Australian Government

Australian Pesticides and Veterinary Medicines Authority

PUBLIC RELEASE SUMMARY

on the Evaluation of the New Active PRODIAMINE in the Product

BARRICADE TURF HERBICIDE

APVMA Product Number 62982

DECEMBER 2010

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PREFACE

The Australian Pesticides and Veterinary Medicines Authority (APVMA) is the Australian Government regulator with responsibility for assessing and approving agricultural and veterinary chemical products prior to their sale and use in Australia.

In undertaking this task, the APVMA works in close cooperation with advisory agencies, including the Department of Health and Ageing, Office of Chemical Safety and Environmental Health (OCSEH), Department of Sustainability, Environment, Water, Population and Communities (DSEWPaC), and State Departments of Primary Industries.

The APVMA has a policy of encouraging openness and transparency in its activities and of seeking community involvement in decision making. Part of that process is the publication of public release summaries for products containing new active constituents.

The information and technical data required by the APVMA to assess the safety of new chemical products and the methods of assessment must be undertaken according to accepted scientific principles. Details are outlined in the APVMA's publications *Ag MORAG: Manual of Requirements and Guidelines* and *Vet MORAG: Manual of Requirements and Guidelines*.

This Public Release Summary is intended as a brief overview of the assessment that has been conducted by the APVMA and of the specialist advice received from its advisory agencies. It has been deliberately presented in a manner that is likely to be informative to the widest possible audience thereby encouraging public comment.

About this document

This is a Public Release Summary.

It indicates that the Australian Pesticides and Veterinary Medicines Authority (APVMA) is considering an application for registration of an agricultural or veterinary chemical. It provides a summary of the APVMA's assessment, which may include details of:

- the toxicology of both the active constituent and product
- occupational exposure aspects
- environmental fate, toxicity, potential exposure and hazard
- efficacy and target crop or animal safety.

Comment is sought from interested persons on the information contained within this document.

Making a submission

In accordance with sections 12 and 13 of the Agvet Code, the APVMA invites any person to submit a relevant written submission as to whether the application for registration of **BARRICADE TURF HERBICIDE**

should be granted. Submissions should relate only to matters that the APVMA is required by legislation to take into account in deciding whether to grant the application. These grounds are **public health aspects, occupational health and safety, chemistry and manufacture, environmental safety,** and **efficacy**. Submissions should state the grounds on which they are based. Comments received outside these grounds cannot be considered by the APVMA.

Submissions must be received by the APVMA by close of business on 15 February 2011 and be directed to the contact listed below. All submissions to the APVMA will be acknowledged in writing via email or by post.

Relevant comments will be taken into account by the APVMA in deciding whether the product should be registered and in determining appropriate conditions of registration and product labelling.

When making a submission please include:

- Contact name
- Company or Group name (if relevant)
- Postal Address
- Email Address (if available)
- The date you made the submission.

All personal and ***confidential commercial information (CCI)***[1] material contained in submissions will be treated confidentially.

Written submissions on the APVMA's proposal to grant the application for registration that relate to the **grounds for registration** should be addressed in writing to:

Contact Officer, Pesticides Program

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[1] A full definition of "confidential commercial information" is contained in the Agvet Code.

Further information

Further information can be obtained via the contact details provided above.

Copies of full technical evaluation reports covering toxicology, occupational health and safety aspects, and environmental aspects are available from the APVMA on request.

Further information on public release summaries can be found on the APVMA website:
http://www.apvma.gov.au

1 INTRODUCTION

Applicant

Syngenta Crop Protection Pty Ltd

Details of Product

It is proposed to register Barricade Turf Herbicide, containing prodiamine (480 g/L) as a suspension concentrate formulation. The product is intended for pre-emergent control of weeds in established turf. Prodiamine is a new active ingredient for the Australian turf industry.

The toxicological characteristics of prodiamine have previously been submitted and considered by NDPSC at its February 1995 meeting and exempted from scheduling. Barricade Turf Herbicide is a member of the dinitroaniline group of herbicides and has the tubulin formation inhibitor mode of action. For weed resistance management this product is a Group D herbicide.

Prodiamine is currently registered for use in USA, Costa Rica, Hong Kong, Japan, Korea (south), Qatar and United Arab Emirates.

Barricade Turf Herbicide offers an advantage over currently registered turf products for the control of the two target weeds with excellent residual action. This means that the proposed dose rate will allow season long control with a single application, minimising the number of applications.

This publication provides a summary of the data reviewed and an outline of the regulatory considerations for the proposed registration of Barricade Turf Herbicide and approval of the new source of active constituent, prodiamine.

2 CHEMISTRY AND MANUFACTURE

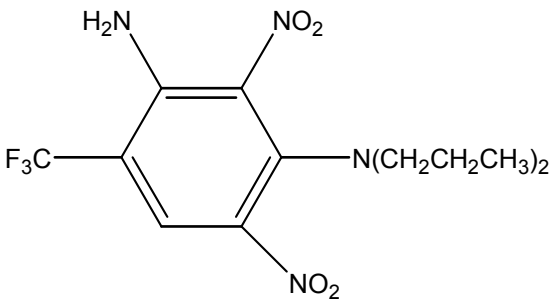
2.1 Active Constituent

Manufacturing Site

The active constituent Prodiamine is manufactured by Elgine Fine Chemicals Inc, 2114 Larry Road, Elgin, South Carolina, USA.

Chemical Characteristics of the Active Constituent

The chemical active constituent Prodiamine has the following properties:

Common Name:	Prodiamine (BSI, E-ISO approved)
IUPAC Name:	5-dipropylamino-α,α,α-trifluoro-4,6-dinitro-*o*-toluidine; 2,6-dinitro-N^1,N^1-dipropyl-4-trifluoromethyl-*m*-phenylenediamine
CAS Name:	2,4-dinitro-N^3,N^3-dipropyl-6-(trifluoromethyl)-1,3-benzenediamine
CAS Registry Number:	29091-21-2
Molecular Formula:	$C_{13}H_{17}F_3N_4O_4$
Molecular Weight:	350.3
Structure:	

APVMA Active Constituent Standard for Prodiamine Active Constituent

Constituent	Specification	Level
Prodiamine	Prodiamine	Not less than 905 g/kg

2.2 Product

Distinguishing name	Barricade Turf Herbicide
Formulation type	Suspension concentrate
Active constituents concentrations	Prodiamine 480 g/L

Physical and Chemical properties of the Product

Appearance	Mobile liquid with red to dark red colour
Odour	Characteristic fruity odour
Acidity/Alkalinity	pH 4-7 (1% dilution)
Density	1.065
Emulsion characteristics	Max. 0.1 mL oil/cream separation after 30 minutes standing
Persistent foam (1:4 dilution)	Max. 60 mL foam after 1 minute
Viscosity	40-60 mPa.s
Flash point	Not applicable
Flammability	Not flammable
Explosive properties	Not explosive
Oxidising properties	No oxidising properties
Corrosive hazard	Not applicable
Dielectric breakdown voltage	Not applicable, formulation is not intended for use around electrical equipment.
Dangerous goods classification	Not dangerous good according to the Australian Code of Transport of Dangerous Goods by Road and Rail.

Recommendation

Based on a review of the chemistry and manufacturing details provided by the applicant, registration of Barricade Turf Herbicide is supported.

3 TOXICOLOGICAL ASSESSMENT

3.1 Summary

Prodiamine is an existing approved active ingredient in the Australian market; however, no products containing prodiamine are currently registered. Prodiamine is part of the dinitroaniline herbicide family, which disrupt the mitotic processes in plant cell division. The product BARRICADE Turf Herbicide is a suspension concentrate formulation containing the active ingredient prodiamine at 480 g/L. It is used for the pre-emergent control of Crowsfoot grass and Summer grass, two weeds which often grow amongst established turf.

Prodiamine is a low oral, dermal and inhalational toxicant. It is a low skin and eye irritant, and it is not a skin sensitiser.

BARRICADE Turf Herbicide has low acute oral, dermal and inhalational toxicity. It is minimally irritant to rabbit skin and eye, and it is a moderate to high-level skin sensitiser in guinea pigs.

Short-term dermal toxicity studies in rabbit revealed that prodiamine was a slight skin irritant, but not a dermal toxicant. Dietary sub-chronic studies in rat and dog revealed increased liver weight and decreased reproductive organ weights, as well as and minor changes in serum enzyme and protein levels.

A chronic study with prodiamine in dog did not reveal significant toxicological events, though liver, thymus and haematological toxicity was observed at higher doses. Two combined chronic/carcinogenicity studies in mouse and rat noted no significant changes in carcinogenicity rates, but liver toxicity at high doses was observed.

Prodiamine is unlikely to be genotoxic or neurotoxic. The chemical was neither a reproductive nor a developmental toxicant.

Occupational Health and Safety

Workers may be exposed to the product when opening containers, mixing/loading and application of the product, cleaning up spills and maintaining equipment, or re-entering treated areas. The main route of exposure to the product will be dermal contact, with limited inhalation exposure while preparing and using the product.

Based on the risk assessment conducted, First Aid Instructions, Warning Statements and General Safety Precautions, Safety Directions and Re-handling statement have been recommended and shown on the product label.

Conclusion

Based on an assessment of the toxicology and occupational health and safety, it was considered that there should be no adverse effects on human health from the use of BARRICADE Turf Herbicide when used in accordance with the label directions.

3.2 Summary Of The Evaluation Of Toxicological Studies

The toxicological database for prodiamine, which consists primarily of toxicity tests conducted using animals, is quite extensive. In interpreting the data, it should be noted that toxicity tests generally use doses that are high compared with likely human exposures. The use of high doses increases the likelihood that potentially significant toxic effects will be identified. Findings of adverse effects in any one species do not necessarily indicate such effects might be generated in humans. From a conservative risk assessment perspective however, adverse findings in animal species are assumed to represent potential effects in humans, unless convincing evidence of species specificity is available. Where possible, considerations of the species specific mechanisms of adverse reactions weigh heavily in the extrapolation of animal data to likely human hazard. Equally, consideration of the risks to human health must take into account the likely human exposure levels compared with those, usually many times higher, which produce effects in animal studies. Toxicity tests should also indicate dose levels at which the specific toxic effects are unlikely to occur. Such dose levels as the No-Observable-Effect-Level (NOEL) are used to develop acceptable limits for dietary or other intakes (ADI and ARfD) at which no adverse health effects in humans would be expected.

Toxicokinetics and Metabolism

[^{14}C]-labelled prodiamine administered by the oral route was rapidly absorbed, metabolised and excreted in Sprague Dawley rats. After 24 hours, approximately 70 % of the total dose was excreted, with faecal excretion accounting for 65–90 % and urinary excretion accounting for 7–30 % of the total dose after 4 days. Tissue and carcass retained approximately 0.5–1.4 % of the total administered dose after 4 days. No evidence of bioaccumulation was found upon repeat-dose administration. Primary metabolites of prodiamine included a mix of conjugated and polar metabolites, formed through a range of N-dealkylation, ring cyclisation, phenyl ring hydroxylation and conjugation mechanisms.

Acute Toxicity

Prodiamine is a low oral (LD_{50} > 5000 mg/kg bw), low dermal (LD_{50} > 2000 mg/kg bw) and low inhalational (LC_{50} > 2560 mg/m^3) toxicant. It is a low skin and eye irritant, and not a skin sensitiser.

