
Quotient algae E50 = 2.4 µg/L	12.5	15.8	5	4.1	<4.2[2]	<4.2[2]

[1] Limit of quantification for the study was 10 µg/L. [2] Quotient based on the LOQ in the study. Dark shading Q > 0.5, light shading 0.5 > Q >0.1.

Table 79 clearly shows that when areas close to flowing water are treated with diuron, in this case sides of a ditch, there are significant levels of diuron in the water from runoff. It is unclear exactly how well these USA results may relate to the Australian situation but given the rainfall, it is considered that could be representative of high rainfall areas on the Queensland coastal fringe during the wet. In order to see the effect of different rates and the likely concentrations in natural receiving water rather than the drainage channels, Table 80 was generated assuming a 1:2 dilution (33% dilution) in the receiving waters, i.e. assuming that the drainage ditch flows into a natural stream. This gives the quotient at rates relevant to Australian uses based on Table 79, calculated using direct proportions.

Table 80: Quotients for algae at application rates used in Australia in receiving water (1:2 dilution) over 52 days from the measured concentrations in Table 79.

Days After Treatment	Rates, kg/ha							
	0.45	**1.8**	**3.6**	**4**	**10**	**16**	**36**	**75**
9	0.14	0.56	1.10	1.24	3.08	4.93	11.09	23.09
13	0.18	0.70	1.40	1.55	3.89	6.23	14.04	29.25
34	0.05	0.23	0.45	0.50	1.24	1.98	4.43	9.23
48	0.05	0.18	0.36	0.41	1.01	1.62	3.62	7.54
61	0.05	0.18	0.36	0.41	1.04	1.64	3.69	7.70

[1] Measured concentration is less than the limit of quantification of 10 μg/L. Dark shading Q > 0.5. light shading 0.5 > Q >0.1.

Table 80 shows that there is a high risk (Q = >0.5) to algae from runoff at concentrations of 3.6 kg ac/ha or greater. This risk is high and unacceptable for at least 34 days. At higher rates (>10 kg ac/ha) the risk lasts for at least 7 weeks, constituting chronic exposure and is unacceptable.

Even at lower rates of 1.8 kg ac/ha, the quotient is between 0.1 and 0.5 and lasts for at least 25 days. Previously a quotient of 0.5 was considered just acceptable with a single exposure. But as this result is based on actual measured water concentrations, larger areas are likely to be treated (data in this trial is from just an area of 0.048 ha), and there is a chronic exposure, a quotient of >0.1 is considered to show an unacceptable risk. Further, the application practices used in this trial (target area being the slopes and tops of the channels) are not typical for Australian practices, where the Department of the Environment and Heritage understands the common practice is to treat the entire channel including the bottom. Therefore, there could be higher environmental levels from Australian practices and the American data is likely to underestimate the exposure levels in Australia, further justifying the use of quotient of 0.1 for the determination of acceptable/unacceptable risk.

As part of the Arkansas study, an automatic sampler was used to take samples during flow events over a 24-hour period. The maximum concentration of diuron in water was 130 μg/L, which occurred 5 days after treatment and remained between 110-130 μg/L for 20 hours. This is a high level and it is clearly hazardous to algae and duckweed and could be hazardous to invertebrates (Q = 0.41-0.48). The last positive sample (>10 μg/L) taken by the automatic sampler occurred 93 days after treatment. The concentration was 10 μg/L. These results clearly show that diuron will run off from treated areas during rainfall and at concentrations of concern. Using a dilution factor of 1:2 for receiving waters, as done previously, gives peak concentrations of 37-43 μg/L and levels of up to 3.3 μg/L for approximately 90 days or so. It should be noted that this does not include diuron in sediment, which was not sampled during these flow events.

While there was a significant level of diuron in the runoff water, levels in the sediment in the channel and directly below the application site were comparably higher, and over ~180 days ranged from 0.31 to 1.61 mg/kg in the 0-15 cm core (excludes day 0 as this could be due to spraydrift). Levels further down stream were lower but reached 0.26 mg/kg approximately 25 metres below the treatment area, again a reasonably high level. It should be noted that 0.26 mg/kg for 0-15 cm corresponds to approximately 500 g ac/ha, at the lower end of the label application rates but well above all the EC25s for seedling emergence and plant vegetative vigour in the non-target plants given in Section 9.3.2.3. At the last downstream sampling area (52 metres downstream), the maximum level of diuron was 0.11 mg/kg (equivalent to 215 g ac/ha). The sediment in the ditch will likely be hazardous to aquatic plants.

It is concluded by the Department of the Environment and Heritage that the field study conducted in Arkansas shows that from applications to ditches at rates of 13.4 kg ac/ha there is a clear risk to downstream non-target algae and aquatic plants. As the current labels give rates of from 10-75 kg ac/ha, the risk from these higher rates is unacceptable unless runoff from treated areas can be retained on site, eg in cotton fields/farms where all runoff water and sediment is contained within the retention pond. Further, the treatment area in this study was small (7.6 X 64 metres) and limited to the slopes and tops of the ditch compared to typical Australian situations where kilometres of irrigation ditches are treated, including the bottom of the channels (though labels do not indicate which part of the channels/ditches are to be treated) and therefore the risk is expected to be higher.

Irrigation Ditch Model

The above field data, while showing an unacceptable risk, does not represent typical Australian use. The Department of the Environment and Heritage has previously used the following as a model for treatment of a channel. The channel is 500 m long, trapezoidal-shaped 2.0 m wide at the top and 1.0 m wide at the basewithside and has a water carrying zone 75 cm deep (total volume of water 562 m^3). The wetted surface of this channel would be 1,401 m^2, [(1 m base + 2 sloping sides each ~ 0.9 m long) X 500, 0.14 ha]. If the channel is filled, held (72 hours) and then drained (flushing the channel), as given in the label directions[17], and that the water released carries off 10% of the applied diuron in the wet area, the EEC resulting in the water released would be 0.249 mg/L of diuron for the lowest label rate (10 kg ac/ha) and 1.79 mg/L at the highest rate (72 kg ac/ha). Table 81 gives the results.

Table 81: EEC and quotients for simple channels model (500 m long, trapezoidal-shaped 2.0 m wide at the top, 1.0 m wide at the base and 75 cm deep (total volume 562 m^3).

Rates, kg ac/ha	Australian channel treatment[1]				USA channel treatment[2]			
	72	**10**	**1.8**	**0.9**	**72**	**10**	**1.8**	**0.9**
EEC, µg/L	1790	249	44.8	22.4	1154	160	28.8	14.4
Q algae	745	104	18.7	9.3	481	66	12.0	6.00
Q for algae in receiving waters[3]	247	34	6.2	3.1	159	22	4.0	2.0

[1]Sides and bottom of wetted area of channel. [2]Only sides of wetted area of channel. [3]A 1:2 dilution for freshwater. Dark shading Q > 0.5. light shading 0.5 > Q >0.1.

[17] Label directions are: 'Apply during the non-crop season and when channel is not in use. Soil should be moist and preferably bare, ie after regrading and cleaning channels. Apply prior to expected seasonal rainfall so as to fix it into the soil. If 50-100 mm of rain has not fallen after application and it is necessary to use the irrigation channel, fill it with water and allow to stand for 72 hours, then drain off the water in the channels and run to waste.'

Even allowing a 1:2 dilution in receiving water, there is a risk to invertebrates (Q = 0.5) and an extreme risk to algae (Q = 34) at the current lowest rates. Changing the management practices and just treating the side of the trapezoidal shape channel in the above model, i.e. as done in the USA, the area treated is reduced to 901 m^2 and the EEC for lowest label rate is 160 μg/L. In order to reach a somewhat acceptable risk (Q ~ 1.0) by reducing in the application rate, and assuming the above conditions, the maximum rate needs to be reduced to 0.45 kg ac/ha or less.

In the model it is assumed that 10% of the diuron applied to the wetted soil in the channel was mobilised. The Department of the Environment and Heritage has no information on a measured value here but notes that in the soil adsorption/desorption studies (see Section 0) 7 to 40% of the diuron on the soil (from adsorption) was remobilised after 5 washings. This shows that diuron is readily remobilised and does not bind irreversibly. Also, in the California study where diuron was applied to highway verges, 8.3% of the applied diuron was washed off in one rain event. Therefore, the assumed 10% loss of diuron is considered reasonable. The model also assumes that the term on the label directions '... and run to waste.' (see footnote 17) after the channels/drain is filled would allow the water in the channels/drain to be run to a nearby creek/river.

Conclusion
Based on the field results in the USA, the risk to algae is acceptable at 0.45 kg ac/ha, a higher risk at 1.8 kg ac/ha, which is marginal and at 3.6 kg ac/ha, the risk is higher and unacceptable (see Table 80). The simple ditch model used above indicates that a rate of 0.45 kg ac/ha (half of 0.9 kg ac/ha; Q = 1.5) might be acceptable, which is supported by the field data from the USA. There is also a chronic risk at rates ≥0.9 kg ac/ha (Q > 0.1, see Table 80), which was considered unacceptable. Therefore the Department of the Environment and Heritage recommends that the application rate to irrigation and drainage ditches be reduced to a maximum rate of no more than 0.45 kg ac/ha per annum and applications are restricted to the sides and tops of the channels and ditches, as is current practice in the USA. It is recognised that at this rate diuron is probably not efficacious and if this rate for channels and drains is not acceptable, it is recommended that application to channels and drains be removed from all registered labels.

Rights-of-way, commercial and industrial areas
While there is little or no information on concentration of diuron in runoff waters in Australia for right-of-ways commercial and industrial areas, there is limited information from overseas.

In California, concentrations of diuron (applied at 3.6 kg ac/ha, 2.4 m wide band) in highway runoff were measured during both simulated (13 mm in 1 h) and natural rainfall during winter storms (Powell, Neal and Leyva, 1996). At two sites, 5-12% and 17-46% of the applied water ran off with diuron concentrations ranging from 144-1175 and 348-1770 μg/L respectively. Total mass of diuron leaving the plots in runoff accounted for up to 5.4% of the applied diuron. In the UK the routine monitoring of pesticides show that concentrations of diuron reach 51 μg/L in freshwater (see Table 19) and the higher levels occurred in urban areas where it is used to control weeds in rights-of-way situations (diuron is not registered for use in agricultural crops in the UK).

It is concluded that these two overseas studies noted here clearly indicate that runoff from rights-of-way, commercial and industrial areas where diuron has been used is contaminated with diuron at concentrations of concern. From the Californian result, the runoff modelled in Table 71 would appear to be reasonable. Therefore assuming average Kd values and noting

that algae are expected to recover from single exposures, the maximum application rate recommended is 1.8 kg ac/ha for right-of-ways commercial and industrial areas per annum. As there needs to be a recovery period for algae, it is recommended that there is at least 6 months between multiple applications at split rates (0.9 kg ac/ha).

9.4.2.3 Spraydrift

Spraydrift is being briefly considered as it can be a significant route of environmental exposure and contribute to the overall loading in natural water systems and therefore contribute to the apparent level of runoff.

The risk and extent of spraydrift can be minimised if applications are made under suitable meteorological conditions and with appropriate equipment, as advised on the label. However, it must be assumed that some spraydrift will occur and hence contamination of soil and water outside the target areas.

Assuming a worst-case spraydrift scenario of 10% of a single application reaching the aquatic environment via spraydrift (Urban and Cook 1986), the resulting EECs for the maximum and minimum application rates are given in Table 82 together with the quotients for fish, invertebrates, duckweed and algae. The quotients remain greater than 0.1 for most fish, all invertebrates and for duckweed and algae the risk quotients are very high and further refinement is needed.