The formulated product BARRICADE Turf Herbicide, containing 480 g/L prodiamine, showed low acute oral (LD_{50} > 5000 mg/kg bw), dermal (LD_{50} > 5000 mg/kg bw) and inhalational (LC_{50} > 2550 mg/m^3; 4 hour nose-only exposure) toxicity in rats. It was minimally irritating to rabbit skin and eye, and a moderate to high-level skin sensitiser in guinea pigs.

Short-term Toxicity

In New Zealand White rabbits, prodiamine administered at 0, 125, 500 or 1000 mg/kg bw for 21 days by the dermal route revealed that prodiamine was a slight skin irritant, but otherwise did not cause notable signs of toxicity. The NOEL was established at 1000 mg/kg bw/day, the highest dose tested in this study.

In CD rats administered prodiamine by the dietary route at 0, 400, 1200 or 4000 ppm for 13 weeks, no clinical signs of toxicity were noted. Body weight and food consumption were depressed in animals administered 4000 ppm prodiamine. Haematology and clinical chemistry was unremarkable at all test doses. Liver and kidney organ weights were elevated in high-dose groups administered 4000 ppm prodiamine, but

histopathological examination did not reveal treatment-related abnormalities. A NOEL was established at 1200 ppm (equivalent to 80 mg/kg bw/day) based on the effects seen at the highest dose.

In beagle dogs administered prodiamine by the dietary route at 0, 200, 600 or 2000 ppm for 13 weeks, increased liver weight and decreased reproductive organ weights, as well as minor changes in serum enzyme and protein levels were noted in animals administered 2000 ppm prodiamine. Decreased haematocrit, haemoglobin, erythrocyte count and prothrombin time, as well as increased leukocyte count and elevated platelets were observed in animals administered 600 or 2000 ppm prodiamine. Centrilobular necrosis was observed in males administered 2000 ppm prodiamine, and increased incidence of foci of mononuclear cells in livers of male and female animals administered 2000 ppm prodiamine were noted. A NOEL was established at 200 ppm (equivalent to 5 mg/kg bw/day) based on the described effects at higher doses.

Long-Term Toxicity

In a chronic study, where dogs were administered prodiamine by the dietary route at 0, 200, 600 and 2000 ppm/day for 52 weeks, glutamic-pyruvic transaminase levels were significantly lower than controls in all treatment groups compared to controls, while glutamic-oxaloacetic transaminase levels were significantly lower than controls at 2000 ppm. Liver weights were significantly higher in a number of animals treated with 2000 ppm prodiamine. Male thymus weights were significantly lower than controls in animals administered 600 and 2000 ppm prodiamine. Histopathological examination revealed a marginal reduction in the cortex of male animals administered 2000 ppm prodiamine. A NOEL was established at 5 mg/kg bw/day based on the liver, thymus and haematological effects at higher doses.

In a combined chronic/carcinogenicity study, where mice were administered prodiamine by the dietary route at 0, 7.5, 75 and 750 mg/kg bw/day for 99 weeks, an increased incidence of mortality was observed in animals administered 750 mg/kg bw/day prodiamine. Body weight gain was significantly lower at this highest dose, and haematological examination showed increased neutrophil counts in females administered the highest dose at week 52, as well as increased neutrophil counts and reduced lymphocyte counts in males administered the highest dose at weeks 78 and 99. At termination, mean liver weights were significantly increased in females at all test doses; slight but not statistically significant increases in liver weights were noted only in males administered 750 mg/kg bw/day prodiamine. Kidney weights were significantly reduced in female animals administered 75 and 750 mg/kg bw/day prodiamine. An increased incidence of male liver tumours was noted in all treatment groups, though this was not of statistical significance. The incidence of subcutaneous fibrosarcoma was significantly increased above controls in males administered 750 mg/kg bw/day prodiamine, though no dose-response relationship was found. No NOEL was established due to the increased liver weights in all treated female animals.

In a combined chronic/carcinogenicity study, where rats were administered prodiamine by the dietary route at 0, 2.5, 10, 40 or 160 mg/kg bw/day for 108 weeks, body weight gain was reduced in males administered 160 mg/kg bw/day prodiamine, and minor haematological and clinical chemistry changes were noted in animals administered 40 or 160 mg/kg bw/day prodiamine. GPT and GOT enzyme activity was decreased in animals administered 40 and 160 mg/kg bw/day prodiamine, and alkaline phosphatase activity for animals administered 160 mg/kg bw/day prodiamine was reduced for males at 52 week and for females at 76 and 104 weeks. Cholesterol levels were increased in females administered 160 mg/kg bw/day prodiamine at 26, 52 and 78 weeks. Liver weights were significantly increased in female animals administered 40 and 160

mg/kg bw/day prodiamine at week 52; similar increases were observed at study termination in male animals administered 40 mg/kg bw/day prodiamine, and in all animals administered 160 mg/kg bw/day test item. The NOEL was established at 10 mg/kg bw/day based on the liver toxicity observed at higher doses.

Reproduction and Developmental Toxicity

In a two generation reproduction study in rats administered prodiamine at 0, 5, 20 or 200 mg/kg bw/day, a NOEL of 5 mg/kg bw/day was established based on increased liver weights in F2 male weanlings at 20 mg/kg bw/day and both adults and weanlings at 200 mg/kg bw/day.

In a developmental study, where CD rats were administered prodiamine orally at 0, 20, 60 or 200 mg/kg bw/day on days 6-15 of gestation, no notable signs of toxicity or animal mortality were noted. Maternal body weight was reduced in animals administered 200 mg/kg bw/day. Reproductive parameters were unremarkable. A maternal NOEL was established at 60 mg/kg bw/day, and a foetal NOEL was established at 200 mg/kg bw/day (the highest dose tested).

In a developmental study, where NZW rabbits were administered prodiamine orally at 0, 25, 75 and 125 mg/kg bw/day on days 6-18 of gestation, no notable signs of toxicity were noted. Pregnancy rate was lower in animals administered 125 mg/kg bw/day prodiamine compared to controls. Body weight change was decreased in animals administered 75 mg/kg bw/day prodiamine, and negative in animals administered 125 mg/kg bw/day. Reproductive parameters not related to pregnancy rate were normal, and necropsy examinations did not reveal notable abnormalities. A maternal NOEL was established at 25 mg/kg bw/day, and a foetal NOEL was established at 125 mg/kg bw/day (the highest dose tested).

Genotoxicity

Prodiamine was considered to be weakly mutagenic in an Ames test, with one strain reporting a weak positive response. The lack of A-T reversion-sensitive strains diminishes the quality of the data in the test. A guideline-compliant *in vitro* mammalian cell mutation assay produced a negative mutagenic response. This is in contrast to a previously assessed study reported in 1987, where mutagenic activity was noted at 13 and 17 µg/mL in the absence of metabolic activation. The significance of this difference is unknown, but given the current study exhibits full compliance with modern test guidelines, the weight of evidence suggests that prodiamine does not induce forward mutations and is not mutagenic.

The submitted *in vivo* micronucleus test produced a negative result (i.e. prodiamine did not induce a clastogenic effect. Therefore, despite the weak positive response in the Ames test and the different results in separate *in vitro* mammalian cell mutation assays, the weight of evidence suggests that prodiamine is unlikely to be mutagenic.

Special Studies

Neurotoxicity studies

In an acute neurotoxicity study, SD rats (10/sex/dose) were administered a single dose of prodiamine (0, 80, 400 or 2000 mg/kg bw) by oral gavage. Acute oral administration of prodiamine at 2000 mg/kg bw resulted in altered neurological function at 5 hours post-administration. This included reductions in locomotor activity, alertness, frequency of rearing response and rectal temperature, as well as increases in palpebral closure and frequency of animals walking on toes. However, these effects were limited in frequency and more isolated in occurrence at days 7 and 14, and were not considered toxicologically significant at those time points. Acute administration of prodiamine at doses up to and including 400 mg/kg bw did not result in altered neurological behaviour at any point during the study.

In a repeat-dose neurotoxicity study, SD rats were administered prodiamine at 0, 250, 1000 or 4000 ppm (equivalent to 0, 17.97, 71.54 and 291.69 mg/kg bw/day for males; 0, 21.04, 83.92 and 342.54 mg/kg bw/day for females) for 13 weeks. No mortalities were found in animals at all doses tested. No clinical signs of toxicological relevance were observed. The neurotoxicity examinations at the different time points reported an increase in the quantitative measure of motor activity in females administered 4000 ppm at weeks 4 and 8, an increased incidence of behavioural change (seen as walking on toes) in females administered 1000 and 4000 ppm test item at weeks 8, as well as an increase in forelimb grip strength in males and hindlimb splay in females administered 1000 and 4000 ppm at week 13. However, the limited incidence of change in behavioural parameters and similarity to pre-test values, as well as the absence of other notable clinical signs suggested that overall these findings were not of toxicological significance. The weight of evidence suggested that prodiamine was not neurotoxic upon repeat administration at doses up to and including 4000 ppm (291.69 mg/kg bw/day in males, 342.54 mg/kg bw/day in females).

Examination of the study protocols in both neurotoxicity studies found deviations which diminished the quality of the data presented. However, based on available data, it is unlikely that prodiamine is neurotoxic.

Other studies

In an in-house designed short-term study investigating thyroid activity, prodiamine (0, 16.8, 63.0 or 681.2 mg/kg bw/day) was administered to female Wistar rats (6–18/dose) for six weeks by the dietary route, with a sub-set of six animals in control and high-dose groups retained for a recovery phase. Animals administered prodiamine at 16.8 mg/kg bw/day did not present with adverse effects. Administration of prodiamine to animals at up to and including 63 mg/kg bw/day did not alter the metabolism, excretion and elimination of thyroid hormones or alter thyroid function, though toxicologically significant effects were noted at this dose. A NOEL was established at 16.8 mg/kg bw/day based on the thyroid-related effects examined. A general NOEL was not able to be established due to incomplete data collection for haematology, clinical chemistry and histopathology parameters.

3.3 Public Health Standards

Poisons Scheduling

The National Drugs and Poisons Schedule Committee (NDPSC) considered the toxicity of the product and its active ingredients and assessed the necessary controls to be implemented under States' poisons regulations to prevent the occurrence of poisoning.

On the basis of its toxicity, the NDPSC decided in 1995 that “due to the low acute toxicity profile and mild reversible liver effects in chronic studies the scheduling of prodiamine was not appropriate”. This decision suggests that the committee considered that prodiamine should be an unscheduled chemical (i.e. equivalent to an Appendix B entry) in the Standard for the Uniform Scheduling of Drugs and Poisons (SUSDP). There are provisions for appropriate warning statements and first-aid directions on the product label.

NOEL/ADI /ARfD

The Acceptable Daily Intake is that quantity of an agricultural compound which can safely be consumed on a daily basis for a lifetime and is based on the lowest NOEL obtained in the most sensitive species. This NOEL is then divided by a safety factor which reflects the quality of the toxicological database and takes into account the variability in responses between species and individuals.

The ADI for prodiamine was established at 0.05 mg/kg bw/day based on a NOEL of 5 mg/kg bw/day in a 52 week study by the oral route in dog and using a default 100-fold safety factor in recognition of the extensive toxicological database available for prodiamine.

Acute Reference Dose (ARfD)

The acute reference dose is the maximum quantity of an agricultural or veterinary chemical that can safely be consumed as a single, isolated, event. The ARfD is derived from the lowest single or short term dose which causes no effect in the most sensitive species of experimental animal tested, together with a safety factor which reflects the quality of the toxicological database and takes into account the variability in responses between species and individuals.

Because this product will not be used on food producing crops and will not be consumed by food-producing animals, no ARfD is required to be established at this time.

4 OCCUPATIONAL HEALTH AND SAFETY ASSESSMENT

Health hazards

Prodiamine is of low acute oral, dermal and inhalation toxicity. It is a slight skin and eye irritant, and not a skin sensitiser.

Prodiamine is not listed in Safe Work Australia's (SWA) Hazardous Substances Information System (HSIS) Database (2009). With the available toxicology information, prodiamine is not classified as a hazardous substance according to NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 2004).

BARRICADE Turf Herbicide has low acute oral, dermal and inhalation toxicity. It is minimally irritating to the eyes and skin, and is a moderate to high-level skin sensitiser. It is not listed in the HSIS Database (2009). With the available toxicology information, BARRICADE Turf Herbicide is classified as a hazardous substance according to NOHSC *Approved Criteria for Classifying Hazardous Substances* (2004) with the following risk phrase:

R43	May cause sensitisation by skin contact

Formulation, packaging, transport, storage and retailing

BARRICADE Turf Herbicide will be formulated overseas and imported into Australia in the final packaged form. The product will be packaged in 5 or 10 L high density polyethylene (HDPE) containers. Transport workers and store persons will handle the packaged products and could only become contaminated if packaging was breached.

Use pattern

BARRICADE Turf Herbicide is a herbicide used on turf grasses in publicly accessible locations such as golf courses, bowling greens and sporting fields. BARRICADE Turf Herbicide is intended to be used at 4 L product/ha in a minimum of 500 L water/ha.

Application of BARRICADE Turf Herbicide to large areas such as golf courses or sporting fields would utilise vehicle-mounted spray equipment such as ground booms. Application to smaller areas such as bowling greens would utilise small-scale application equipment such as backpack or low-pressure hand wand/hand gun sprayers.

Exposure during use

Lawn care professionals, golf course and sporting field curators and their employees will be the main users of the product. Workers may be exposed to the product when opening containers, mixing/loading, application, and cleaning up spills, maintaining equipment and entering treated areas. The main route of exposure to the product will be by dermal contact, with limited inhalation exposure while preparing and using the product.

There are no worker exposure studies on prodiamine or the product BARRICADE Turf Herbicide available for assessment. In the absence of worker exposure data, the OCSEH used the Pesticide Handler Exposure Database (PHED) Surrogate Exposure Guide (1998) to estimate the worker exposure during mixing/loading and application based on the maximum product use rate according to the Australian use pattern. The estimation in conjunction with toxicology data demonstrated that workers should wear cotton overalls buttoned to the neck and wrist (or equivalent clothing) and elbow-length chemical resistant gloves, when preparing and using the product.

Exposure during re-entry

Exposure to the product as a result of activities on treated turf is expected. Based on the exposure assessment for re-entry to treated areas, the following re-entry statement is proposed: “Do not allow entry into treated areas until spray has dried, unless wearing cotton overalls buttoned to the neck and wrist (or equivalent clothing) and elbow-length chemical resistant gloves. Clothing must be laundered after each day's use.”

Recommendations for safe use

Users should follow the First Aid Instructions, Warning Statements, Safety Directions and Re-handing statement on the product label.

Conclusion

The registration of the product BARRICADE Turf Herbicide, containing prodiamine 480 g/L, for the pre-emergent control of Crowsfoot grass and Summer grass in established turf, is supported.

BARRICADE Turf Herbicide can be used safely if handled in accordance with the instructions on the product label and any other control measures described above. Additional information is available on the product MSDS.

5 ENVIRONMENTAL ASSESSMENT

5.1 Environmental fate summary

Hydrolysis

Prodiamine was stable to hydrolysis in buffers of pH 4, 7 and 9 over a 30 day period at 24-26°C where less than 10% of test substance was hydrolysed. In saltwater (pH 8.0), slight hydrolysis occurred with 92% of the original amount of prodiamine remaining after 30 days. Hydrolysis in waters at environmental pHs or in sea water is not expected to be a major route of degradation of prodiamine in the aquatic environment.

Aqueous Photolysis

Photolysis of prodiamine in sterile natural water and pH 7 buffer solution using simulated sunlight conditions resulted in 100% loss of prodiamine in the sterile natural water within 24 hours and a 91.5% loss of prodiamine in the pH 7 buffer over the same time period. The respective half-lives were approximately 0.7 and 1.3 days. The three major degradates were benzimidazole derivatives. Prodiamine in salt water exposed to light with an intensity of 2.4 times that of natural sunlight underwent rapid degradation with an aquatic photolysis half-life of 7.6 minutes. The major photodegradation products were the dealkylated N-despropylprodiamine, further benzimidazole derivatives and transitory polar compounds. Aqueous photolysis of prodiamine is expected to be a significant route of degradation in the environment with ready and significant degradation of the parent occurring.

Soil Photolysis

Prodiamine mixed with a loam soil and exposed to natural sunlight degraded with the formation of three degradation products (N-despropylprodiamine, N,N-didespropylprodiamine and a N-despropylbenzimidazole), along with an increasing amount of unidentifiable material. The soil photolysis half-life was determined as between 50 to 63 hours. A second soil photolysis study using simulated sunlight showed that prodiamine degraded readily, decreasing from 97.9% of the applied radioactivity at time 0 to 13.2% at day 14. The half-life was 5.2 days with the formation of amino-benzimidazoles which further degrade to form significant amounts of soil-bound residues. Soil photolysis may be expected to be a significant route of degradation of prodiamine in the environment.

Photodegradation in Air

Based on reactions of prodiamine with hydroxy radicals in the troposphere, the atmospheric photodegradation half-life of prodiamine was calculated to be 5.35 hours. While prodiamine is very slightly volatile, any reaching the troposphere would undergo fast degradation by photochemical processes.

Aerobic Soil Metabolism

In a laboratory study, soil incorporated prodiamine declined over time such that after 365 days, 7.2% of the originally applied prodiamine remained with a calculated soil half-life of 57 days. The major degradate was 6-amino-2-ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazole which made up 29.6% of the originally applied prodiamine after 365 days (declined slightly from the 9 months peak). A reduced prodiamine and despropyl-prodiamine (both less than 5% of the applied radioactivity) were also present after 365 days. The amount of unextractable soil material increased over time to be 36% of the applied radioactivity at 365 days. Soil applied prodiamine was shown to be extensively degraded under aerobic soil conditions.

Anaerobic Soil Metabolism

In a 30 day aerobic/63 day anaerobic soil crossover study, 6.4% of the originally applied prodiamine remained after 93 days with small amounts (all less than 5% of the applied radioactivity) of the 6-amino-1-propyl-benzimidazole and 4-amino-1-propyl-benzimidazole formed by cyclisation of the prodiamine; reduced prodiamine and despropylprodiamine were also present at that time. The aerobic/anaerobic the soil half-life of prodiamine was 30 days and, under anaerobic conditions, 12.7 days (but based on limited data points). Coupled with the ready degradation of the prodiamine in the anaerobic phase was a large increase in soil unextractable material, making up 54.4% of the applied radioactivity at 93 days. Soil applied prodiamine is extensively degraded under anaerobic soil conditions.

Aerobic and Anaerobic Aquatic Metabolism

The route and rate of degradation of radiolabelled prodiamine under aerobic and anaerobic conditions was investigated in two natural contrasting water sediment systems maintained under dark conditions. Under aerobic conditions over a 99 day study period there was rapid movement of radioactivity to the sediment and increasing amounts of unextractable radioactivity in the sediment as time progressed; after 99 days the unextractable radiolabelled material in one water/sediment system made up 56.4% of the applied radioactivity and, in the other water/sediment system, 76.5% of the applied radioactivity. Volatiles accounted for 2.6% of the applied radioactivity at day 99 in one system and 1.5% at the same time in the other. Similar results were seen in the anaerobic study with respective amounts of 83.7 and 79.3% of the applied radioactivity being present as unextractable sediment associated material in the two test systems. Volatiles accounted for 0.12% of the applied radioactivity at day 99 in one system and 0.03% at the same time in the other.

Prodiamine dissipated rapidly from the water phases in the aerobic and anaerobic studies in both water/sediment systems (in the aerobic waters there was <2% remaining at day 99 with prodiamine not measurable thereafter while in the anaerobic waters, there was <1% prodiamine left by day 28 in both systems).

No major metabolites were detected in the aerobic water phases. In the associated sediments, one system contained an unidentified metabolite at 10.7% of the applied radioactivity at day 14 but declining to 1.4% by day 28. In the second sediment, this material was detected at a maximum of 1.7% at day 28. In the anaerobic water phases, an unknown at a maximum (16.93% of the applied) at day 7 was detected in one system but then decreasing to be not measurable at day 62. In all cases, this compound was thought to be an amino derivative of prodiamine formed by reduction of one of prodiamine's nitro groups. There were a number of other metabolites/degradates present but all individually less than 10% of the applied radioactivity. These results were mirrored in the second system's water phase (the main unknown was present at a maximum of 3.2% at day 14). In the anaerobic sediments, the degradates/metabolites found mirrored the anaerobic water results in both cases (one main metabolite, the likely amino prodiamine derivative, present at 3.46% on day 7 in one sediment and 4.17% on day 14 in the other sediment plus polar radioactivity, small amounts of other degradates/metabolites as in the anaerobic waters, none of which individually exceeded 3% of the applied radioactivity.

Prodiamine DT50 values in the aerobic water phase were 1.4 days in both systems and 1.9 and 5.1 days in the anaerobic water phases. Total system DT50 values were 14.7 and 14.3 days in the aerobic system and 3.4 and 6.6 days in the anaerobic systems. Total system DT90 values in one of the aerobic systems was 540.9 days and, in the other, 93.5 days. Total system DT90 values in the two anaerobic water/sediment systems were 11.4 and 21.9 days.

In aerobic and anaerobic water/sediment systems, prodiamine is expected to readily break down and/or partition to the sediment followed by further degradation accompanied with increasing amounts of unextractable sediment material. Mineralisation is not expected to be significant.

Volatility

Prodiamine placed on the soil surfaces underwent less than 10% loss of starting material over 14 days and soil applied formulations of prodiamine are not likely to undergo significant volatility losses from the soil surface. This is consistent with the very slight volatility predicted from the vapour pressure value of 2.93 X 10^{-6} Pa at 25°C. Other non-standard investigations confirmed that prodiamine is readily and strongly adsorbed to dry and moist soils and, once applied, the prodiamine only very slowly volatilises from soil with soil moisture levels not significantly affecting the volatilisation.

Batch equilibrium desorption (soil mobility)

Measurements of soil mobility of prodiamine by batch equilibrium adsorption/desorption studies showed that the majority of soil applied prodiamine is expected to be strongly adsorbed to the soil with Koc values in one study with four soils ranging from 9310 to 19540, indicative of prodiamine being immobile once adsorbed to soils, while another study with two soils reported Koc values of 5442 and 5654. Aged residues on prodiamine on a loam soil had a Koc value of 6070, indicative of aged prodiamine residues retaining their soil immobility. A further batch equilibrium desorption study using clay loam and loam soils gave adsorption Koc values based on the Freundlich isotherm model of 2710 and 3580, indicative of slight soil mobility (Koc of 2000 to 5000). Soil adsorbed prodiamine is expected to be immobile or at worst, show slight mobility.

Soil column leaching

This was confirmed by a soil column leaching study using freshly applied and aged radiolabelled prodiamine. Fresh and aged prodiamine was found to remain primarily in the top 2 cm of the four different soil columns with no measurable radioactivity found in the leachates. In a second aged soil column study, prodiamine applied to a loam soil and aged for 30 days showed that some 70% of the applied radioactivity after 30 days was prodiamine with the remainder associated primarily with known degradation products. Following column chromatography of this aged prodiamine/soil, 1.1% of the applied radioactivity was in the leachate while 89.5% was retained in the soil and 0.23% on the column (primarily in the top 2 cm). Prodiamine was the major leachate material (0.27% of the applied radioactivity). Koc values calculated in the study confirmed prodiamine as being immobile in soil (Koc 5195), while its degradates were either immobile or showed low mobility.