Table 82: Maximum and minimum EECs for 10% spraydrift and range of uses and corresponding quotients

Agricultural situation	EEC 10% spraydrift mg/L	Quotient, Sensitive EC50s [1]			
		fish	invert	duckweed	algae
Orchards	Min. 0.12	0.17	0.75	8	50
	Max. 0.24	0.34	1.5	16	100
Broadacre	Min. 0.03	0.04	0.19	2	12.5
	Max. 0.12	0.17	0.75	8	50
Rights-of-way, commercial and industrial areas	Min. 0.27	0.38	1.69	18	112
	Max. 2.4	3.4	15	16	1000
Irrigation and drainage channels	Min. 0.67	0.94	4.2	45	279
	Max. 5.0	7.0	31	333	2083
Sugarcane	Min. 0.12	0.17	0.75	8	50
	Max. 0.24	0.34	1.5	16	100

[1] EC50s used are fish 0.71 mg/L, invertebrates 0.16 mg/L, duckweed 15 µg/L and algae 2.4 µg/L. Dark shading Q > 0.5. light shading 0.5 > Q >0.1.

Ground-rig

Two models were used to evaluate the spraydrift from ground-rig application, the German or Ganzelmeier model (Rautmann *et al* 2001) and Agdrift. Table 83 has the spraydrift, resultant EECs at maximum rates and quotients for 50, 100 and 200 metres away from the site of spraying using the Ganzelmeier model for field crops using a medium spray quality. As application in orchards is via boom spray to control weeds on the ground, the field spraydrift values were used rather than the data generated using an orchard axial sprayer. Table 84 is for AgDrift with a ground boom at 50 cm or less in height using medium droplets (fine/medium boundary curve in AgDrift).

Examining the results in Table 83**,** it is clear that the quotients based on the Ganzelmeier model show that there is unlikely to be a hazard to fish and invertebrates with a 50-metre

spraydrift buffer zone. There is a slight but acceptable risk to duckweed (Q = 0.1 or less) for orchards, broadacre and sugarcane with a 50 metre buffer and a 100 metre buffer for non-agricultural areas. There is a risk (Q < 0.5) to algae from broadacre use at 50 metres and for orchards and sugarcane there is a high risk at 50 metre but slightly lower at 100 metres. However, there's an unacceptable risk to algae from high application rates, i.e. rights-of-way, commercial areas and irrigation/drainage channels. Included in Table 83 and Table 84 is the percentage of species that will be protected at the given EECs and for orchards and sugarcane it is clear that even at 200 metres only 95% of species would be fully protected from any effects of diuron, based on the acute data.

Table 83: The EECs from maximum use rates and quotients based on the Ganzelmeier crop data.

Agricultural situation	Distance from sprayer	Percent drift	Max. EEC µg/L	% Species protected[2]	Quotient, Sensitive EC50s [1]			
					fish	invert	duckweed	algae
Orchards	50	0.06	1.44	80%	0.00	0.01	0.10	0.60
	100	0.03	0.72	90%	0.00	0.00	0.05	0.30
	200	0.016	0.38	95%	0.00	0.00	0.03	0.16
Broadacre	50	0.06	0.72	90%	0.00	0.00	0.05	0.30
	100	0.03	0.36	95%	0.00	0.00	0.02	0.15
	200	0.016	0.19	99%	0.00	0.00	0.01	0.08
Rights-of-way, commercial and industrial areas	50	0.06	14.4	<80%	0.02	0.09	0.96	6.0
	100	0.03	7.2	<80%	0.01	0.05	0.48	3.0
	200	0.016	3.84	<80%	0.01	0.02	0.26	1.6
Irrigation and drainage channels	50	0.06	30	<80%	0.04	0.19	2.0	12
	100	0.03	15	<80%	0.02	0.09	1.0	6.2
	200	0.016	8	<80%	0.01	0.05	0.53	3.3
Sugarcane	50	0.06	1.44	80%	0.00	0.01	0.10	0.60
	100	0.03	0.72	90%	0.00	0.00	0.05	0.30
	200	0.016	0.38	95%	0.00	0.00	0.03	0.16

[1] EC50s used are fish 0.71 mg/L, invertebrates 0.16 mg/L, duckweed 15 µg/L and algae 2.4 µg/L.
[2] From Table 69; ≤0.22 µg/L is 99% protection; ≤0.6 is 95%; ≤1.0 is 90%; ≤2.0 is 80% and >2.0 is <80%. Dark shading Q > 0.5, light shading 0.5 > Q >0.1.

Table 84: The EECs from maximum use rates and quotients based on the Agdrift low ground boom, fine to medium/coarse spray, 90% percentile data.

Agricultural situation	Distance from sprayer	Percent drift from AgDrift	Maximum EEC µg/L	% Species protected[4]	Quotient, sensitive EC50s			
					fish	invert	Duck weed	algae
Orchards[1]	50	0.16	3.8	<80%	0.01	0.02	0.25	1.58
	100	0.10	2.4	<80%	0.00	0.01	0.16	1.00
	200	0.05	1.2	80%	0.00	0.01	0.08	0.50
Broadacre[2]	50	0.22	2.64	<80%	0.00	0.02	0.18	1.10
	100	0.14	1.68	80%	0.00	0.01	0.11	0.70
	200	0.08	0.96	90%	0.00	0.01	0.06	0.40
Rights-of-way, commercial and industrial areas[3]	50	0.06	14.4	<80%	0.02	0.15	1.0	6.0
	100	0.03	7.2	<80%	0.01	0.04	0.50	3.00
	200	0.01	2.4	<80%	0.00	0.01	0.16	1.00
Irrigation and drainage channels[3]	50	0.06	30	<80%	0.07	0.19	2.00	12.5
	100	0.03	15	<80%	0.03	0.09	1.00	6.3
	200	0.01	5	<80%	0.01	0.03	0.33	2.08
Sugarcane[2]	50	0.22	5.28	<80%	0.01	0.03	0.35	2.20
	100	0.14	3.36	<80%	0.00	0.02	0.22	1.40
	200	0.08	1.92	80%	0.00	0.01	0.13	0.80

[1] Model used 10 swaths. [2] Model used 20 swaths. [3] Model used 2 swaths. [4] From Table 69; ≤0.22 µg/L is 99% protection; ≤0.6 is 95%; ≤ 1.0 is 90% ≤ 2.0 is 80% and >2.0 is <80%. Dark shading Q > 0.5, light shading 0.5 > Q >0.1.

In Table 84, based on the AgDrift models (note that the number of swaths sprayed changes depending on situation with only 2 swaths used for rights-of-way etc and channels), there is an unacceptable risk to duckweed at the higher application rates (rights-of-way etc and irrigation channels) at 100 metres. For algae there is an unacceptable risk for all applications and potential buffers to 200 metres except for broadacre applications, where it is mitigable. A 200-metre buffer for broadacre crops would be protective for at least 90% of all species but the same buffer would only protect 80% of species or less in all other situations including sugarcane. The risk is higher from the AgDrift data compared to the Ganzelmeier results. The difference between the two models can be explained by noting that AgDrift is based on typical usage patterns in the US and includes worst-case data while Ganzelmeier is based on European usage and under ideal conditions to minimise spraydrift (best agricultural practice).

Both Table 83 and Table 84use a water depth of just 15 cm. For streams and other water bodies of high conservation values, i.e. with long-term flows, a water depth of 30 cm may be more appropriate for most situations but not necessarily all. However, due to the wide geographic distribution of use of diuron and to ensure adequate protection of shallow swamps or streams, especially during dry spells, DEH is using 15 cm.

From the Ganzelmeier results, a 100-metre buffer for broadacre and 200-metre spraydrift buffer for orchard, and sugarcane crops would fully protect at least 95% of all species from any impacts and it is protective of the most sensitive algae species (Q ~0.2). Phytoplankton with short life cycles and high rate of reproduction recover from herbicide impacts, even high impact events, with return frequencies of days to weeks, especially if there are no persistent residues (Solomon, 1999). Therefore, a quotient of 0.5 is acceptable to Department of the Environment and Heritage provided the frequency of impact events is at least a few weeks apart. Hence, a buffer of 100 metre is considered acceptable for orchard and sugarcane crops where applications are likely to be months apart, although it would only fully protect 90% of species. No practical buffer would be protective for rights-of-way, commercial areas and irrigation/drainage channels at the maximum rates allowed on the label. However, if the maximum label rate were reduced to 20 kg ac/ha, then a 200-metre spraydrift buffer would give an EEC of 1.33 µg/L and Q ≅ 0.5 for algae. Note that for late applications to sugarcane, just before canopy closure, the application is directed onto the soil between the rows of cane and below the growing top of the cane which will reduce any spraydrift.

From the AgDrift results, a buffer of 200 metres for orchard and broadacre crops would only protect approximately 90% of species and would protect algae but the same buffer for sugarcane would be not protective for algae would only be protective for 80% of species.

The Department of the Environment and Heritage concludes that taking into account both the AgDrift and Ganzelmeier data, a 100 metre buffer is the minimum required to protect aquatic systems from use of diuron in orchards and broadacre but 200 metres is required for sugarcane (after harvest or when new cane growth is small and when replanting). For directed application to sugarcane before canopy closure, spraydrift is anticipated to be lower but as the Department of the Environment and Heritage does not have any information on the spraydrift under these conditions, a 50 metre is recommended as a default.

Note that the above conclusions are based on the current label rates and do not take into account the lower rates recommended later in this report due to aquatic risk from run-off.

Aerial

On the labels aerial application for wheat and other winter grains at rates of up to 280 g ac/ha is specifically allowed. However, it is considered that for most winter grains diuron would be applied by ground rigs. Aerial application is only likely under unusual circumstances, such as prolonged wet weather, and fields are too wet for ground rigs. The only other situation where aerial application is mentioned on the diuron labels or is likely is for use of Dropp Ultra (diuron at 60 g/L; thidiazuron 120 g/L), a cotton defoliant. The application rate is 150 to 400 mL/ha (9 to 48 g ac/ha) and there are large spraydrift buffers for citrus in flush (8 km) and lettuce (800 metres). There is no information for Dropp Ultra on droplets sizes but as the label gives directions for tank mixing with organophosphates, it is assumed that application will likely be done using fine droplets. Spraydrift was evaluated using the AgDrift model at tier 3. Table 85 has the spraydrift, resultant EEC and quotient for several distances away for the site of spraying. Note that the ASEA boundary spray quality curve very fine/fine (137 μm VMD) was used as worst case.

Table 85: Concentration of spraydrift from aerial application (Tier 3) to cotton in water 15 cm deep and resulting quotient for algae (EC50 = 2.4 μg/L).

	AgDrift, very fine/fine, vmd = 137 μm			
	200 m	**300 m**	**400 m**	**600**
% spraydrift	6.5	5.0	4.35	3.18
Concentration, μg/L	2.6	2.0	1.74	1.27
Quotient algae	1.08	0.83	0.72	0.53

[1]The very fine/fine boundary curve is worst case for fine quality spray. Dark shading Q > 0.5. light shading 0.5 > Q >0.1.

The results in Table 85 clearly indicate a risk to algae and to achieve an acceptable risk (i.e. Q < 0.5) for a fine spray, a buffer of at least 600 metres is needed when Dropp Ultra containing diuron is used as a cotton defoliant. This does not take into account the effect of the other active (thidiazuron) or if it is tank mixed. Note that there would only be one application at the end of the growing season.

If the aerial application to wheat remains on the label, the EECs are 4.4 times those in Table 85, i.e. at 600 metres the concentration in water is 5.59 μg/L and there is a high risk to algae. To get a Q = 0.5, AgDrift shows that a buffer of >1500 metres is required but this is outside the range of AgDrift and it tends to overestimate the drift at 800 metres or greater. Using coarser droplets (medium vmd 294 μm) a 750-metre spraydrift buffer is required to protect nearby waterways (assumes 15 cm deep water). Note that as aerial application is only expected when the wheat paddocks are to wet for ground applications, there will be an increased risk from runoff that will be considered later.

There are label warnings not to allow spraydrift to contaminate any off-target water bodies (eg ponds, streams, lakes, rivers or waterways). Nevertheless, if aerial application to wheat is to remain on the labels, then the labels should specify a spray quality, i.e. medium or coarse, together with the related spraydrift buffer to protect aquatic areas from spraydrift. It is suggested that when spraying with a medium spray, a 750-metre buffer is used or with a coarse spray, a 500-metre buffer is used.