Field Dissipation

Some seven studies were presented which were placed in this field dissipation category. All were conducted in the 1970s and 1980s.

The degradation of prodiamine (as a 50% WP formulation) applied to dry soil surfaces was investigated at two Californian locations which showed that surface applied prodiamine degraded over a 57 day period with DT50s of 7-30 days but with soil incorporated prodiamine undergoing no substantial degradation in that period. When conducted under different climatic conditions and with two different soils in trays, the ready degradation on the soil surface was confirmed (DT50s of 7 to 28 days) whereas when soil incorporated, DT50s of 36 to 38 days were noted. However, the lack of experimental detail for this study make interpretation of the incorporated soil results uncertain. Summaries of concentrations of prodiamine found in

orchard and vineyard soils in the US after treatment with prodiamine (also followed by incorporation) showed that in orchards significant amounts (up to close to 40%) of the applied prodiamine can remain in the soil for up to at least 15 months after application, with the percentages remaining not indicated as being related to the initial application. In the vineyards, while residues were persistent in the top 0-7.6 and 7.6-15 cm soil layers, they did decrease over time. The orchard and vineyard results showed that the amount of prodiamine in the deeper soil layers was always less than that in the top soil portion with most residues in the 15-30 and 30-46 cm soil profiles <0.01 ppm. Such results indicate that leaching of prodiamine is unlikely to be of concern.

A field dissipation study of prodiamine incorporated into a sandy loam demonstrated that prodiamine degrades under field conditions with the formation of 6-amino-1-propyl-benzimidazole the major degradate, which itself also degrades. Neither parent or degradate showed significant movement below the 10-20 cm soil profile. The determination of DT50 values for prodiamine were made difficult by levels of residues found in the soil in the early sampling periods (days 0, 1 and 7) being considerably lower than those seen from day 15 onwards and the first order degradation kinetics had poor goodness of fit. The DT50 values reported were 113 days based on all the measured data or 55 days if early data measurements were omitted. When a commercial prodiamine formulation was applied to established common Bermuda grass turf present in a dormant state, no clear degradation of the prodiamine occurred and the prodiamine levels found in the 0-10 cm layer did not show a smooth dissipation curve when plotted against time. A DT50 of 230 days was determined but the lack of degradation places doubt on this value. The irregular dissipation and lengthy DT50 were attributed to the lack of soil microbial activity because of application in the US winter season.

An early (1976), semi-field, non-standard study in trays examined the persistence of prodiamine on irrigated and flooded soil surfaces. The study demonstrated that soil applied prodiamine undergoes a rapid initial degradation which appears to be independent of whether watering in or rain occurs shortly after or some time after application which at worst only slowed degradation slightly. However, the exposures took place in sunlight and soil photolysis as the principal method of degradation rather than soil degradation may have been occurring.

In a greenhouse study, radiolabelled prodiamine was incorporated into a sandy loam under aerobic and anaerobic conditions. After 150 days in the aerobic soil, very little of the radiolabel was found in the 5-10.2 cm soil layer (8.1% of that in the 0-5 cm layer). After a further 150 days, the amount of radiolabel in the top 5 cm was unchanged from the amount present at 150 days and the amount present in the 5-10.2 cm layer was 15.6% of that in the 0-5 cm layer [0.075 versus 0.48 ppm], indicating little vertical movement. In the anaerobic soil, the majority of the radiolabel remained in the top 0-5 cm with <5% of the applied radioactivity in the lower soil profile (5 to 15.2 cm). In the aerobic soil, the DT50 was 218 days and in the anaerobic soil, 32 days. Movement of prodiamine and its degradation products to the lower soil portions was essentially insignificant under both aerobic and anaerobic conditions. Degradation in aerobic soils was much slower than in anaerobic soils with the soil prodiamine concentration after 400 days being 30.5% of the initial concentration under aerobic conditions but only 5.9% after 120 days under anaerobic conditions.

Soil incorporated prodiamine degrades more slowly than surface applied prodiamine with <10% of the initially applied prodiamine degraded 57 days after application compared to ~70% degradation in surface applied prodiamine, also 57 days after application. Similarly, in a second series of trials, 10 to 29% of the incorporated prodiamine had degraded 21 days after application whereas 40 to 71% of the surface applied material had degraded by that time. This slower degradation is reflected in DT50 values in incorporated soils being longer than those in surface applied soils, e.g. DT50 values of 7 to 30 days were reported for the surface, i.e. unincorporated, prodiamine in these trials with the DT50s for the soil incorporated prodiamine

not being determined because of the lack of any substantial degradation. In a second study, the prodiamine incorporated into the soil had DT50 values of 36 to 38 days, whereas the surface applied prodiamine DT50s were 7 to 28 days. In field studies were watering in after application occurred, DT50s of 113 and 230 days were recorded, with the latter being for a field study in which the prodiamine was applied to turf under actual field conditions. As such it represents a real world situation and will be used for the risk assessment of the proposed use of Barricade Turf Herbicide

Overall, the fate of prodiamine in soil is expected to involve degradation with variable DT50s in aerobic soils (7 to 230 days) but faster degradation in anaerobic soils (DT50 32 days). Prodiamine residues can be expected to persist in the soil.

Bioaccumulation

Four studies relating to the uptake, depuration and bioaccumulation of prodiamine in fish species were presented. When channel catfish were exposed to prodiamine that had been aerobically aged on a sandy loam, followed by flooding and a water/soil aging period before addition of the fish, it was found that prodiamine highly bioconcentrated in whole fish (day 42 BCF of 1340) and inedible fish portions (day 42 BCF of 1430), where high bioconcentration equates to a BCF >1000. In a dynamic (flow-through) 42 day study conducted to determine the bioconcentration of radiolabelled prodiamine and bluegill sunfish (*Lepomis macrochirus*), the bioconcentration factor for whole fish was 1400 with the half-life for clearance 3.39 days. Radiolabelled prodiamine was found to be the principal component of the fish radioactivity with smaller amounts of despropyl prodiamine and five other unknowns, all present after 28 days exposure at individually less than 10% of the total sample radioactivity. In a second flow-through study with the bluegill sunfish, a 28 day exposure phase and a 14 day depuration phase, the BCF of 1182 in whole fish is indicative of prodiamine being highly bioconcentrating, but with an estimated time for 50% clearance of the prodiamine from the fish of 2.8 days.

5.2 Environmental effects

Avian toxicity

An acute oral study with the bobwhite quail and sub-chronic (5 day dietary exposure) studies with the mallard duck and the bobwhite quail were reported. In the acute oral study, there were no mortalities in the control or any of the test groups. All birds (control and test groups) appeared normal in appearance and behaviour for the duration of the study. There were no compound related effects on body weight or feed consumption. The bobwhite quail acute oral LD50 of >2250 mg prodiamine/kg body weight indicates the chemical is practically non-toxic to birds via acute oral uptake (i.e. the LD50 is greater than 2000 mg active constituent/kg body weight). In the eight day dietary exposure test with bobwhite quail, the birds were exposed to 0, 464, 1000, 2150, 4640 and 10,000 ppm of prodiamine in their diet for five days and then maintained on a prodiamine free diet for three days. In the prodiamine exposed birds, there was one mortality in the 10,000 ppm treatment group at day 4 of the exposure period. Wing droop and mild depression was seen in birds at the 10,000 ppm level and the 8 day LC50 was set at >10,000 mg prodiamine/kg feed and the 8 day NOEC for adverse effects at 4640 mg prodiamine/kg feed. When mallard ducks were exposed to the same concentrations of prodiamine in the feed for five days, the prodiamine exposed birds had no mortality and exhibited no symptoms of toxicity or behavioural abnormalities and the 8 day LC50 was set at >10,000 mg prodiamine/kg feed and the 8 day NOEC for adverse effects at 2150 mg prodiamine/kg feed. Prodiamine in the feed is practically non-toxic to birds. Twenty-one week subchronic reproduction studies with the bobwhite quail and the mallard duck, in which the birds were exposed to

nominal dietary concentrations of 50, 350 and 1000 ppm, reported there were no observed adverse effects on adult health or survival or on any reproductive parameter that could be related to the prodiamine exposure and a survival/reproduction NOEC of 1000 ppm was established.

Aquatic toxicity

In the aquatic toxicity studies, there were reports of prodiamine precipitation and turbidity being present on numerous occasions with this associated with the maximum water solubility of the prodiamine having been exceeded. In such instances caution is needed in interpretation of the data as the true exposure concentration is unknown.

Fish

Rainbow trout exposed to nominal concentrations of 1.0 to 100 mg prodiamine/L in a static 96 hour study exhibited adverse effects such as surfacing and sounding at all test concentrations with a 96 h LC50 of 6.6 mg prodiamine/L (nominal). All test solutions contained surface film and precipitate indicating the solubility of the prodiamine had been exceeded and the LC50 of uncertain validity. A second study with the rainbow trout was conducted with radiolabelled carbon 14 prodiamine at mean measured concentrations of 84 to 829 µg/L in a 96 hour flow-through experiment. There was a creamy, yellow material seen throughout the test at the air/water interface in the mixing chambers and test chambers associated with the three highest test concentrations. No sublethal effect or mortalities were seen in any of the control or test fish over the 96 hour exposure period and the 96 hour LC50 is set at >829 µg prodiamine/L.

In a 96 hour static acute fish toxicity study, bluegill sunfish (*Lepomis macrochirus*) were exposed to nominal prodiamine concentrations of 18 to 320 mg/L. A yellow precipitate was reported as seen in all test solutions. The 96 hour LC50 was determined as 68 mg/L but the presence of precipitate gave doubt over the true concentrations of prodiamine the fish were exposed to. Because all surviving fish at the lowest test concentration were showing signs of excitability at 96 hours, the 96 hour NOEC was set at <18 mg/L. A 96 hour flow-through study with the bluegill sunfish was conducted with radiolabelled carbon 14 prodiamine at nominal concentrations of 80, 130, 220, 360 and 600 µg/L (mean measured: 94, 144, 213, 354 and 552 µg/L). Once again, there was a creamy, yellow material seen throughout the test at the air/water interface in the mixing chambers and test chambers associated with the three highest test concentrations. No sublethal effects or mortalities were seen in any of the control or test fish over the 96 hour exposure period and the 96 hour LC50 is set at >552 µg prodiamine/L.

Common carp were exposed to the highest amount of the prodiamine which could be dissolved in test water at a loading of 1 mg/L in a 96 hour static study with the 0 to 96 hour mean measured concentration being determined as 4.8 µg prodiamine/L with the test medium a clear solution throughout the entire test duration. In the control, solvent control and test concentration of 4.8 µg prodiamine/L, there was no mortality or other visible abnormalities seen in any of the fish over 96 hours and the 96 hour LC50 was set as >4.8 µg prodiamine/L (mean measured). The toxicity of a 40% prodiamine formulation to the carp was also tested in a 96 hour static acute study. Exposure levels were 29.2, 70.0, 91.0, 118, 154 and 200 mg of formulation/L. Test solutions were prepared by adding/mixing the necessary amount of formulation to the test aquaria. A water control was also run. The prepared test solutions were slightly yellow, turbid and with precipitate present. After 96 hours there was 90% mortality at 154 mg formulation/L and 100% at 200 mg/L. Control fish and fish at the 29.2 and 70.0 mg/L test levels showed no abnormal behaviour over the 96 hours of the exposure period and the NOEC was set the latter value. The 96 hour LC50 was 139 mg formulation/L.

Two studies were reported on the saltwater sheepshead minnow. The first was a 96 hour static renewal study in which the sheepshead minnow were exposed to nominal concentrations of 10, 18, 32, 56, 100 and 180 mg prodiamine/L. All solutions containing prodiamine had an orange precipitate at the surface and the bottom of the chambers with the amount increasing with the concentration. There was 100% mortality in the nominal 180 mg/L fish at 48 hours. No mortality occurred in any of the controls or other test solutions over the 96 hours of the study period. The 96 h NOEC was set at 10 mg/L as a result of abnormal behaviour (surfacing, loss of equilibrium, being on the bottom of the tank, etc.) seen in higher test concentrations at least one observation interval. The 96 hour LC50 was determined as 130 mg prodiamine/L (nominal). The presence of precipitate again shows that the solubility of the prodiamine had been exceeded and highlights the need for caution in the interpretation of the results from such studies. The second study was designed to evaluate the acute toxicity of ^{14}C-prodiamine to the sheepshead minnow under flow through conditions over a 96 hour test period. The mean measured exposure concentrations were 0.058, 0.10, 0.15, 0.28 and 0.45 mg prodiamine/L (respectively, for the prodiamine solutions, 74, 77, 68, 78 and 75% of nominal). A yellow precipitate was seen in the mixing chamber for all prodiamine treatments, indicating the water solubility was exceeded despite the use of a relatively high cosolvent level to aid dispersion. Sheepshead minnow in the controls and all test solutions had no overt signs of toxicity and there were no mortalities. The 96 h LC50 value was >0.45 mg prodiamine/L (mean measured), the highest value tested.

The low solubility of the prodiamine in water (0.013 mg/L) has confounded the interpretation of these results as the effects seen could result from the physical presence of prodiamine in the water rather than to its intrinsic toxicity. Based on the lowest LC50 determined, >4.8 µg prodiamine/L, in carp where there were no mortalities observed, prodiamine may be expected to be non-toxic to fish at the limit of its water solubility of 0.013 mg/L.

An early life stage flow-through toxicity study commencing with newly fertilised rainbow trout eggs exposed to mean measured concentrations of 5.9 to 96 µg prodiamine/L showed adverse effects on larval growth from day 32 post-hatch. Based on the statistically significant reduction in growth at 25 µg prodiamine/L, the study NOEC (for growth of rainbow trout larvae) was set at 12 µg prodiamine/L with prodiamine moderately toxic to the early life stage of trout (NOEC 10 – 100 µg prodiamine/L).

Aquatic invertebrates

In a static, 48 hours study, *Daphnia magna* were exposed to exposed to nominal concentrations of prodiamine (91.3%) of 5.6, 10, 18, 32, 56 and 100 mg/L (nominal) with the aid of a co-solvent. Erratic behaviour in the 18 to 100 mg/L concentrations was seen in all daphnia at 24 hours and there were 60% of the daphnia dead at 48 hours at 100 mg/L, and 80 to 100% at 32 and 56 mg/L. All surviving daphnia, even at the lowest test concentration of 5.6 mg/L exhibited erratic behaviour at that time. A yellow precipitate was formed on the bottom of the test vessels in the higher concentrations and the erratic behaviour of the daphnids was considered probably due to the presence of undissolved material in the water. The 48 hour LC50 was 29 mg prodiamine/L and the 48 h NOEC for abnormal behaviour, <5.6 mg/L. In a second 48 hour static study, daphnia were exposed to radiolabelled ^{14}C-prodiamine at mean measured concentrations (0-48 hours) of 11, 19, 31, 51 and 83 µg prodiamine/L with all test solutions reported as being clear. There were no daphnid mortalities in any of the controls or prodiamine solutions at 3, 24 or 48 hours. At 48 hours, all prodiamine solutions had erratically swimming daphnids (from 75 to 100% of the daphnid were affected. The 48 hour EC50 was >83 µg prodiamine/L (mean measured) and the 48 hour NOEC for adverse effects was <11 µg prodiamine/L.

In a 48 hour acute flow-through study, *D. magna* were exposed to ^{14}C-prodiamine at 92, 152, 243, 388 and 658 µg/L. A creamy yellow material was seen at the air/water interface of the mixing and test chambers of the three highest test concentrations. There were no daphnid mortalities or immobilisations in any of the control or test solutions and the 48 h EC50 was set at >658 µg prodiamine/L (mean measured concentration). The NOEC (immobilisation and other adverse effects) was set at 658 µg prodiamine/L. The toxicity of a 40% prodiamine formulation to daphnids at concentrations of nominal concentrations of 1.00, 3.16, 10.0, 31.6 and 100 mg formulation/L was tested over a 48 hour period under static conditions. The test solutions in the 3.16 to 100 mg/L range all had yellow suspensions and precipitate in the containers at the start of the exposure with these observations remaining over the 48 hours. The 1.00 mg/L test solution was clear and colourless. No immobility or symptoms of lethargy, reduced activity or hyperactivity were seen in daphnids in the 1.00 and 3.16 mg/L concentrations. Immobility (90 and 100% at 31.6 and 100 mg/L, respectively) and other adverse symptoms were seen in up to 100% of the daphnia at the higher test concentrations. The 48 hour EC50 was set at 19.1 mg formulation/L and the 48 hour NOEC for absence of adverse effects at 3.16 mg/L but the presence of suspended material and precipitate in the test vessels calls for caution in the interpretation of these results.

A 96 hour static study the mysid shrimp were exposed to nominal prodiamine concentrations of 1.0, 1.8, 3.2, 5.6 and 10 mg/L of synthetic seawater. All test solutions were reported as having prodiamine concentrations at the surface film at time 0 and precipitate at this time in all concentrations except at 10 mg/L. At 96 hours, there had been 100% mortality at the 10 mg/L concentration and 70 and 20% in the 5.6 and 3.2 mg/L test concentrations respectively. There were no deaths at the lower test concentrations and there were no adverse behaviour seen in any of the mysids exposed to these test concentrations. The 96 hour LC50 was 4.4 mg prodiamine/L (nominal) with a 96 hour NOEC for mortality and adverse effects of 1.8 mg prodiamine/L. In a second study, mysid were exposed to mean measured concentrations of 0.045, 0.065, 0.12, 0.20 and 0.31 mg/L in a flow through system for 48 hours. A yellow precipitate was seen in the mixing chamber of all test concentrations, indicating water solubility of the prodiamine was exceeded. Mortality in prodiamine test concentrations ranged from 0 to 10% and no adverse behaviour was seen in any of the surviving mysids. The 96 h LC50 was set at >0.31 mg prodiamine/L and the 96 h NOEC for adverse effects at 0.045 mg prodiamine/L.

Three studies on the acute toxicity of prodiamine on oysters were presented. The first examined effects on oyster embryos while the others were based on effects on the oyster's shell growth. In the 48 hour static acute study using a cosolvent with eastern oyster embryos exposed to nominal prodiamine concentrations of 0.47 to 6.0 mg/L, prodiamine was highly toxic with a 48 hour EC50 of 0.60 mg prodiamine/L.

In the shell regrowth studies, eastern oysters were exposed to prodiamine in two 96 hour flow-through studies with the effect on shell growth considered. The exposure concentrations were 0.11, 0.15, 0.19, 0.2 and 0.40 mg/L (20 to 42% of nominal) in the first study and 0.057, 0.10, 0.16, 0.28 and 0.53 mg/L (73 to 88% of nominal) in the second.

In the first study, undissolved prodiamine, as a precipitate, was present in all chemical and splitter cells of the diluter apparatus over 96 hours but no undissolved prodiamine was seen in the test aquaria. In the second, a yellow precipitate was seen in the 0.53 mg/L mixing chamber.

In the first study, no oyster mortalities were recorded over the 96 hours but at 0.40 mg prodiamine/L there was reduced feeding and reduced production of faecal matter at 24 hours in the oysters at that test level. No other similar effects were seen in any of the control or prodiamine exposed oysters.

Shell growth at 0.40 mg prodiamine/L was reduced by 32% compared to the solvent control and was found to be statistically significantly different, resulting in 96 h EC50 for inhibition of shell regrowth being set as >0.40 mg prodiamine/L. In the second study there were no mortalities and all oysters appeared normal. The 96 h EC50 for shell regrowth was 0.37 mg prodiamine/L. Based on the 0.37 mg/L value, prodiamine is highly toxic to oysters.

The low solubility of the prodiamine in water (0.013 mg/L) confounds the interpretation of these acute aquatic invertebrate toxicity results where insolubility/precipitation were reported as the effects seen could result from the physical presence of prodiamine in the water rather than to its intrinsic toxicity. Based on the lowest endpoint determined, the 48 h daphnid EC50 of >83 µg/L, prodiamine may be expected to be non-toxic to aquatic invertebrates at the limit of its water solubility of 0.013 mg/L.

There were three chronic/reproductive studies with *Daphnia magna* presented, with their being either semi-static (static renewal) or flow-through in design and conducted over 21 days. In these studies, survival and reproduction of a parent daphnid generation were recorded and the results used to determine the chronic toxicity of prodiamine to the daphnid. Cosolvents were used in two of the studies to aid in dissolving the prodiamine while the third was based on dilutions of a saturated prodiamine solution and did not require the use of a cosolvent. Mean measured exposure concentrations used in the three studies were respectively, 1.5 to 65 µg prodiamine/L (cosolvent used), 3.3 to 41 µg prodiamine/L (cosolvent used) and 0.23 to 16 µg prodiamine/L (no cosolvent required). The 21 day NOECs (based on parent daphnid survival or growth and reproduction based on the total number of young produced) for the three studies were, respectively, 1.5 (reproduction), 6.2 (growth) and 6.6 (reproduction) µg prodiamine/L. Based on the reproduction NOECs, prodiamine is highly toxic to daphnid reproduction.

Algae and aquatic plants

When the freshwater green alga *Pseudokirchneriella subcapitata* was exposed to mean measured concentrations of 0.23, 0.45, 1.13, 3.0 and 5.0 µg prodiamine/L in a static 96 hour study using a cosolvent, significant inhibitory effects seen on growth (biomass and growth rate) at concentrations ≥1.13 µg prodiamine/L. All test solutions were clear throughout the exposure period and cell morphology was unaffected following exposure to concentrations ≤1.13 µg prodiamine/L. The 96 hour ErC50 was determined as 4.0 µg prodiamine/L and prodiamine is very highly toxic to aquatic algae.

The freshwater green alga *Scenedesmus subspicatus* was exposed to nominal concentrations of 0.003 to 3.0 mg prodiamine/L (3 to 3000 µg/L) in a static, 96 hours study with the aid of a cosolvent. At ≥0.03 mg/L, 100% growth inhibition was observed with the few remaining cells at these concentrations were very enlarged. At 0.01 mg/L, 86% growth inhibition was seen with some of the cells enlarged at this concentration. No significant growth inhibition and no misshapen cells were seen at 0.003 mg/L and in the blank control. There was no indication that solubility problems occurred over the range of test concentrations. The 24-96 hour ErC50 was estimated to be between 3 and 10 prodiamine/L, again showing prodiamine is very highly toxic to alga.