9.4.2.4 Leaching

Leaching potential can be easily predicted using a nomogram based on the mobility and persistence, (Gustafson, 1989). Use of the laboratory data for persistence (laboratory half-lives in soil of 20-372 days) and sorption (Koc 418-1666) gives GUS scores 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 lysimeters data showed only limited leaching, which was confirmed in the field studies. Those conducted in Europe showed very limited leaching of diuron with no evidence of movement below 20 cm (see Section 0; Pogány, 1993). The US data also showed limited leaching with no detections below 30 cm except at one sandy site in California where diuron showed leaching down to 60 cm (Tweedy, 1999 and Stevenson, 1990b). In Australia field studies, conducted in sugarcane at Bundaberg, diuron was detected in ground water at maximum concentration of ~6 µg/L (Simpson and Hargreaves, 2001). This is higher than would be expected from the overseas studies, possibly indication that diuron has higher mobility in Australian soils.

Diuron was also found in the MIA in tile drain water at levels up to 28 µg/L (Bowmer *et al*, 1998). The tile drains in the MIA are porous pipes at approximately 2 metres deep and are designed to keep the watertable below the root zone. In the MIA 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 despite the overseas field lysimeters studies and general field studies showing the diuron is not likely to leach in most circumstances and only limited leaching in sand soils to 60 cm deep. However, the Australian field data indicates that diuron is leaching to at least 2 metres and is found in ground waters in several areas. The use of diuron in sandy soils or soils with shallow water tables needs to be restricted or at least reduced. Due to previous concerns with respect to runoff from various crops (sugarcane and citrus), reduced rates have already been recommended that will also reduce the concentration of diuron in leachate. Therefore a separate recommendation is not required specifically to control leaching.

9.4.2.5 Multiple Applications

The label directions for some crops (apples and pears, pawpaw and cotton) clearly indicate at least two applications are allowed, often at split rates or with the second application at half rates. For most other crops there are no directions on the number of sprays allowed, although it is implied that there is expected to be only one spray per season/year.

Though analysis of the risk to the environment is based on a single application, the use of field data has reduced the need to recalculate to allow for an extra application. Considering the relatively long degradation rates in some soils (half-lives up to 372 days) and water/sediment systems (half-lives up to 232 days), additional applications of diuron will significantly increase the environmental risk. It is recommended that only one application of diuron should be allowed per season/year on the label at maximum rates. If two applications are to be made, these should be at a split rate and the total should not be greater than the maximum label rate for the crop.

9.4.3 Risk to Terrestrial Organisms

9.4.3.1 Invertebrates

The risk to honey bees is expected to be slight to low at application rates of <3.6 kg/ac/ha as at the application rate of 3.6 kg ac/ha (equivalent to 36 µg ac/cm^2) the quotient is 0.25,

assuming that a honeybee is approximately 1 cm^2 in surface area (Davis and Williams 1990). As application is normally by ground rig, direct overspraying of bees is not expected. Irrigation and drainage channels and rights-of-ways, commercial and industrial areas where higher rates are used are not generally attractive to bees and therefore the exposure to bees in these areas is expected to be lower. Again this risk would be reduced by the removal of high rate uses from the labels.

No data regarding the toxicity of diuron to earthworms were made available. However diuron has been described as being non-toxic to earthworms, (http://pubs.cas.psu.edu/freepubs/pdfs/uc182.pdf).
No other information on soil organisms or soil micro-organisms was available.

9.4.3.2 Birds

Based on the typical diet of northern bobwhite quail and the EEC of diuron in food items when oversprayed, the concentration of diuron in the diet can be calculated for a single application (Urban and Cook 1986). With the dietary LD_{50} for quail of 1730 mg ac/kg bw the quotient can then be calculated (see Table 86).

Table 86: Avian EEC and risk quotients.

Agricultural situation	Min-max rates kg/ha	EEC in food items, mg/kg wt.		Quotient [1]	
		Quail	mallard	quail	mallard
Orchards	1.8-3.6	189-377	70-140	0.11-0.22	<0.03
Broadacre	0.45-1.8	47-189	17-70	0.03-0.11	≤0.01
Rights-of-way, commercial and industrial areas	Initially 4-36 retreatment at 3.1-16	419-3771	155-1396	0.24-2.18	0.03-0.28
Irrigation and drainage channels	10-75	1048-7857	388-2908	0.61-4.54	0.08-0.58
Sugarcane	1.8-3.6	189-377	70-140	0.11-0.22	<0.03

[1]LC50 used were 1730 mg/kg food for quail and 5000 mg/kg for mallards

There is no risk to quails from overspray at <1.8 kg ac/ha and a slight risk to quails from feeding on food items directly oversprayed at between 1.8 to 3.6 kg ac/ha. Assuming only 50% of the birds diet is actually oversprayed, the hazard to quails and mallards is low and acceptable for all applications at 3.6 kg ac/ha. However, that is not the case for the two high application rates where, even with consideration that half of the diet is not sprayed, there is a slight to high risk to quails, Q = 0.12-2.27 (unacceptable at 16.5 kg ac/ha, Q = 0.5) and a slight risk to mallards.

The label conditions for application to rights-of-way, commercial and industrial areas and irrigation and drainage channels do not appear to be sufficient to prevent overspraying when avian food items, i.e. seed heads, insects, could be present. Further, no evidence was presented that diuron has a repellent effect and it is assumed that birds will eat food items that have been sprayed. Therefore, it is concluded that with the current label there is a slight risk to birds when used to treat non-agricultural situations, especially at rates greater than 3.6 kg ac/ha and that the risk is unacceptable at rates of >16.5 kg ac/ha. This risk would be lowered to an acceptable level if high application rate uses were removed from the labels due to runoff risks as recommended later in this report.

9.4.3.3 Terrestrial Plants

When used according to label directions, the exposure to non-target vegetation should be limited to spraydrift or runoff. In tests using both dicotyledon and monocotyledons seedlings (see Table 67), the most sensitive was tomato seedlings with EC25 of 2.2 g/ha but another five species (wheat, pea, soybean, cucumber and sugar beet) were also very sensitive, with EC25s ranging from 6 to 16 g/ha. Note that the US EPA has recently set its level of concern for terrestrial plants using EC25 data with Q = 1 (US EPA 2004). The US EPA uses this approach as the endpoints are effects, not mortality, and therefore there is the possibility of recovery.

For aerial application to wheat and cotton at maximum rates of 280 and 48 g ac/ha, the EC25 of 2.2 g/ha corresponds to 0.8 and 5% of the respective application rates. For application to wheat with medium spray quality, AgDrift (using fine/medium boundary curve) shows that at 620 metres the spraydrift is 0.8% of the application rate, i.e. 2.24 g/ha and quotient is 1. For the cotton application at 48 g ac/ha with a fine spray (boundary curve fine/very fine used), at 220 metres the spraydrift is 5% of the application rate, corresponding to 2.2 g/ha, and quotient = 1. Note that wheat seedlings are sensitive to diuron and in the vegetative vigour test had an EC25 of 13 g/ha yet the label would allow over spraying at 280 g ac/ha, presumably without damage to the crop.

For ground rig applications, the Ganzelmeier data (field crops) shows that at 20 metres the spraydrift is 0.15% of the application rate for broadacre crops (maximum label rate = 1.8 kg ac/ha) this corresponds to 2.7 g/ha and Q ~ 1. Using AgDrift (medium spray, low boom) at 150 metres the spraydrift is 0.12% of applied and Q = 1.

There are few, if any, reports concerning damage to non-target plants from using diuron, which would appear to show that users are well aware to the toxicity of diuron to non-target plants and take appropriate precautions or that plants affected by spraydrift recover and there is no long tem damage.

9.4.4 Antifouling use of Diuron

The use of diuron in anti-fouling paints impact on the Great Barrier Reef Lagoon, the contribution of diuron for this source have been examined. The use of diuron on vessels <25 metres in length has been revoked in the UK, Demark and the east coast of Sweden (Kevin, McHugh and Waldock, 2002).

The anti-fouling paints containing diuron are used on a range of vessels including large ships but in Australia a large use is for yachts and other recreational vessels that are moored, as well as commercial and naval vessels. The situation modelled using a large marina situated on the coast near the GBR and is based on Gold Coast City Marina, Coomera, Queensland. This marina has an area of ~3.2 ha (8 ac), depth of 5 m (unusually deep to cater for larger yachts) and capacity for of the order of 100 vessels of various sizes (Leigh-Smith, 2001). For the purposes of the model, a low tide depth of 3 m and high tide depth of 4 m were assumed, with 100 yachts having an average wetted area of 40 m^2 continuously occupying the area of the marina.

To obtain an estimate of the leach rate of diuron it is assumed that the hull is coated with an anti-fouling paint at 25 g diuron/m^2. This corresponds closely with likely maximum application rates given in Table 21 and with one by Wattyl. It is assumed that there is an

effective lifetime of the paint of one year. This would imply an average leach rate of ~68 mg/m^2/day for diuron if it is assumed that all the active ingredient is exhausted over the life time of the paint.

The classical 'tidal prism' approach assumes complete mixing due to tide and a continuous loading of the contaminant, given:

g	=	load introduced per tidal cycle (μg)
P	=	Tidal Prism volume (exchange volume - i.e. difference between low and high tide), including river flow (L)
V	=	Low Tide volume (L)
P+V	=	High Tide volume (L)
R = P/P+V	=	Exchange ratio, i.e. the fraction of well mixed water that would be removed from the estuary
d	=	Decay rate of the pollutant per tidal cycle (as %)
y=[1-R](1-d)	=	Fraction remaining after one tidal cycle
gy	=	Amount of pollutant remaining after 1st cycle (μg)
Css*	=	Steady State Concentration (μg/L) = gy/V(1-y)

* Batley *et al* (1989) gives derivation of Css = gy/V(1-y)

Table 87 gives estimates of steady-state concentrations for the marina allowing for degradation. The Department of the Environment and Heritage has used 6% as the degradation per tidal cycle for the decay rate (actually the dissipation rate of diuron from water using $t_{1/2}$ of 4.2 days from Table 30). The marina has a tidal exchange of 25% per tidal cycle. The predicted steady state concentration (Css) is 3.46 μg/L (Table 87). The risk quotient is 1.44 for green algae. It is also above the LOEC endpoints for seagrass (0.1 μg/L), crustal algae and corals. It is concluded that within the modelled marina the steady state concentration of diuron is high enough to indicate a potential risk to marine organisms.

While the above calculations show that diuron use in antifouling paints could affect marine organisms, a marina generally does not have high conservation values and therefore this is of less concern. However, the area outside of the marina is of more concern. Allowing for a 1:10 dilution, used by the Department of the Environment and Heritage for industrial chemicals entering seawater (this may be generous for some marinas and given that the GBR lagoon is a high conservation area) the localised concentration outside of the marina is 0.35 μg/L. An effect on algae is unlikely (risk quotient 0.15) at this level, however it is still above the LOEC for seagrasses, crustose coralline algae and corals.

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 (eg collection of waste material from bunded areas of the slipways/dry-docks involved and disposal of appropriately 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 Department of the Environment and Heritage is aware of modern marinas with well designed facilities containing sumps and filters to remove fouling and other waste material, although it is unclear as to the proportion of such well designed facilities compared to more basic facilities, especially in small centres adjacent to the Great Barrier Reef). Nonetheless, users will need to comply with relevant State environmental regulations and local government requirements, though controls are likely to be less comprehensive than for drydocks handling large ships, where handling of TBT waste has been important.

Table 87: Estimated steady-state concentrations (μg/L) for a model Australian marina and the calculated acute hazard quotient (Q) for the most sensitive test species, rainbow trout.