Exposure of the freshwater diatom, *Navicula pelliculosa*, to dilutions of a saturated solution of prodiamine (mean measured concentrations of 0.19, 0.32, 0.66, 2.7, 6.7 and 21 µg prodiamine/L) for 96 hours resulted in statistically significant reductions in algal growth at 6.7 and 21 µg prodiamine/L and the establishment of the 0-96 hour ErC50 as 4.8 µg prodiamine/L (indicative of very high algal toxicity). Algal cells exposed to 0.19 to 2.7 µg prodiamine/L appeared normal with respect to the control cells at that time. At 6.7 and 21 µg

prodiamine/L, a proportion of the algal cells had ruptured cell walls. There was again no indication of solubility problems over the range of test concentrations.

The marine diatom, *Skeletonema costatum*, also exposed to dilutions of a saturated solution of prodiamine (nominally 0.78, 1.56, 3.13, 6.25, 12.5, 25, 50 and 100% of saturation but with mean measured concentrations of 0.31, 0.17, 0.70, 1.20, 2.19, 1.15, 1.14 and 6.29 µg prodiamine/L) for 96 hours with all test solutions reported as clear and colourless or near colourless. The variability of the mean measured results is indicative of the difficulties of working with the low solubility prodiamine and the results may be attributed to adsorption of prodiamine to the test equipment or to degradation via photolysis.

At concentrations up to 12.5% saturation, the algal cells appeared normal with respect to control cells. At 25% saturation, a proportion of the cells were smaller than the controls while at 50 and 100% saturation, no algal cells were observed. Growing the exposed algae in a recovery phase showed prodiamine was algistatic at 25% saturation but algicidal at higher levels of exposure. The 0-96 hour ErC50 was set at 4.1 µg prodiamine/L and prodiamine is very highly toxic to the saltwater diatom.

Exposure of the green alga *Pseudokirchneriella subcapitata* to nominal concentrations of 2 to 200 µg/L of a formulation containing 40% prodiamine (with all test concentrations clear and colourless) for 72 hours under static conditions resulted in extensive inhibition of growth at 200 µg formulation/L after 48 hours and little growth at that time in the 63.2 µg formulation/L. Algal cell morphology at these concentrations showed swelling and deformations present. The 48-72 hour ErC50 was 51.8 µg formulation/L with the formulation being highly toxic to alga.

In contrast to the above results, when *Anabaena flos-aquae*, a cyanobacteria, was exposed in a 96 hour study to nominal concentrations of 1.02 to 100% saturated solutions of prodiamine (mean measured concentrations of 0.19 to 16 µg prodiamine/L with all test concentrations clear and colourless without insolubility issues), no adverse effects on algal growth were recorded at any test concentration and the 96 hour ErC50 was >16 µg prodiamine/L with prodiamine not toxic to this alga at the limits of the water solubility of prodiamine.

Duckweed exposed to 1.02 to 100% saturated solutions of prodiamine (mean measured concentrations of 0.23 to 22 µg prodiamine/L) for seven days with renewal of the test solutions at days 3 and 5 had little effect on duckweed growth compared to that of the controls. The EC50 values were not able to be determined because of absence of effect and it is set as >22 µg prodiamine/L. Prodiamine, to the limit of its water solubility, is not toxic to duckweed.

Non-target terrestrial invertebrates

Honey bees

Prodiamine, via contact study in which honey bees were exposed to up to 100 µg prodiamine/bee showed very slight toxicity to the treated bees with 24 and 48 hour LD50 values >100 µg prodiamine/bee. In a second contact study the bees were exposed to 600 to 1000 ppm of prodiamine, the 24 and 48 hour LD50s were, respectively, 941 and 894 ppm. In an acute oral and contact toxicity study to the honeybee conducted to current requirements there was nil mortality at 24 and 48 hours after the bees were fed prodiamine at a measured dose of 108.9 µg/bee and nil mortality at the same times after the bees had been treated with 100 µg prodiamine/bee via dorsal application to the thorax of the treated bees. The 48 hour oral LD50 is set at >109 µg prodiamine/bee and the 48 hour contact LD50 at 100 µg prodiamine/bee. Prodiamine is shown to be very slightly toxic to honey bees via the acute oral and contact routes.

Earthworms

In a 14 day acute study, adult earthworms were exposed to prodiamine concentrations of 125, 250, 500 and 1000 mg/kg soil dry weight. No mortalities occurred in any of the earthworms over the 14 days and the 14 day LC50 is >1000 mg prodiamine/kg soil dry weight. No abnormal behaviour or toxic symptoms were seen in any of the control or prodiamine exposed earthworms but there was a statistically significant weight reduction compared to untreated earthworms seen in the earthworms exposed to the 1000 mg/kg treated soil after 14 days resulting in the 14 day NOEC for weight loss being set at 500 mg prodiamine/kg soil dry weight. No chronic earthworm study is available.

Beneficial insects

When aphid mummies parasitised by the predatory wasp *Aphidius colemani* were immersed for 5 seconds in a 610 mg/L prodiamine solution (determined as equivalent to a 244 g prodiamine/ha treatment) there were no adverse effects seen on emergence of the young wasps from the mummies and the wasps that emerged showed no abnormalities. Similar exposure of larvae of the green lacewing (*Chrysoperla formosa*) and the ladybird beetle (*Coccinella septempuntata*) resulted in no adverse effect on larval survival or time to pupation.

Soil microorganisms

When a loamy sand soil was treated with prodiamine at rates of 7.99 and 26.46 mg prodiamine/kg soil dry weight (equivalent to 6 and ~20 kg prodiamine technical/ha), and effects on the activity of soil microflora were examined with respect to nitrogen transformation (mineralisation) and carbon turnover (respiration) in a laboratory test conducted over 28 days, there were no adverse effects (deviations from the untreated control soil of <25%) on either of these parameters.

Phytotoxicity

In a study to examine the effects of prodiamine as a 65% WG formulation of seedling emergence and vegetative vigour, six dicots species (carrot, cucumber, lettuce, radish, soybean and tomato) and four monocot species (corn, oat, ryegrass and onion) were exposed to concentrations of 1.1, 3.4, 6.7, 11, 22, 45, 100, 210, 410, 840 and 1680 g prodiamine/ha. With water control and formulation blanks also tested. The data obtained from the emergence tests included the total number of seedlings emerged at each observation (weekly), the percent emergence, shoot length and dry shoot weight measurements, and phytotoxicity observations. Vegetative vigour test data included the length of shoots, replicate dry shoot weight, and phytotoxicity effects ratings. The length measurements were made after approximately three weeks of testing. The main effect of Barricade 65WG on plants from the emergence and vegetative vigour test was noted as stunting, chlorosis, leaf rolling, and some epinasty (excessive growth on the upper side of a leaf causing a downward bending of the plant leaf).

The results of the study with the 65WG indicated effects on growth were observed on all species tested except carrot, corn, and soybean. Ryegrass was considered the most sensitive plants in the emergence test having NOECs of 22.4 g prodiamine/ha for emergence shoot length and for emergence dried shoot weight. This is the same as for tomato percentage emergence. In the vegetative vigour test, cucumber and tomato were most sensitive with the same shoot weight NOEC value of 44.8 g prodiamine/ha. However, the tomato emergence dried shoot weight NOEC can be set at <22.4 g/ha because no testing at 11.2 g/ha was done. Consequently, there is some evidence pointing to NOECs of less than 22.4 g/ha and, as a result, the

cucumber vegetative vigour phytotoxicity result of 11.2 g/ha will be used as the plant phytotoxicity endpoint in the risk assessment to non-target terrestrial plants.

5.3 Risk Assessment

With respect to the proposed use patterns, exposure to birds (and small mammals) to prodiamine residues would primarily be via the eating of treated turf and of seed or insects that were in the turf when it was sprayed with the formulated material. Based on the estimated dietary intakes of prodiamine by birds (and small mammals) following the proposed application of Barricade Turf Herbicide at the maximum use rate of 1.92 kg prodiamine/ha and comparison of such values with the relevant subchronic dietary LC50 or NOECs, risk to birds (and small mammals) through eating of prodiamine contaminated feed has been shown to be acceptable.

Risk assessment based on a direct overspray of waterbody indicated unacceptable risk for aquatic species (fish, aquatic invertebrates, algae and aquatic plants) from exposure to prodiamine when applied at the maximum label rate of 1.92 kg/ha. A refinement of the risk assessment based on a 10% spraydrift event showed acute aquatic risk remained unacceptable to all trophic levels. Modelling of spraydrift according to the AgDRIFT ground spray mode showed that acute aquatic risk is acceptable when using a coarse spray droplet size category and a downwind no spray zone of 120 metres is specified. With respect to the compulsory tank mix of Barricade Turf Herbicide with Monument Liquid Turf Herbicide (100 g trifloxysulfuron sodium/L) to control winter grass with reduced prodiamine rates, modelling showed that when trifloxysulfuron sodium is applied at the label rate of 30 g/ha, acute aquatic risk is acceptable when using a coarse spray droplet size category when a downwind no spray zone of 20 metres. Because this distance is significantly less than the 120 metre downwind no spray zone already established for prodiamine, no additional downwind no spray zone distance is indicated as needed for the compulsory tank mix. Chronic risk to species in the water column was modelled and shown to be acceptable with a down wind no spray zone of 115 metres. As this value is below the no spray zone of 120 metres required for acceptable acute aquatic risk, chronic aquatic toxicity should be acceptable. Modelling movement to sediment using predicted sediment concentrations (PECs) and a predicted no effect concentrations (PNEC) indicated acceptable benthic risk would occur from the proposed Barricade use pattern provided a 120 metre downwind buffer is observed.

Aquatic risk from runoff of prodiamine was modelled taking into account field runoff, the low water solubility, foliar interception, binding of prodiamine to soils/sediments and field half-lives of prodiamine. This modelling indicated that the acute risk to aquatic ecosystems from the run-off of prodiamine in the runoff water and in the sediment washed from treated turf was mitigable with respect to aquatic invertebrates and aquatic plants but unacceptable to fish and algae. Refinement of the runoff modelling based on more specific turf scenarios showed aquatic risk from runoff from turf growing operations and playing surfaces was acceptable based on the relatively limited treatment areas involved and slopes likely to be <4%. Golf courses, while containing areas likely to be sloped, also had mitigable aquatic risk once factors such as fairways typically making up one third of a golf course were considered. Risk is expected to be acceptable provided labelling restraints are adopted. The permitted tankmix of Barricade Turf Herbicide and Monument Liquid Herbicide to control winter grass has the potential, because of the presence of trifloxysulfuron sodium to adversely impact aquatic plants, and, to a lesser extent, algae as a result of runoff. Adherence to recommended label restraints relating to runoff will assist in the reduction of the risk to aquatic plants and algae.

Risk to honeybees from prodiamine applied at the maximum proposed use rate is indicated as acceptable as is risk from trifloxysulfuron sodium when applied at the maximum rate proposed for the compulsory tank mix with the Barricade product.

Risk assessment based on the predicted environmental concentration and either the earthworm LC50 value showed that the proposed use of Barricade Turf Herbicide is not expected to cause unacceptable risk to earthworms. While prodiamine can be expected to persist in the soil, the soil DT90 values reported or determined were not considered sufficiently robust to show the European Communities' requirement for a reproduction test if the DT90 in field studies is above 365 days had been met. Because earthworms are important for turf health, and because no other standard tests on beneficial non-target invertebrates in turf were presented close to the maximum rate permitted on the label, a label statement that it cannot be ruled out that BARRICADE® Turf Herbicide may have an adverse effect on non-target beneficial turfgrass invertebrates where such IPM is practised has been recommended.