Parameter	
Decay/adsorption rate per tidal cycle	**6%**
Total wetted area of treated hulls (m^2)	4000
Leach rate per day (mg ai/m^2/d)	68
g (load, mg/tidal cycle)	2.72×10^5
y (fraction remaining after 1 tidal cycle)	0.15
P (tidal prism volume, L)	3.24×10^7
V (low tide volume, L)	9.71×10^7
Css (steady state concentration, μg/L)	**3.46**
Hazard quotient for algae using EC50	**1.44**

Dark shading Q > 0.5. light shading 0.5 > Q >0.1.

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, with waste from well controlled facilities going to approved landfill and some degradation also occurring in collection sumps. 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. Such release should be minimised as far as possible.

A Code of Practice has been developed by the ANZECC (Australia and New Zealand Environment and Conservation Council) for the use of antifouling paints, which has been published (ANZECC, 2000). These guidelines should be promoted by registrants of diuron containing antifouling paints as part of their stewardship for these paints. Appropriate guidance for the application and maintenance of vessel antifouling coatings may also be available from State environmental agencies (eg NSW EPA 1999; Vic EPA 1998).

The UK Advisory Committee on Pesticides reviewed antifouling use of diuron 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). 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. The measured levels in open marinas, more typical of Australian marinas, ranged from <1 to 613 ng/L with an average of 170 ng/L (see Table 58). The UK modelled data showed levels of 2254 ng/L (100% of all boat using diuron antifouling paints), similar to that in Table 87.

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 Fitzory River (0.9 μg/kg) and in interdial seagrass at Pallarenda (0.8 μg/kg dw). The Fitzory 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 antifouling uses in marina and ports etc. In addition, the Fitzory River has a substantial area of the catchment (2790 km^2, 2% of catchment) used for horticultural crops (GBRMPA, 2001).

It is concluded by Department of the Environment and Heritage that the antifouling use of

diuron does make a contribution of the overall load of diuron in the Great Barrier Reef Lagoon. Although, the field evidence to support this is confounded by other non-agricultural uses of diuron. However, due to the fact that the level of contribution is expected to be relatively small compared to that coming from agricultural sources and allowing for a 1:10 dilution factor, the retention of the use of diuron in antifouling paints is considered acceptable.

9.5 References

ACP, 2000. UK Advisory Committee on Pesticides, meeting on 7 September, 2000. http://www.hse.gov.uk/hthdir/noframes/pest49.htm

ACP, 2002. UK Advisory Committee on Pesticides, 'Environmental Risk Assessment of Booster Biocides in Antifouling Products', August 2002.

ANZECC (2000). Code of Practice for Antifouling and In-water Hull Cleaning and Maintenance. Australian and New Zealand Environment and Conservation Council, Australian Transport Council, Australian Maritime Safety Authority, Maritime Safety Authority of New Zealand. BP1287, May 2000.

APVMA (2002). Diuron Review Scope Document. http://www.apvma.gov.au/chemrev/diuron_scope.pdf

Attaway, H H, Camper, N D and Paynter, M J B (1982). Anaerobic Degradation of Diuron by Pond Sediment. *Pesticide Biochemistry and Physiology,* **17**, 96-101.

Australian Agriculture, 1995. Australian Agriculture: the complete reference on rural industry (1995) Douglas F ed, fifth edition. National Farmers' Federation. Morescope Publishing Pty Ltd., Hawthorn East, Victoria.

Australian Bureau of Meteorology (1997). Australian climate data. National Climate Centre, Bureau of Meteorology, Commonwealth of Australia. World Wide Web site "http://www.bom.gov.au/".

Bell A (2001). Effects of Photosystem II-Inhibiting Herbicides on Four Mangrove Species. Honours thesis submitted to Department of Botany, University of Queensland.

Bergström, L F, Bramble Jr, F Q, Aronsson P, Brücher, J and Norwood, G I (1996). Leaching of [Phenyl(U)-14C]Diuron in Scandinavian Soils Using Field Lysimeters. Swedish University of Agricultural Sciences and E. I. du Pont de Nemours & Co Inc, Wilmington, Delaware. Du Pont Report No. AMR 4584

Bowmer, K H; Korth, W; Scott, A; McCorkelle, G and Thomas, M (1998). Pesticide Monitoring in the Irrigation Areas of South-Western NSW. CSIRO Land and Water, Technical Report 17/98. Available at http://www.clw.csiro.au/publications/technical98/tr17-98.pdf

Bramble Jr. F Q, Behmke F D and Norwood, G I (1998). Batch Equilibrium (Adsorption/desorption) of 14C-Diuron, Fenuron and N'-(3-chlorophenyl)-N,N-Dimethylurea on Soil. -97.

Bramble Jr. F Q, Behmke F D, Frizzell, R S and Norwood, G I (1998-interrim report). Field Soil Dissipation of Diuron Following Application of Karmex DF Herbicide. E. I. du Pont de Nemours & Co Inc., Delaware. Report No. AMR 4383-97.

Bramble, F Q and Norwood, G I (1994). Supplement No 1 To: The Degradation of [Phenyl(U)-^{14}C]Diuron in Soil Under Aerobic Conditions. Inveresk Research International, Scotland. E. I. du Pont de Nemours & Co Inc., Delaware. Report No. AMR 2603-93 Supplement No. 1

Brumhard, B, Konig Th and Sommer, H (1998). Adsorption/Desorption of Desmethyl-Diuron on Difference Soils. Bayer AG, Leverkusen, Germany. Report No. MR 575/96

Campbell E, Palmer M, Shao Q and Wilson D (2000). Mathematic and Information Sciences, CSIRO. See http://www.cmis.csiro.au/Envir/burrlioz/.

Cantin, N E (2004). Implications of Reduced Photosynthetic yields caused by the Herbicide Diuron for Coral Reproduction and Larval Metamorphosis. Presented to the 10th International Coral Reef Symposium Okinawa, Japan, 2004. Department of the Environment and Heritage has only seen the abstract.

Cooper, B (1994). Central and Northwest Regions Water Quality Program, 1993/94 Report. NSW Department of Land and Water Conservation, Sydney, NSW. Report No. TS 94.087.

Cooper, B (1995). Central and Northwest Regions Water Quality Program, 1994/95 Report. NSW Department of Land and Water Conservation, Sydney, NSW. Report No. TS 95.087. ISBN 0 7310 2328 5

Cooper, B (1996). Central and Northwest Regions Water Quality Program, 1995/96 Report. NSW Department of Land and Water Conservation, Sydney, NSW. Report No. TS 956.048. ISBN 1327-1032

De Vries, R (1996). Determination of the Metabolism and Degradation Rate of Diuron in Soil. NOTOX, Netherlands. NOTOX Project No. 157826. Owner: Agrichem, The Netherlands (presented by Bayer CropScience Pty Ltd).

Dewez D, Marchand M, Eullaffroy P and Popovic R (2002). Evaluation of the Effects of Diuron and Its Derivatives on *Lemma gibba* using a Fluorescence Toxicity Index. *Environmental Toxicology* **17**, 493-501.

Doyle, R C, Kaufman D D and Burt, G W (1978). Effect of Dairy Manure and Sewage Sludge on ^{14}C-Pesticide Degradation in Soil. *J. Agric. Food Chem.,* **26**, 987-989.

Duke NC, Bell AM, Pedersen DK, Roelfsema CM, Godson LM, Zahmel KN, Mackenzie J and Bengston-Nash S (2003). Mackay Mangrove Dieback - Investigations in 2002 with Recommendation for Further Research, Monitoring and Management. September 2003. Marine Botany Group, Centre for Marine Studies, the University of Queensland. Report to the Queensland Department of Primary Industries, Northern Fisheries Group and the Community of the Mackay Region. (Available on Internet website http://www.marine.uq.edu.au/marbot/significantfindings/mangrovedieback.htm).

Duke NC, Roelfsema C, Tracey D and Godson L (2001). Preliminary investigation into dieback of mangroves in the Mackay Region: initial assessment and possible causes. Mangrove Ecosystem Research and Marine Botany Group, Botany Department, the University of Queensland. Report to the Queensland Fisheries Service, Northern Region and the Community of the Mackay Region. (Available on Internet website http://www.marine.uq.edu.au/marbot/significantfindings/mangrovedieback.htm).

Ellis, P A and Camper, N D (1982). Aerobic Degradation of Diuron by Aquatic Microorganisms. *J. Environ. Sci. Health.* B17(3), 277-289.

Environment Australia (2003) Model and Guidance for Estimating Predicted Environmental Concentrations to Surface Water and Soil from Chemicals Released to the Environment Through a Sewage Treatment Plant. Chemical Assessment Section, Environment Australia, Canberra Australia.

Environment Western Australia (1999). State of the Environment Report 1998. Internet http://www.environ.wa.gov.au/pubs/soe/soe19_a.htm

Forster HC, Vasey AJ & Cole CE (1970). Field crops. In: Leeper GW ed, The Australian environment, fourth edition. Commonwealth Scientific and Industrial Research Organisation & Melbourne University Press, Melbourne, Australia, pp 94-119.

Frank, R and Klöpffer, W (1985). UBA Research Report No. 10602046. (Not sighted by the Department of Environment and Heritage)

Gagnon, M (2002). Hepatotoxicity of Diuron to Australian Marine Fish. A complementary study to: Reitsema, T J, Gagnon, M M and Spickett J (2002). An evaluation of the environmental impacts of two antifouling biocides: Toxicity to marine organisms. Report to Natural Heritage Trust, Environment Australia, Canberra.

GBRMPA, 2001. Great Barrier Reef Water Quality Action Plan,. A report to Ministerial Council on target for pollutant loads. http://www.gbrmpa.gov.au/corp_site/key_issues/water_quality/action_plan/

Ham G J (1994). Irrigation and Drainage-A Queensland Perspective. 41st Annual General Meeting, ANCID 11-14 Sept., Kununurra (1994).

Hamilton, D & Haydon, G (1996) Pesticides and Fertilisers in the Queensland Sugar Industry - Estimates of Usage and Likely Environmental Fate. Project: ICM-R&D.94.01. Resource Management Institute, Department of Primary Industries, Indooroopilly, Queensland, January 1996.

Hargreaves PA., Simpson BW, Ruddle LJ. and Packett R. (1999). Persistence and fate of pesticides in sugarcane soils. Proceedings of Australian Society of Sugar Cane Technologists 21:287-293.

Harrington L, Fabricius K, Eaglesham G and Negri, A (2004). Synergistic effect of Diuron and Sedimentation on Photosynthesis and Survival of Crustose Coralline Algae. Marine Pollution Bulletin, in press.

Hausmann S M (1992). Anaerobic Aquatic Metabolism of [Phenyl(U)-^{14}C]Diuron. E. I. du Pont de Nemours & Co Inc, Wilmington, Delaware. Report No. AMR 2067-91.

Hausmann S M (1997a). Aerobic Aquatic Metabolism of [Phenyl(U)-^{14}C]Diuron Supplement 1. E. I. du Pont de Nemours & Co Inc, Wilmington, Delaware. Report No. AMR 2066-91 Supplement 1.

Hausmann S M (1997b). Anaerobic Aquatic Metabolism of [Phenyl(U)-^{14}C]Diuron Supplement 1. E. I. du Pont de Nemours & Co Inc, Wilmington, Delaware. Report No. AMR 2067-91 Supplement 1.

Hausmann S M and Kraut, G M (1992). Aerobic Aquatic Metabolism of [Phenyl(U)-^{14}C]Diuron. E. I. du Pont de Nemours & Co Inc, Wilmington, Delaware. Report No. AMR 2066-91.

Hawkins, D R, Kirkpatrick, D, Shaw, D and Mobbs, J (1989). The Photodegradation of ^{14}C-Diuron in Water. Huntington Research Centre, Cambridgeshire, UK. E. I. du Pont de Nemours & Co Inc., Delaware. Report No. AMR 909-87.

Hawkins, D R, Kirkpatrick, D and Shaw, D (1989). The Hydrolytic Stability of ^{14}C-Diuron. Huntington Research Centre, Cambridgeshire, UK. E. I. du Pont de Nemours & Co Inc., Delaware. E. I. du Pont de Nemours & Co Inc AMR 908-87.

Hawkins, D R, Kirkpatrick, D, Shaw, D and Chan, S C (1990). The Metabolism of [Phenyl(U)-^{14}C]Diuron in Keyport Silt Loam Soil under Aerobic Conditions. Huntington Research Centre, Cambridgeshire, UK. E. I. du Pont de Nemours & Co Inc., Delaware. Report No. AMR 1202-87-8.

Haynes D; Müller J and Carter, S (2000). Pesticides and Herbicide Residues in Sediments and Seagrasses from the Great Barrier Reef World Heritage Area and Queensland Coast. *Marine Pollution Bulletin*, **41**, 279-287.

Haynes D, Ralph P, Pranges J and Dennison B (2000). The Impact of the Herbicide Diuron on Photosynthesis in Three Species of Tropical Seagrass. *Marine Pollution Bulletin*, **41**, 288-293.

Heintze, A (2002). Determination of the Adsorption/Desorption Behaviour of DCPU in Four Different Soils. Arabeitsgemeinschaft GAB Biotechnologie GmbH & IFU Umweltanalytic GmbH, Öschelbronn, Germany. Owners: Bayer AG, Monheim Germany and Griffin (Europe), Belgium. Study Code 20001409/01-PCAD.

Hellpointer, E (1991). Determination of the Quantum Yield and Assessment of the Environmental Half Life of the Direct Photodegradation of Diuron in Water. Bayer AG, Leverkusen Germany.

Hornshuh, M J and Antle, P E (1996). Field Aquatic Dissipation and Transport of Karmex DF Herbicide in Arkansas. Du Pont Laboratories, Wilmington, Delaware; Braun Intertec Corp. Minnesota; Enviro-Test Laboratories, Alberta and ABC Laboratories Inc. Columbia. E. I. du Pont de Nemours & Co Inc, Delaware. Report No. AMR 2617-93.

Jones RL and Kerswell AP (2003). Phytotoxicity of Photosystem II (PSII) herbicides to coral. Marine Ecology Progress Series 261: 149-159.

Jones RJ, Müller J, Haynes D and Schreiber U (2003). Effects of herbicides diuron and atrazine on corals of the Great Barrier Reef, Australia. *Marine Ecology Progress Series* **251**: 153-167.

Kevin V T, McHugh M and Waldock M (2002). Antifouling paint booster biocides in UK coastal waters: Inputs, occurrence and environmental fate. *The Science of the total Environment,* **293**, 117-127.

Kirkwood A and Dowling R (2002). investigation of mangrove dieback in the Pioneer River Estuary, Mackay. Queensland Herbarium, Environment Protection Agency. A report prepared for the Sugar Research Development Corporation, August 2002. Project EPA). (Available via internet).

Leech FJ, KR Helyar & G Geeves (1998). Describing soil pH profiles and their effect on yield of cereal crops. Agronomy - Growing a Greener Future. Proceedings of the 9th Australian Agronomy Conference, Wagga Wagga, NSW, 20-23 July 1998. Http://life.csu.edu.au/argonomy/papers/15/15.html.

Leigh-Smith R (2001). Email response to the Department of the Environment and Heritage, dated March 1 2001 from Mr Ryan Leigh-Smith, Customer Relations, Gold Coast City Marina, Coomera, Queensland.

Levy O, Dubinsky Z and Achituv Y (2003). Photobehavior of stony corals: responses to light spectra and intensity. *Journal of Experimental Biology* 206: 4041-4049. Internet: www.biology.uky.edu/Yan/ Jessica_photo_behavior_coral.pdf

Liu, L Cand Cedeno-Maldanado, A (1974). Effects of Fluometuron, Prometryne, Ametryne and Diuron on Growth of Two *Lemna* Species. *Journal of Agriculture of University of Puerto Rico*, **63**(4), 483-488.

Mackie, J A and Hall B E (1994). The Degradation of [Phenyl(U)-^{14}C]Diuron in Soil Under Aerobic Conditions. Inveresk Research International, Scotland. E. I. du Pont de Nemours & Co Inc Inc., Delaware. Report No. AMR 2603-93.

Marwood CA, Solomon KR and Greenberg BM (2001). Chlorophyll fluorescence as a bioindicator of effects on growth in aquatic macrophytes from mixtures of polycyclic aromatic hydrocarbons. *Environmental Toxicology and Chemistry*. **20**(4):.890–898

McMahon K, Bengston-Nash S, Eagleham G, Müller JF, Duke NC and Winderlich S (2004).Herbicide contamination and the potential impact to seagrass meadows in south-east Queensland, Australia. *Marine Pollution Bulletin*, in press.

Mensink BJWG, Montforts M, Wijkhuizen-Mas′lankiewicz L, Tibosch H, Linders JBHJ (1995) Manual for summarising and evaluating the environmental aspects of pesticides. Report No. 679101022, National Institute of Public Health and Environmental Protection, Bilthoven, The Netherlands.

Mensink, BJWG, de Greef J and Linders JBHJ (1996). How to estimate concentrations of pesticide in surface water semi-quantitatively: an interim report. Report No.: 679102011. National Institute of Public Health and the Environment, Bilthoven, The Netherlands.

Müller, J F; Duquesne, NG, J; Shaw, G R; Krrishnamohan, K Manonmanii, K; Hodge M and Eagleham G K (2000). Pesticides in Sediments from Queensland Irrigation Channels and Drains. *Marine Pollution Bulletin*, **41**, 294-301.

Muschal, M (1997). Central and Northwest Regions Water Quality Program, 1996/97 Report. NSW Department of Land and Water Conservation, Sydney, NSW. Report No. CNR97.063. ISBN 1327-1032

Muschal, M (1998). Central and Northwest Regions Water Quality Program, 1997/98 Report. NSW Department of Land and Water Conservation, Sydney, NSW. Report No. CNR98.038. ISBN 1327-1032

NPWRC (undated). Aquatic and Wetland Vascular Plants of the Northern Great Plains. 60. Lemnaceae, the Duckweed Family. US Geological Survey, Northern Prairie Wildlife Research Center. Internet http://www.npwrc.usgs.gov/resource/1999/vascplnt/allspec.htm (April 2004).

NSW EPA (1999). Environmental Guidelines. Best Management Practice for Marinas and Boat Repair Facilities. (NSW) Environment Protection Authority Publication No. EPA 99/60.

Pesticides and Safety Directorate (2002). Advisory Committee on Pesticides: Environmental Risk Assessment of Booster Biocides in Anti-Fouling Products. Available from: Department of Environment, Food and Rural Affairs, Pesticides Safety Directorate, Mallard House, 3 Peasholme Green, York, UK

Pogany, E (1993). Dissipation of Diuron in Soils under Field Conditions (Germany). Bayer AG, Germany. Report No. 2138/91

Råberg S, Nyström M, Erös M and Plantman P (2003). Impact of the herbicides 2,4-D and Diuron on the metabolisms of the coral *Porites cylindrical*. Marine Environmental Research, **56**, 503-514. Abstract available from www.sciencedirect.com.

Powell S, Neal R and Leyva J (1996). Runoff And Leaching Of Simazine And Diuron Used On Highway Rights-Of-Way. Environmental Protection Agency, California. Available at http://www.cdpr.ca.gov/docs/empm/pubs/ehapreps/e9603.htm

Priester, T M (1990). Batch Equilibrium (Adsorption/desorption) and Soil Thin-Layer Chromatography Studies with [carbonyl-^{14}C] Diuron. E. I. du Pont de Nemours & Co Inc, Wilmington, Delaware. Report No. AMR 452-85.

Priester, T M and Chesser, S A (1995). Field Aquatic Dissipation and Transport of Karmex DF Herbicide in California. Du Pont Laboratories, Wilmington, Delaware; Braun Intertec Corp. Minnesota, and Enviro-Test Laboratories, Alberta. E. I. du Pont de Nemours & Co Inc, Delaware. Report No. AMR 2233-91.

Rautmann D, Streloke, M, and Winkler, R (2001). New basic drift values in the authorisation procedure for plant protection products. In Forster, R., Streloke, M. Workshop on Risk Assessment and Risk Mitigation Measures in the Context of the Authorization of Plant Protection Products (WORMM). Mitt. Biol. Bundesanst. Land-Forstwirtsch. Berlin-Dahlem, Heft 383.

Rouchaud, J, Neus, O, Bulcke, R, Cools, K, Eelen H and Dekkers, T (2000). Soil Dissipation of Diuron, Chlorotoluron, Simazine, Propyramide and Diflufenican Herbicides after Repeated Applications in Fruit Tree Orchards. *Arch. Environ. Contam. Toxicol.,* **39**, 60-65.

Salih A, Hoegh-Guldberg O and Cox G (1998). Bleaching responses of symbiotic dinoflagellates in corals: the effects of light and elevated temperature on their morphology and physiology. *In:* Greenwood JG. & Hall NJ, eds (1998). *Proceedings of the Australian Coral Reef Society 75th Anniversary Conference, Heron Island October 1997.* School of Marine Science, The University of Queensland, Brisbane. pp. 199-216.

Schäfer, H (1998). Calculation of DT50 Values of Diuron and its Metabolite Desmethyl-Diuron in Soil under Aerobic Conditions. Bayer AG, Germany. Report MR-427/98.

Simpson, B W and Hargreaves, P A (2001). Pesticide Transport in Sugar Production Systems. Natural Resources and Mines, Queensland Government, Indooroopily Brisbane.

Simpson, B W (2002). River Water Quality in the Pioneer Catchment on February 14-15, 2002. Water Quality Assessment and Protection, Natural Resources and Mines, Queensland Government, Indooroopily Brisbane.

Sims HJ, *et al* (1990). Grain crops. In: Reid RL ed, The manual of Australian agriculture, fifth edition. Butterworths Pty Limited, Sydney, pp 59-120.

Sneikus, J (2001). Aerobic Degradation and Metabolism of Diuron in the Water-Sediment System. Bayer AG, Leverkusen Germany. Bayer Ag and Griffin LLC, Belgium. Bayer Report No. MR-433/01.

Solomon K R (1999). Integrating Environmental Fate and Effects Information: The Key to Ecotoxicological Risk Assessment for Pesticides. In: *Pesticide Chemicstry and Bioscience: The Food-Environment Challenge.* ed Brooks G T and Roberts TR. The Royal Society of Chemistry, Cambridge, UK. Pp 313-326.

Stevenson, I E (1990a). Photodegradation of [Phenyl(U)-^{14}C]Diuron on Soil Under Artificial Sunlight. Biospherics Inc., Maryland and Cambridge Analytical Associates, Inc., Massachusetts. . E. I. du Pont de Nemours & Co Inc Inc., Delaware. Report No. AMR 771-87.

Stevenson, I E (1990b). Field Soil Dissipation of Karmex DF Herbicide. Du Pont Laboratories Inc., Wilmington, Delaware and Enviro-Test Laboratories, Alberta. E. I. du Pont de Nemours & Co Inc., Delaware. Report No. AMR 1145-88.

Tebbutt THY (1992) Principles of water quality control. Fourth edition, Pergamon Press, Oxford, England.

Teisseire H, Couderchet M and Vernet G (1999). Phytotoxicity of Diuron alone and in combination with copper or folpet in duckweed (*Lemna minor*). Environmental Pollution, **106**, 39-45.

Timme, G, Frehse, H and Laska, V (1986). Statistical interpretation and graphic representation of the degradational behaviour of pesticide residues II. Pflanzenschutz-Nachrichten Bayer, 1986, 39 (2), 187-203. Published.

Tomlin CDS ed (1997) The pesticide manual: a world compendium. Eleventh edition, pp 372-374. British Crop Protection Council, Surrey, UK.

Torstensson L et al., 2002. Environmental Problems with the Use of Diuron on Swedish Railways. Pesticide Outlook, June 2002, page 108-111.

Tweedy, B G (1999). Field Soil Dissipation of Diuron Following Application of Karmex DF Herbicide. ABC Laboratories Columbia and Du Pont Laboratories, Delaware. Griffin LLC, Georgia. Griffin Protocol No. GP98-084. Report No. 46305.