When soil was treated with approximately ten times the maximum proposed rate of prodiamine, no unacceptable effects on soil microorganisms mediated carbon and nitrogen turnovers occurred and risk to soil microorganisms from the proposed use of Barricade Turf Herbicide is acceptable. As the maximum soil concentration of trifloxysulfuron sodium resulting from the proposed tank mix with the Barricade product is approximately 43% of the lowest observed effect concentration of trifloxysulfuron sodium on soil microbial activity, no marked effects on soil microbial processes because of the presence on trifloxysulfuron sodium are expected as a result of the tank mix's use.

The risk assessment of the proposed use of Barricade Turf Fungicide with respect to adverse effects on non-target terrestrial plants at the edges of the treated areas has shown risk to be acceptable provided application is with a coarse quality spray with a downwind no spray zone of 10 metres. For the compulsory Barricade Turf Herbicide and Monument Liquid Turf Herbicide tank mix, the risk to non-target terrestrial plants is expected to be acceptable provided applications is with a coarse quality spray with a downwind no spray zone of 60 metres (the current Monument Liquid Turf Herbicide label requirement with respect to protected non-target native vegetation).

6 EFFICACY AND SAFETY ASSESSMENT

6.1 Proposed use pattern

Registration of a 480g/L prodiamine suspension concentrate for the pre-emergent control of Crowsfoot Grass, Summer Grass, Winter Grass and Crab Grass in established turf.

6.2 Summary of Evaluation of Efficacy and Crop safety

The supporting data comprise 14 trial data sets demonstrating efficacy of the candidate against the four target weeds, phytotoxicity observations in these trials, plus a dedicated phytotoxicity trial against 28 warm climate grass species.

The methods used by the three different independent operators of the efficacy trials are very similar – plots 2 – 20 sq m., 3 – 4 replications in a randomised complete block (RCB). Single pre-emergence spray applications were made with a gas pressurized small plot boom sprayer for Barricade and up to three registered industry standard herbicides per trial. Assessments of efficacy were made for up to six months by quantifying the target weed population in quadrats. Results of all trials were statistically analysed. The quantity and quality of trials were considered adequate for this submission by the reviewer.

Barricade was applied at label rates, alone or in combination with Monument Herbicide, against Winter Grass in five trials where it gave significant, commercially acceptable 82 – 100% control compared with untreated plots.

Barricade was applied at the range of label rates in three trials against Crowsfoot Grass. It gave significant, commercially acceptable control of 87 – 99% by all rates in two trials. The third trial gave 85% at the upper rate of 3 L/ha with lower rates of control at 1 – 2 L/ha indicating these rates are more suited to four months control rather than six.

Barricade was applied at the range of label rates in six trials against Crab Grass/Summer Grass, *(D sanguinalis or D ciliatis*, two species which are difficult to separate). It gave significant, commercially acceptable control averaging 90% at upper label rates of 2 - 3 L/ha in all trials. The lower rate of 1 L/ha was similar in four trials but significantly less in two suggesting, as above, that this rate is more suited to only four months control, not six. This is in agreement with the label recommendations.

In all the above trials the Barricade formulation used was the candidate formulation, field conditions reflected the intended use pattern for the product, and the control levels achieved were equivalent or superior to that achieved by four industry standards.

The proposed label accurately lists the target weeds, application rates proven by the efficacy data, and the turf species situations, which have been shown to be safe in the phytotoxicity trial.

Assessment of study/trial data

Details are provided of 14 sets of trial data supporting efficacy, most also with phytotoxicity observations, plus one trial solely on phytotoxicity conducted by the applicant. All efficacy trials were carried out by three independent operators. With the exception of one trial from 1986, all were carried out in 2006 and 2007. The

efficacy trials were in various golf clubs, ovals or other amenity turf areas in NSW, Victoria and Queensland. The main turf grass species in all trials are listed in the table below.

The methodology, considering these trials were carried out by three unrelated operators, is very similar in all trials. Plots from 1 x 2m to 4 x 5m were established in existing turf, duplicated 3 - 4 times and in a randomized complete block configuration. Spray applications, in all but one trial, were by gas pressurized small plot boom sprayers. Application of granules of one industry standard, where described, was by hand held salt type shaker. A single pre-emergence application was made of all treatments then the turf irrigated. All Barricade treatments used the formulation proposed for registration and up to three registered industry standards were used for comparison in all but one trial.

Assessments of efficacy were also by similar means. These were mostly by using quadrats 0.31 x 0.31m, 0.5 x 0.5m or 1 x 1m for either counting plant numbers or tillers of target weed species in these areas or, if quadrats were divided into 100 squares, by scoring for presence or absence of target in each square. In one trial, assessment was made by visually estimating percentage target cover on whole plots. Assessments were repeated at 1 – 2 month intervals up to six months after treatment. Where the target grass is a *Digitaria sp*. it is called *D sanguinalis* in four trials, *D ciliaris* in one trial and *Digitaria spp* in one trial. The applicant's terminology for the target in all these trials is the same – Crab Grass/Summer Grass.

Results of assessments were statistically analysed in all trials by Analysis of Variance, and the significant differences between treatment means shown.

It is concluded by the reviewer that the14 trial sets, which were all successfully completed, were carried out using appropriate trial design in field situations simulating proposed product use and provide adequate quantity and quality support for this application. The one exception is the use in trial 13 of visual, whole plot assessment of a weed population. Despite this crude approach the trial was successful.

Results of the efficacy trials are summarised. Only the treatments using Barricade at its label rate are included so they can be compared directly with the industry standards which were all applied at their label rates. The efficacy tended to be clearly shown by infestation ratings at either four or six months after treatment so either are listed. (Ratings at four months tended to show the adequacy of treatment at lower label rates while ratings at six months showed the continued control, more by upper label rates.) All results have been converted to show the reduction in the target weed grass as a percentage of the untreated control plots.

Crop safety

Observations for phytotoxicity in the above trials did not detect any symptoms on the turf species listed. Furthermore, in a replicated trial where Barricade was applied at twice label rate to 28 cultivars of warm season turf plants and observations made at four weekly intervals, no symptoms occurred.

Resistance management

General Instructions and Resistance Management instructions on the label are appropriate.

7 CONCLUSION

The established turf species listed on the proposed label under “Situation” are those shown to be safe in the phytotoxicity trial. The claims for control of the four target weeds and the rates of Barricade recommended are supported by the efficacy trials in this submission. While most trials on *Digitaria* were on *D sanguinalis* there was one on *D ciliaris*, and these two species are considered difficult to separate, so the combined data sets are adequate to support efficacy claims against both species.

The Application by Syngenta Crop Protection Pty Ltd for the registration of BARRICADE TURF HERBICIDE is supported on efficacy and crop safety grounds when used in accordance with the proposed label instructions and Good Agricultural Practice (GAP).

8 LABELLING REQUIREMENTS

READ SAFETY DIRECTIONS BEFORE OPENING OR USING

Barricade®
Turf Herbicide

syngenta®

ACTIVE CONSTITUENT: 480 g/L PRODIAMINE

GROUP D HERBICIDE

For pre-emergent control of weeds in established turf as per the Directions for Use

5 or 10 LITRES

Syngenta Crop Protection Pty Limited
Level 1, 2-4 Lyonpark Road, Macquarie Park NSW 2113

In a transport emergency dial 000, Police or Fire Brigade
For specialist advice in an emergency only, call 1800 033 111 (24 hours)

APVMA Approval No: 62982/44469
Item number
Date code

TM

DIRECTIONS FOR USE

Restraints
DO NOT blend BARRICADE onto dry fertiliser or any other granular material
DO NOT apply with aircraft or through any type of irrigation equipment
DO NOT apply to turf under stress
DO NOT apply to golf course putting greens
DO NOT apply to newly seeded, sodded or sprigged turf. Delay application until turf is at 100% cover and root system is developed beyond a 3 cm depth
DO NOT apply if heavy rain has been forecast within 48 hours
Spray Drift Restraints
DO NOT apply with spray droplets smaller than a **COARSE** spray droplet size category according to "*APVMA Compliance Instructions for Mandatory COARSE or Larger Droplet Size Categories"* located under this title in the GENERAL INSTRUCTIONS section of this label
DO NOT apply when wind speed is less than 3 or more than 20 kilometres per hour as measured at the application site
DO NOT apply during surface temperature inversion conditions at the application site
DO NOT apply with a nozzle height greater than 50 cm above the ground
Mandatory No-Spray Zones
DO NOT apply if there are aquatic and wetland areas including aquacultural ponds, surface streams and rivers within 120 metres downwind from the application area
DO NOT apply if non-target vegetation is within 10 metres downwind from the application area
DO NOT apply if using Monument® Liquid Turf Herbicide and BARRICADE tank mix for control of winter grass if non-target vegetation is within 60 metres downwind from the application area

Situation	Weeds	Rate	Critical Comments
Established turf: Bahia grass (*Paspalum notatum*), **Buffalo Grass** (*Stenotaphrum secundatum*), **Carpet grass** (*Axonopus affinis, Axonopus compressus*), **Common Couch** (*Cynodon dactylon*), **Hybrid Couch** (*Cynodon dactylon x Cynodon transvaalensis*), **Kikuyu** (*Pennisetum clandestinum*), **Qld Blue Couch** (*Digitaria didactyla*), **Seashore Paspalum** (*Paspalum vaginatun*), **Zoysia** (*Zoysia japonica, Zoysia matrella*)	Crab Grass (*Digitaria sanguinalis*), Summer Grass (*Digitaria ciliaris*)	1 to 3 L/ha	Apply prior to weed emergence in early spring for residual control of up to 6 months. A repeat application (3 to 4 months after initial application) may be needed if lower rates are used in high weed pressure situations or during extended germination periods due to environmental conditions. Refer to Application section for detailed information.
	Crowsfoot Grass (*Eleusine indica*)		Apply prior to weed emergence in early spring. For residual control of up to 4 months use 1 to 2 L/ha. For residual control of up to 6 months use 2 to 3 L/ha. A repeat application (3 to 4 months after initial application) may be needed if lower rates are used in high weed pressure situations or during extended germination periods due to environmental conditions. **Note:** Crowsfoot Grass germinates later than Crab Grass and/or Summer Grass. In situations with multiple weeds present use higher rates to ensure adequate residual control. Refer to Application section for detailed information.

Situation	Weeds	Rate	Critical Comments
Established turf: Bahia grass (*Paspalum notatum*), **Buffalo Grass** (*Stenotaphrum secundatum*), **Carpet grass** (*Axonopus affinis, Axonopus compressus*), **Common Couch** (*Cynodon dactylon*), **Hybrid Couch** (*Cynodon dactylon x Cynodon transvaalensis*), **Kikuyu** (*Pennisetum clandestinum*), **Qld Blue Couch** (*Digitaria didactyla*), **Seashore Paspalum** (*Paspalum vaginatun*), **Zoysia** (*Zoysia japonica, Zoysia matrella*)	Winter Grass (*Poa annua*)	1 to 2 L/ha plus 0.3 L/ha Monument Liquid plus 0.25% v/v non-ionic surfactant	Apply during late summer to early autumn for residual control of up to 6 months. A repeat application (3 to 4 months after initial application) may be needed if lower rates are used in high weed pressure situations or during extended germination periods due to environmental conditions. Refer to Application section for detailed information.
		4 L/ha	Apply prior to weed emergence in late summer to early autumn for residual control of up to 6 months. A repeat application (3 to 4 months after initial application) may be needed if lower rates are used in high weed pressure situations or during extended germination periods due to environmental conditions. Refer to Application section for detailed information.