USGS (1998). Pesticides in Surface and Ground Water of the United States: Summary of Results of the National Water Quality Assessment Program (NAWQA). . US Geological Survey, July 1998. Internet http://ca.water.usgs.gov/pnsp/allsum/.

US EPA 2003. RED for Diuron available at: http://www.epa.gov/oppfead1/endanger/effects/diuron_efed_chapter.pdf

US EPA (2004). US EPA Pesticide Ecotoxicity Database; for further information and contacts for access see http://www.epa.gov/oppefed1/general/databasesdescription.htm.

US EPA (2004b). US EPA GENEEC model: for further information see http://www.epa.gov/oppefed1/models/water/index.htm.

Vic EPA (1998). Cleaner Marinas – EPA Guidelines for Protecting Victoria's Marinas. (Victorian) Environment Protection Authority Publication No. 624.

Williams, M D (1995a). Hydrolysis of ^{14}C-Diuron as a Function of pH at 25°C and 50°C. ABC Laboratories, Inc; Columbia, Missouri. Sanachem Pty Ltd, Durban South Africa. Report No. 42580.

Williams, M D (1995b). Determination of the Aqueous Photodegradation of ^{14}C-Diuron. ABC Laboratories, Inc; Columbia, Missouri. Sanachem Pty Ltd, Durban South Africa. Report No. 42581.

Vic EPA (1998). Cleaner Marinas – EPA Guidelines for Protecting Victoria's Marinas. (Victorian) Environment Protection Authority Publication No. 624.

Yu, W C (1988). Anaerobic Soil Metabolism of [Phenyl(U)-^{14}C]Diuron. Ambridge Analytical Associates, Inc., Boston Massachusetts. E. I. du Pont de Nemours & Co Inc Inc., Delaware. Report No. AMR 552-86.

Zoltán, B (2001a). The acute toxicity of diuron techn. to Rainbow trout (*Onchorhynchus mykiss* walbaum). Laboratory of Hydrobiology, Százhalombatta, Hungary. Owner: North-Hungarian Chemical Works Co Ltd.

Zoltán, B (2001b). The prolonged toxicity of diuron techn. to Rainbow trout (*Onchorhynchus mykiss* walbaum). Laboratory of Hydrobiology, Százhalombatta, Hungary. Owner: North-Hungarian Chemical Works Co Ltd.

Zoltán, B (2001c). The acute toxicity of diuron techn. to Daphnia (*Daphnia magna Straus*). Laboratory of Hydrobiology, Százhalombatta, Hungary. Owner: North-Hungarian Chemical Works Co Ltd.

Zoltán, B (2001d). Diuron Tech. Alga, Growth Inhibition test with *Selenastrum capricornutum* Prins (Starr stock). Laboratory of Hydrobiology, Százhalombatta, Hungary. Owner: North-Hungarian Chemical Works Co Ltd.

9.6 Attachments

Attachment 1

Maps showing sugar production areas in central and northern Queensland and areas sampled by Duke at el (2003) for their mangrove dieback study. The maps have been reproduced from the Duke et al (2003) report and the Figure numbers and descriptions are as appeared in that report.

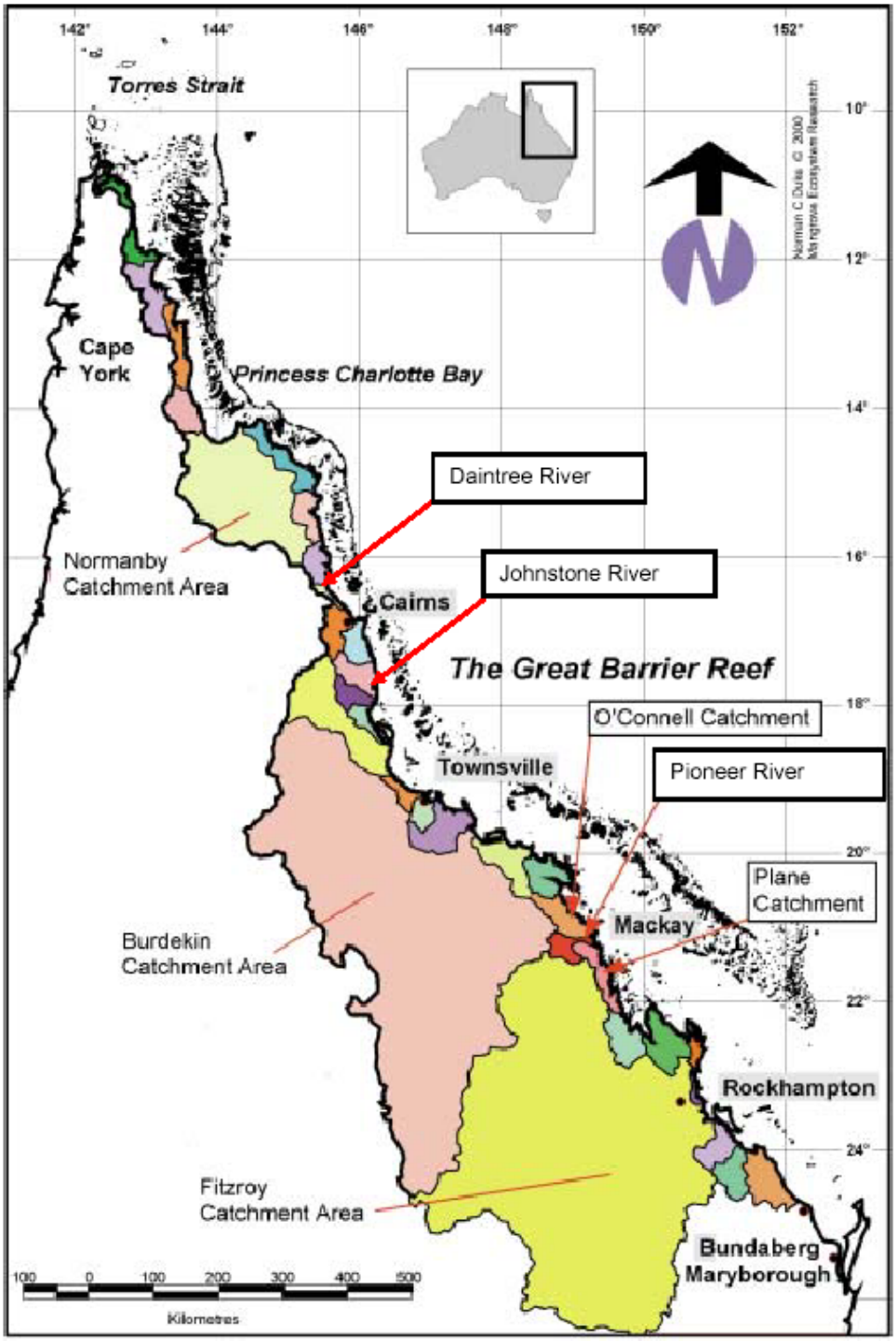


FIGURE 1: Catchment areas along the north and central coast of Queensland showing relative locations of Pioneer (plus McCreadys and Bakers Creeks), Johnstone and Daintree Rivers. These were the estuaries sampled during investigations in 2002.

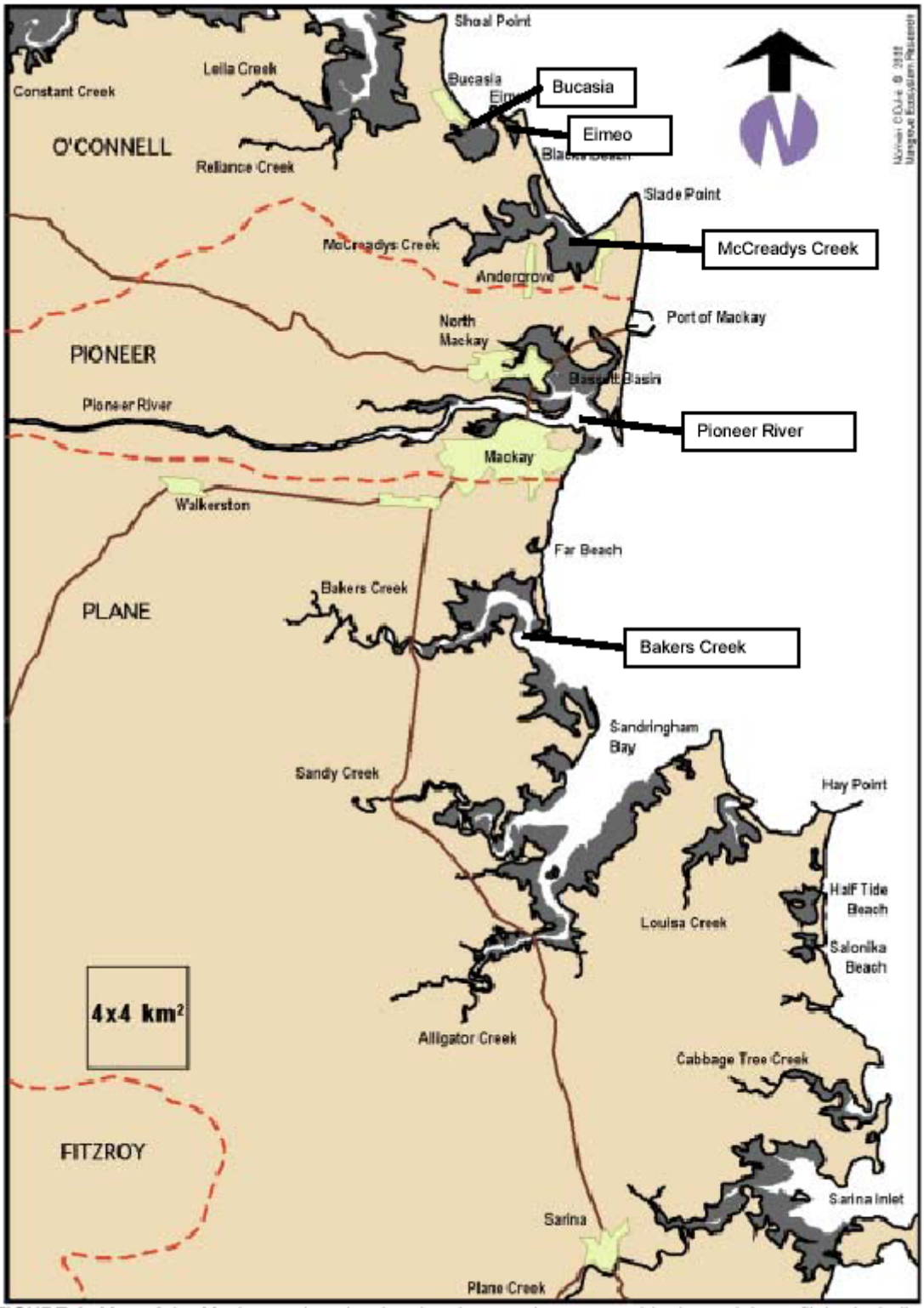


FIGURE 3: Map of the Mackay region showing the six estuaries surveyed in the aerial overflight, including Leila/Reliance Creeks, Bucasia/Eimeo Creeks, McCreadys Creek, Pioneer River, Bakers Creek and Sandringham Bay –Sandy/Alligator Creeks.

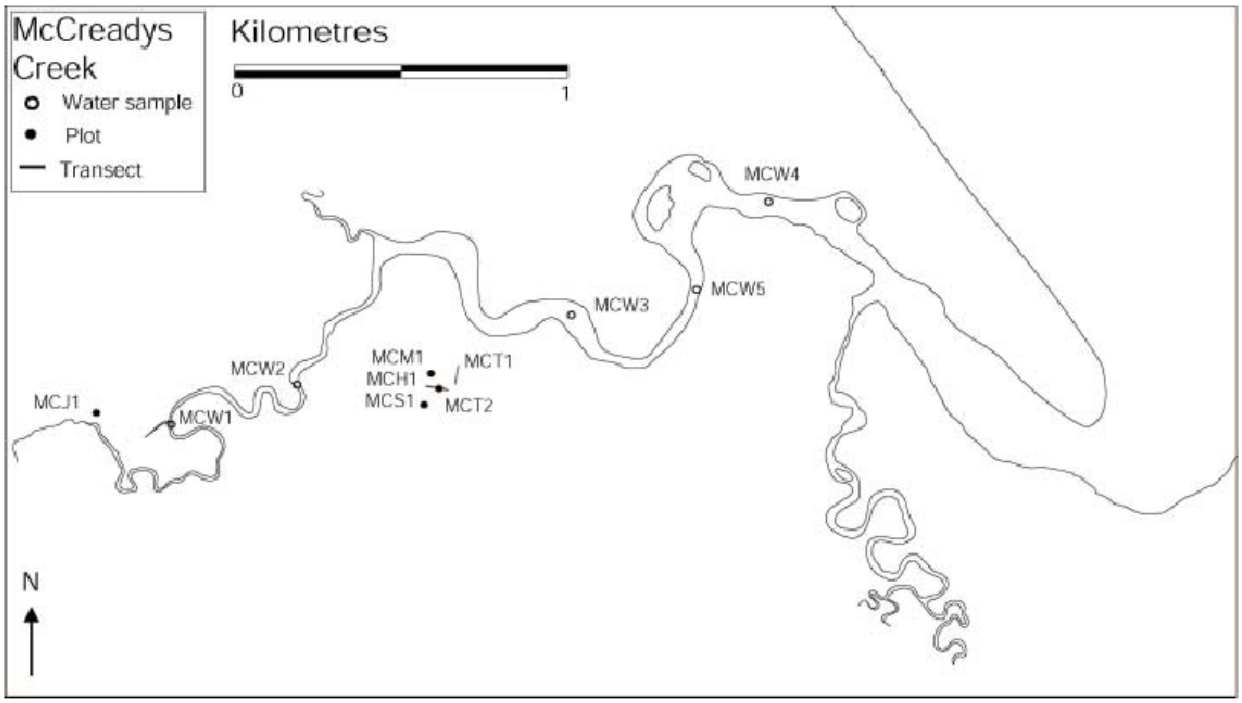


FIGURE 4: McCreadys Creek estuary study sites showing water sampling, plot and transect locations.

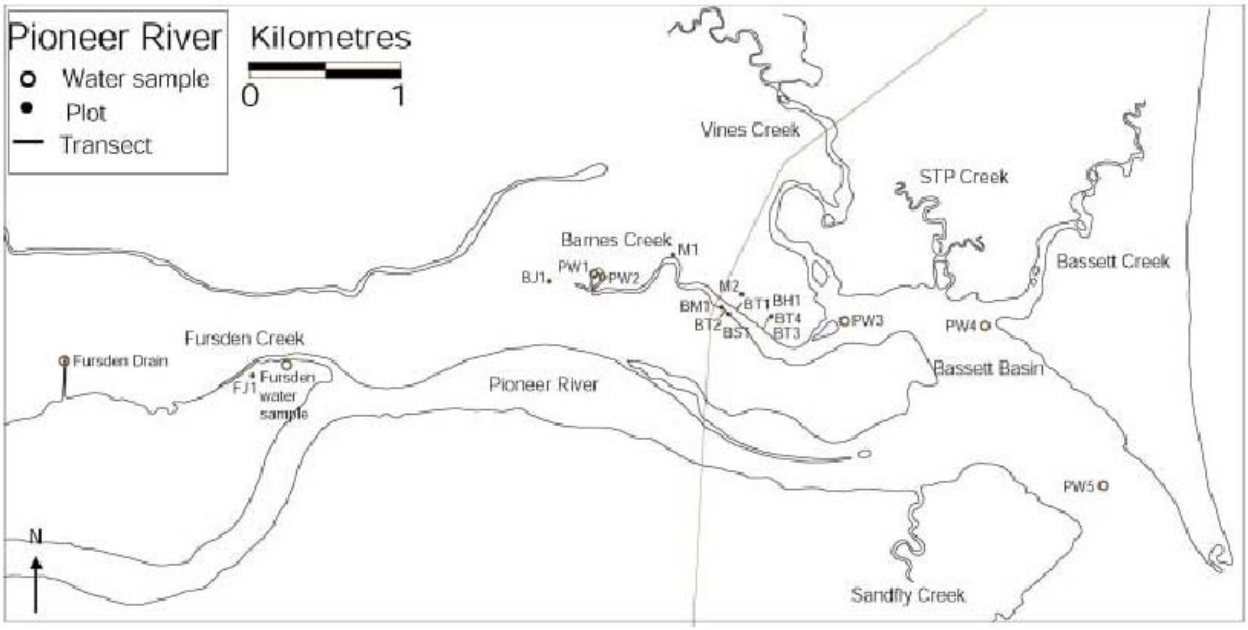


FIGURE 5: Pioneer River estuary study sites showing water sampling, plot and transect locations.

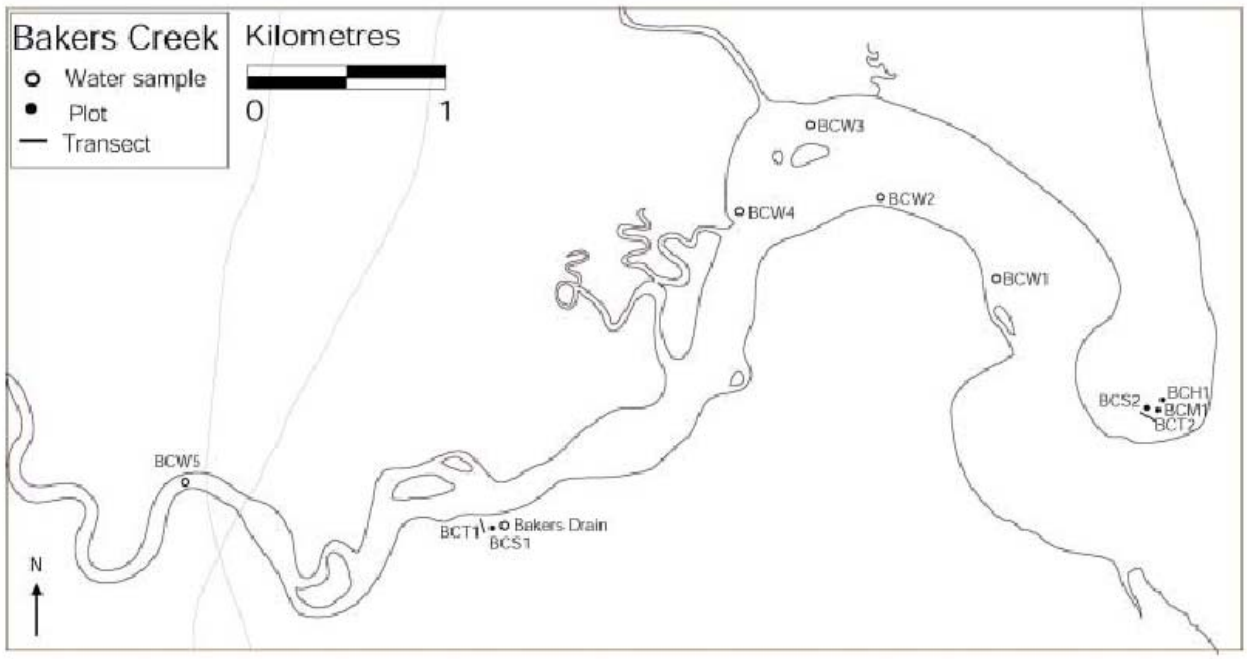


FIGURE 6: Bakers Creek estuary study sites showing water sampling, plot and transect locations.

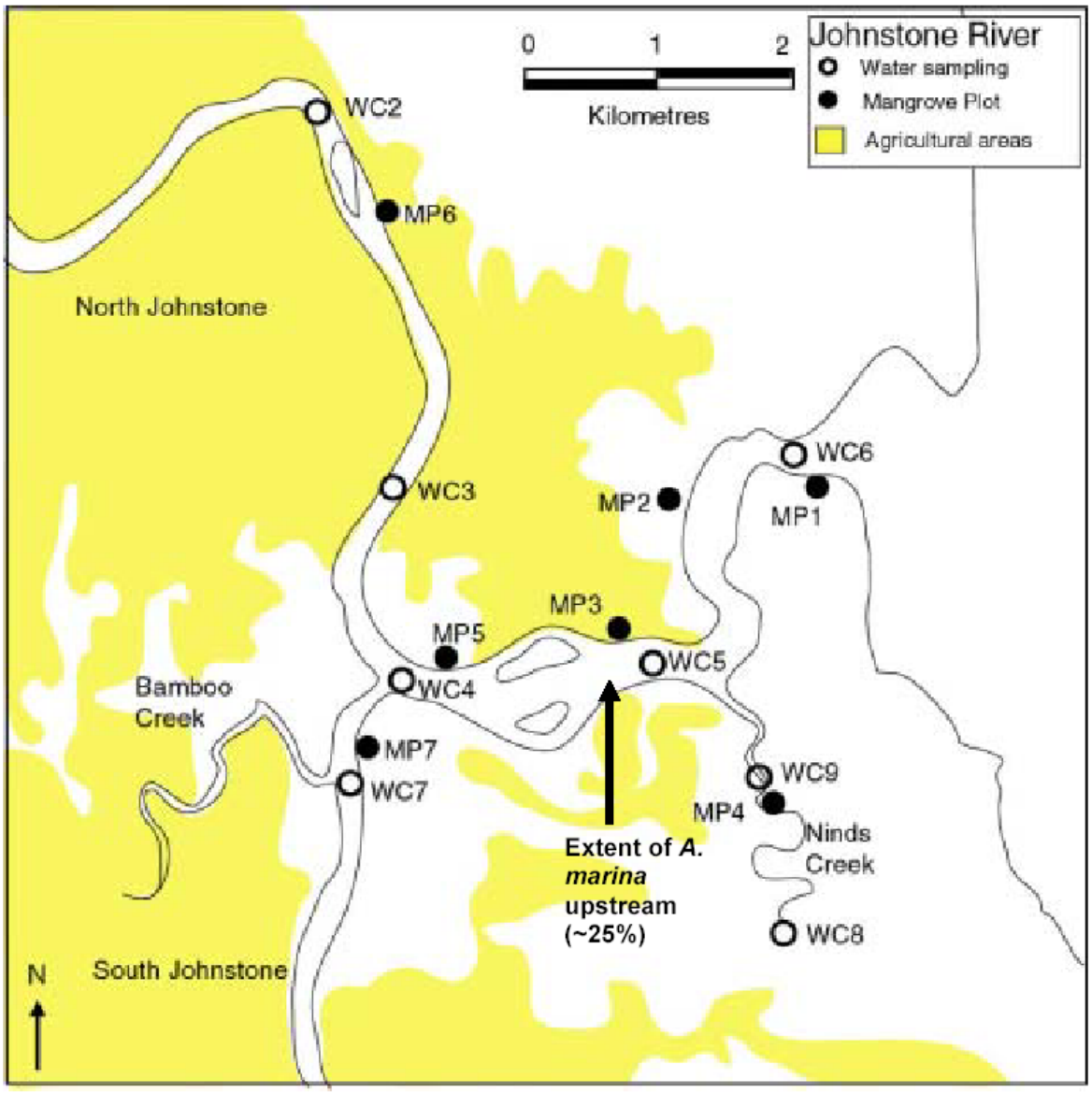


FIGURE 69: Johnstone River mangrove and water sampling sites showing extent of *A. marina* upstream (arrow) from the river mouth (for location see Figure 1).