NOT TO BE USED FOR ANY PURPOSE, OR IN ANY MANNER, CONTRARY TO THIS LABEL UNLESS AUTHORISED UNDER APPROPRIATE LEGISLATION

WITHHOLDING PERIOD: DO NOT GRAZE TREATED TURF/LAWN OR FEED TURF/LAWN CLIPPINGS FROM ANY TREATED AREA TO POULTRY OR LIVESTOCK

GENERAL INSTRUCTIONS

BARRICADE is a selective pre-emergent herbicide that provides residual control of grass weeds in established turf. BARRICADE controls susceptible weeds by preventing growth and development of newly germinated weeds. Weed control is most effective when BARRICADE is activated by at least 6 mm of rainfall or irrigation before weed seeds germinate and within 7 days after application.

Mixing
Add the required quantity of BARRICADE directly to a spray tank containing 2/3 of the required spray volume. Add the rest of the water and ensure the mix is thoroughly agitated before application.
Monument Liquid tank mix
Add Monument Liquid and non-ionic surfactant after BARRICADE, then add the rest of the water and ensure the mix is thoroughly agitated before application. Refer to Monument Liquid label for specific mixing instructions.

Application

DO NOT apply with aircraft or through any type of irrigation equipment

Apply prior to weed emergence in early spring (summer weeds) or late summer to early autumn (*Poa annua*). Ensure product placement as close to soil surface as possible. Total application volume should not be lower than 500 L/ha. Use extremely coarse droplets [Turbo FloodJet* (TF5) or TurfJet* (TTJ10)], use strainers with no less than a 50-mesh rating. Wash in with at least 6 mm rain or irrigation within 7 days of application. Spray nozzles should be uniformly spaced and of the same size, and should provide accurate and uniform application. To ensure accuracy, calibrate sprayer at the beginning of the season before use and recalibrate frequently. Apply at a volume of greater than 500 L water/ha. Observe sprayer nozzles frequently during the spraying operation to ensure that the spray pattern is uniform. Avoid overlapping of spray runs. Ensure that boom height for broadcast application does not exceed 50 cm above the leaf blades of the turf. Avoid application under conditions when uniform coverage cannot be obtained or when spray drift may occur.

Monument Liquid tank mix

Ensure even product placement. Total application volume should be 400 to 800 L/ha. Use coarse droplets [AIXR* (11004 or 10005) or Turbo Teejet* (11004 or 10005)]. Wash in with at least 6 mm rain or irrigation within 7 days after application. Refer to Monument Liquid label for specific application instructions.

APVMA Compliance Instructions for Mandatory COARSE or Larger Droplet Size Categories

These instructions inform users of this chemical product how to lawfully comply with the requirement of a COARSE or larger spray droplet size category for spray application.

Spray droplet size categories are defined in the ASAE S572 Standard (newer name may also be shown as ASABE) or the BCPC guideline. Nozzle manufacturers may refer to one or both to identify droplet size categories, but for a nozzle to comply with this requirement, the manufacturer must refer to at least one.

Complying with the label requirement to use a specific droplet size category <u>means</u> using the correct nozzle that will deliver that droplet size category under the spray operation conditions being used. The APVMA has approved only the following specific methods for choosing the correct nozzle. Use one of the methods specified in these instructions to select a correct nozzle to deliver a COARSE or larger droplet size category.

<u>Mandatory instructions for ground applications for COARSE droplet size or larger categories</u>

USE ONLY nozzles that the nozzles' manufacturer has rated to deliver a COARSE, a VERY COARSE or an EXTREMELY COARSE droplet size category as referenced to ASAE S572 or BCPC. Choose a nozzle specified to provide the droplet size required in the label Spray Drift Restraints. DO NOT use a higher spray system pressure than the maximum the manufacturer specifies for the selected nozzle to deliver the droplet size category required in the label Spray Drift Restraint.

Compatibility

As formulations of other manufacturers' products are beyond the control of Syngenta, and water quality varies with location, all mixtures should be tested prior to mixing commercial quantities. BARRICADE is compatible with Monument Liquid.

Clean up

After tank mixing with Monument Liquid refer to the Monument Liquid label for spray tank cleaning instructions.

Replanting interval

DO NOT replant any crop, ornamentals or overseed with cool season grasses for winter cover to treated areas for a period of 6 months after application.

Herbicide Resistance Warning

GROUP	D	HERBICIDE

BARRICADE Turf herbicide is a member of the dinitroaniline group of herbicides and has the tubulin formation inhibitor mode of action. For weed resistance management this product is a Group D herbicide. Some naturally occurring weed biotypes resistant to BARRICADE and other Group D herbicides may exist through normal genetic variability in any weed population. The resistant individuals can eventually dominate

the weed population if these herbicides are used repeatedly. These resistant weeds will not be controlled by BARRICADE or other Group D herbicides. Since the occurrence of resistant weeds is difficult to detect prior to use, Syngenta Crop Protection Pty Limited accepts no liability for any losses that may result from the failure of BARRICADE to control the resistant weeds. Advice as to strategies and alternative treatments that can be used should be obtained from your local supplier, consultant, local Department of Agriculture, Primary Industries Department or a Syngenta representative.

Integrated Pest Management
The possible effects of BARRICADE on integrated pest management (IPM) strategies in the turf industry have not been studied at the proposed rates. However, based on available information, it cannot be ruled out that BARRICADE may have an adverse effect on non-target beneficial turfgrass invertebrates where such IPM is practised.

PRECAUTION
Re-entry Period
Professional operators
DO NOT allow entry into treated areas until spray has dried, unless wearing cotton overalls buttoned to the neck and wrist (or equivalent clothing) and chemical resistant gloves. Clothing must be laundered after each day's use.
Public
DO NOT allow entry into treated areas until spray has dried.

PROTECTION OF CROPS, NATIVE AND OTHER NON-TARGET PLANTS

DO NOT apply under weather conditions, or from spraying equipment, that may cause spray to drift onto nearby susceptible plants/crops, cropping lands or pastures. Avoid applications to areas where product may accumulate under the drip line of trees or where product may come into contact with roots of desirable plants.

PROTECTION OF WILDLIFE, FISH, CRUSTACEANS AND ENVIRONMENT
Very toxic to aquatic life. DO NOT contaminate streams, rivers or waterways with the chemical or used containers. DO NOT apply if heavy rain has been forecast within 48 hours. DO NOT apply to waterlogged soil. DO NOT irrigate to the point of run-off within 3 days of application. DO NOT apply to turf which is not well established.

STORAGE AND DISPOSAL
Store in the closed, original container in a cool, well ventilated area. DO NOT store for prolonged periods in direct sunlight. Triple rinse containers before disposal. Add rinsings to spray tank. DO NOT dispose of undiluted chemicals on site. If not recycling, break, crush or puncture and deliver empty packaging to an approved waste management facility. DO NOT burn empty containers or product.

SAFETY DIRECTIONS
May irritate the eyes and skin. Repeated exposure may cause allergic disorders. Sensitive workers should use protective clothing. Avoid contact with eyes and skin.
When opening the container, preparing spray and using prepared spray wear:
- **cotton overalls buttoned to the neck and wrist (or equivalent clothing)**
- **elbow-length chemical resistant gloves**

If product on skin, immediately wash area with soap and water. Wash hands after use. After each day's use wash gloves and contaminated clothing.

FIRST AID
If poisoning occurs, contact a doctor or Poisons Information Centre. Phone 131 126.

MATERIAL SAFETY DATA SHEET
If additional hazard information is required refer to the Material Safety Data Sheet. For a copy phone 1800 067 108, or visit our website at www.greencast.com.au or www.syngenta.com.au

MANUFACTURER'S WARRANTY AND EXCLUSION OF LIABILITY

Syngenta has no control over storage, handling and manner of use of this product. Where this material is not stored, handled or used correctly and in accordance with directions, no express or implied representations or warranties concerning this product (other than non-excludable statutory warranties) will apply. Syngenta accepts no liability for any loss or damage arising from incorrect storage, handling or use.

Product names marked ® or ™, the ALLIANCE FRAME the SYNGENTA Logo and the PURPOSE ICON are Trademarks of a Syngenta Group Company

* Trademark

Batch No.	
Date of Manufacture	

BARCODE

ABBREVIATIONS

ac	active constituent
ADI	Acceptable Daily Intake (for humans)
AHMAC	Australian Health Ministers Advisory Council
ai	active ingredient
BBA	Biologische Bundesanalstalt fur Land – und forstwirschaft
bw	bodyweight
d	day
DAT	Days After Treatment
DT_{50}	Time taken for 50% of the concentration to dissipate
EA	Environment Australia
E_bC_{50}	concentration at which the biomass of 50% of the test population is impacted
EC_{50}	concentration at which 50% of the test population are immobilised
EEC	Estimated Environmental Concentration
E_rC_{50}	concentration at which the rate of growth of 50% of the test population is impacted
EUP	End Use Product
Fo	original parent generation
g	gram
GAP	Good Agricultural Practice
GCP	Good Clinical Practice
GLP	Good Laboratory Practice
GVP	Good Veterinary Practice
h	hour
ha	hectare
Hct	Heamatocrit
Hg	Haemoglobin
HPLC	High Pressure Liquid Chromatography *or* High Performance Liquid Chromatography
id	intradermal
im	intramuscular

ip	intraperitoneal
IPM	Integrated Pest Management
iv	intravenous
in vitro	outside the living body and in an artificial environment
in vivo	inside the living body of a plant or animal
kg	kilogram
K_{oc}	Organic carbon partitioning coefficient
L	Litre
LC_{50}	concentration that kills 50% of the test population of organisms
LD_{50}	dosage of chemical that kills 50% of the test population of organisms
LOD	Limit of Detection – level at which residues can be detected
LOQ	Limit of Quantitation – level at which residues can be quantified
mg	milligram
mL	millilitre
MRL	Maximum Residue Limit
MSDS	Material Safety Data Sheet
NDPSC	National Drugs and Poisons Schedule Committee
ng	nanogram
NHMRC	National Health and Medical Research Council
NOEC/NOEL	No Observable Effect Concentration Level
OC	Organic Carbon
OM	Organic Matter
po	oral
ppb	parts per billion
PPE	Personal Protective Equipment
ppm	parts per million
Q-value	Quotient-value
RBC	Red Blood Cell Count
s	second

sc	subcutaneous
SC	Suspension Concentrate
SUSDP	Standard for the Uniform Scheduling of Drugs and Poisons
TGA	Therapeutic Goods Administration
TGAC	Technical grade active constituent
T-Value	A value used to determine the First Aid Instructions for chemical products that contain two or more poisons
µg	microgram
vmd	volume median diameter
WG	Water Dispersible Granule
WHP	Withholding Period

GLOSSARY

Active constituent	The substance that is primarily responsible for the effect produced by a chemical product
Acute	Having rapid onset and of short duration.
Carcinogenicity	The ability to cause cancer
Chronic	Of long duration
Codex MRL	Internationally published standard maximum residue limit
Desorption	Removal of an absorbed material from a surface
Efficacy	Production of the desired effect
Formulation	A combination of both active and inactive constituents to form the end use product
Genotoxicity	The ability to damage genetic material
Hydrophobic	Water repelling
Leaching	Removal of a compound by use of a solvent
Log Pow	Log to base 10 of octonol water partitioning co-efficient
Metabolism	The conversion of food into energy
Photodegradation	Breakdown of chemicals due to the action of light
Photolysis	Breakdown of chemicals due to the action of light
Subcutaneous	Under the skin
Toxicokinetics	The study of the movement of toxins through the body
Toxicology	The study of the nature and effects of poisons

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