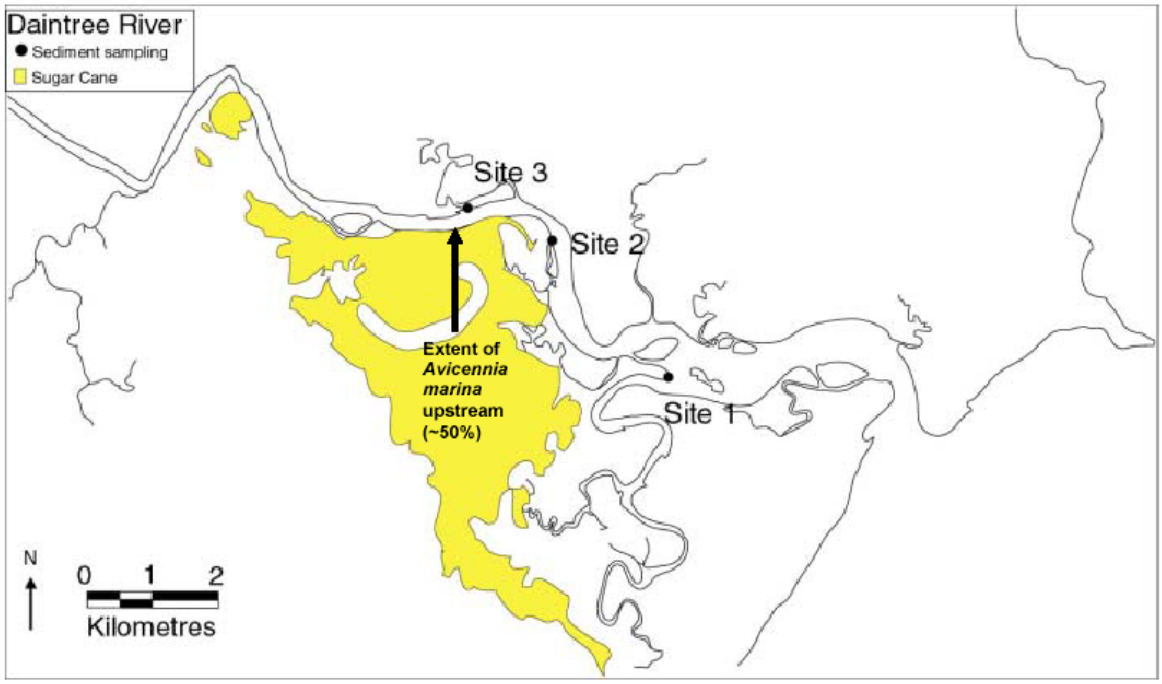
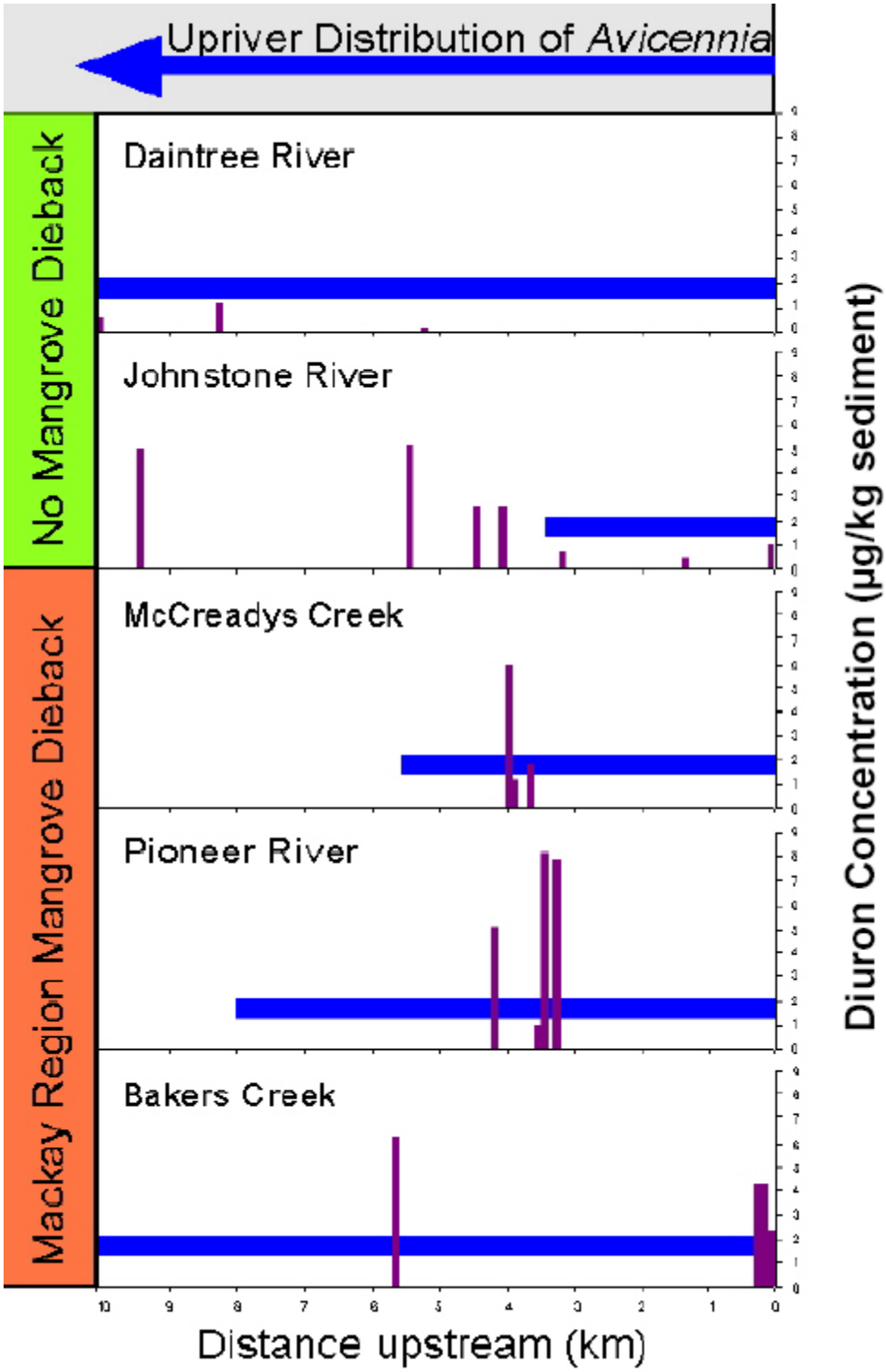


FIGURE 70: Daintree River mangrove sediment sampling sites and areas of sugar cane farming showing extent of *A. marina upstream* (arrow) from the river mouth (for location see Figure 1).

Attachment 2

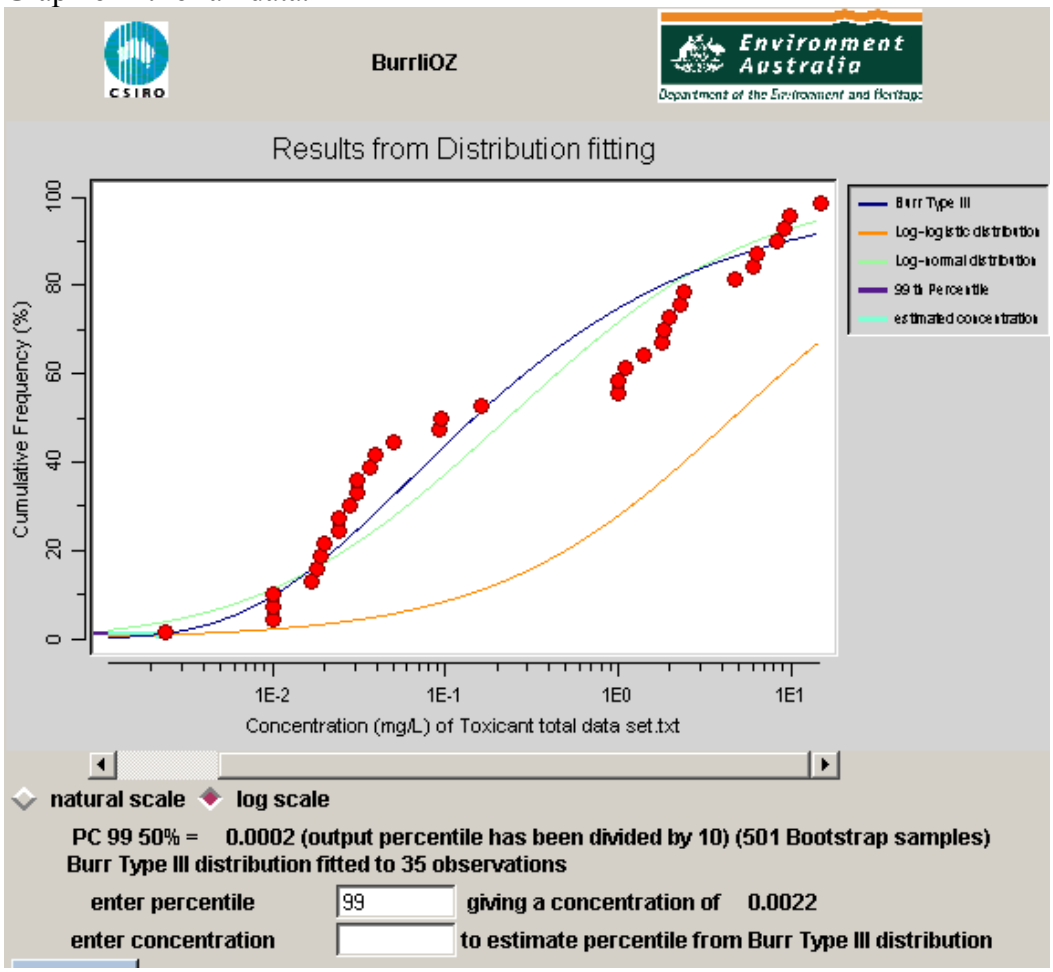
Graphic of distribution of *Avicennia marina* and concentration of diuron taken from Duke *et al* (2003).



Attachment 3

The BerrilOZ data fits are given below for all the entire data. From the Barr type 3 curves, fitted to the data sets, the 99th percentile point was determined by the BerrilOZ program (output not given).

Graph of fit for all data.



The fit of the data to the Barr type 3 curves is not the best when using all the data set but when fitted to the fish, invertebrate and alga data sets the fit to the individual 3 data sets is much better.

Attachment 4

Using the US EPA GENEEC 2.0 model (US EPA, 2004), the EEC were calculated as a comparison to the Department of the Environment and Heritage's screening level assessment. Several parameters/factors are used, including number of applications, Kd, solubility, spray zones etc. In order to keep it comparable, only a single application is considered and there was 100 metre spraydrift buffer to minimise the effect of spraydrift and examine runoff principally. Table 1 gives the EEC and quotient in the same formate as used in Table 70 to allow direct comparisons.

Table 1. The EEC and risk quotients using GENEEC 2.0 model.

Agricultural situation	Min-max rates Kg/ha	EEC µg/L		Risk Quotient. 95% protection [1]					
				fish		invert		algae	
		min	max	mim	max	min	max	min	max
Orchards	1.8-3.6	61.9	123.7	0.11	0.22	0.23	0.46	11.4	22.9
Broadacre	0.45-1.8	15.5	61.9	0.03	0.11	0.06	0.23	2.87	11.4
Rights-of-way, commercial and industrial areas	Initially 4-36 retreatment at 3.1-16	137.4	1237	0.25	2.21	0.51	4.58	25.5	229
Irrigation and drainage channels	10-75	343.6	2577	0.61	4.60	1.27	9.54	63.6	477
Sugarcane	1.8-3.6	61.9	123.7	0.11	0.22	0.23	0.46	11.5	22.9

The input parameters used were:

- Kd = 2.9 (Kf value)
- $t_{1/2}$ aerobic soil = 372 days
- $t_{1/2}$ aerobic aquatic metabolism = 232 days
- $t_{1/2}$ aquatic photolysis = 30 days
- 1 application
- ground boom spraying with 300 ft (100 metre) no spray zone

The large spraydrift buffer that was used to minimise the input to the pond from spraydrift. The other parameters are from the fate section of this report and are worst case.

Attachment 5

The BerrilOZ data fits are given for all the seedling vigour data set. From the Barr type 3 distribution curves the 95th and 90th percentile points were determined by the BerrilOZ program.