Diuron and the Great Barrier Reef

– A review of the latest science

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One of more than a thousand turtles that washed up on the Great Barrier Reef coast in 2011
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Summary

Diuron has been shown to be an unmanageable pesticide in the GBR catchments due to its toxicity, persistence, ability to travel long distances from its point of application and its sub-lethal impacts. Its continued registration contravenes the aims of the Australian Pesticides and Veterinary Medicines Authority (APVMA) and therefore must be cancelled to protect the Great Barrier Reef and its catchments.

Introduction

The role of the Australian Pesticides and Veterinary Medicines Authority (APVMA) is to ensure that all registered products "will have no harmful or unintended effects on people, animals, the environment or international trade[1]". Although under review since 2002, the continued registration of diuron contradicts this role as it has clearly been shown to have *harmful* and *unintended* effects on the marine and freshwater environment. Numerous scientific publications demonstrating both its presence in, and negative effects on, aquatic ecosystems have been released since the diuron review process began and many have been published in the last few months of 2011 and early 2012 providing compelling Australian evidence about the environmental fate and effects of diuron in the Great Barrier Reef. The combined result of these studies is that diuron:

- Represents a clear threat to the health of marine and freshwater ecosystems
- Is the dominant herbicide entering the Great Barrier Reef (GBR) and its catchments
- Is persistent in the environment and so cannot be controlled seasonally
- Acts in concert with other pesticides and stressors
- Is reducing the resilience of ecosystems such as the Great Barrier Reef

The following summary highlights arguments for the removal of diuron from use within the catchments of the Great Barrier Reef and signals that other catchments may also be at risk.

The toxicity of Diuron in the environment is well understood

Diuron's toxicity as a pesticide is well understood in both plants and animals. The USEPA based ECOTOX database lists almost 600 records of toxicology endpoints (e.g. mortality, reduced photosynethsis, lowest effect concentration, etc) for a range of both terrestrial, freshwater and marine plants and animals. The Great Barrier Reef Marine Park Authority (GBRMPA) list more diuron toxicology data in their water quality guidelines documentation than for any other pesticide (GBRMPA 2010), with concentrations as low as 0.05 µg/L documented as having detrimental effects.

[1] Taken from APVMA website: http://www.apvma.gov.au/about

Diuron is persistent and cannot be managed within its application area

Although diuron will degrade in the environment, the rate at which degradation occurs is highly variable depending on the conditions present. In one study conducted according to USEPA guidelines the half life was recorded at more than 500 days (cited in APVMA 2011). The review undertaken as part of the development of the Great Barrier Reef Marine Park Authority (GBRMPA) water quality guidelines identify a typical half life of between 5 and 370 days depending on conditions (GBRMPA 2010).

These relatively long half-lives suggest that containment of diuron in its place of application will likely be impossible. Even restricting application to the dry season in North Queensland (for example) will not prevent its entry into the surrounding aquatic environment as its slow degradation will likely result in it remaining available through to the following wet season (Brodie, Wolanski et al. 2012). In addition, in areas where irrigated sugar plantations exist (such as the Burdekin), the highest herbicide concentrations (including diuron) have been detected in waterways during the dry season (Davis, Thorburn et al. 2012). The presence of diuron in GBR marine waters throughout the year (Shaw, Furnas et al. 2010; Kennedy, Schroeder et al. 2012) and not just in flood plume conditions, demonstrates the persistence of diuron in tropical marine waters and the chronic threat it presents on top of the acute threat in flood plume conditions (Lewis, Schaffelke et al. 2012).

In a recently released study investigating the effectiveness of "best management practices" in the sugar industry at controlling the release of PSII herbicides to the environment, diuron (and hexazinone) were demonstrated to be much harder to control than atrazine and ametryn (Masters, Rohde et al. 2012). The study also demonstrated that it took 122 days and five significant rainfall events (>24 mm), for the concentration of diuron in farm runoff to meet ANZECC water quality criteria even using best management practices.

Diuron metabolites are just as toxic as the diuron

The dominant metabolites produced in the degradation of diuron are DCPMU, mCDPMU and DCPU. Although there is limited data available, all of these metabolites have been shown to be toxic to various organisms. DCPMU, mCDPMU and DCPU have been rated as: highly toxic; highly toxic; and moderately toxic respectively to the green algae (*Desmodesmus subspicatus*) in a study conducted to OECD Guidelines. DCPMU has been found to be almost four times more toxic than diuron itself in a microbial study while DCA, another metabolite was found to be 140 times as toxic (APVMA 2011).

Diuron has been consistently detected in the Great Barrier Reef ecosystem

Diuron has been consistently detected along the length of the Great Barrier Reef (GBR) ecosystem, possibly 100's of km from its point of application. It has been detected in both the wet and the dry seasons and is the dominant PSII herbicide detected within the GBR in both seasons (Lewis, Brodie et al. 2009; Shaw, Furnas et al. 2010; Johnson, Brando et al. 2011; Kennedy, Schroeder et al. 2012; Smith, Middlebrook et al. 2012). Being consistently detected in dry season monitoring suggests that it is either remaining in the environment throughout the wet and into the dry seasons as a result of its moderately long half life and stability from hydrolysis in water (Brodie, Wolanski et al. 2012), or that it is also being released into the GBR in the dry season, meaning a ban on wet season application would be ineffective. Pesticides (dominated by diuron), together with sediment and nutrients, are the three main pollutant categories of concern within the GBR (Johnson, Brando et al. 2011). Figure 1 shows an example of pesticide monitoring within the GBR demonstrating the presence of diuron in both the wet and dry seasons.

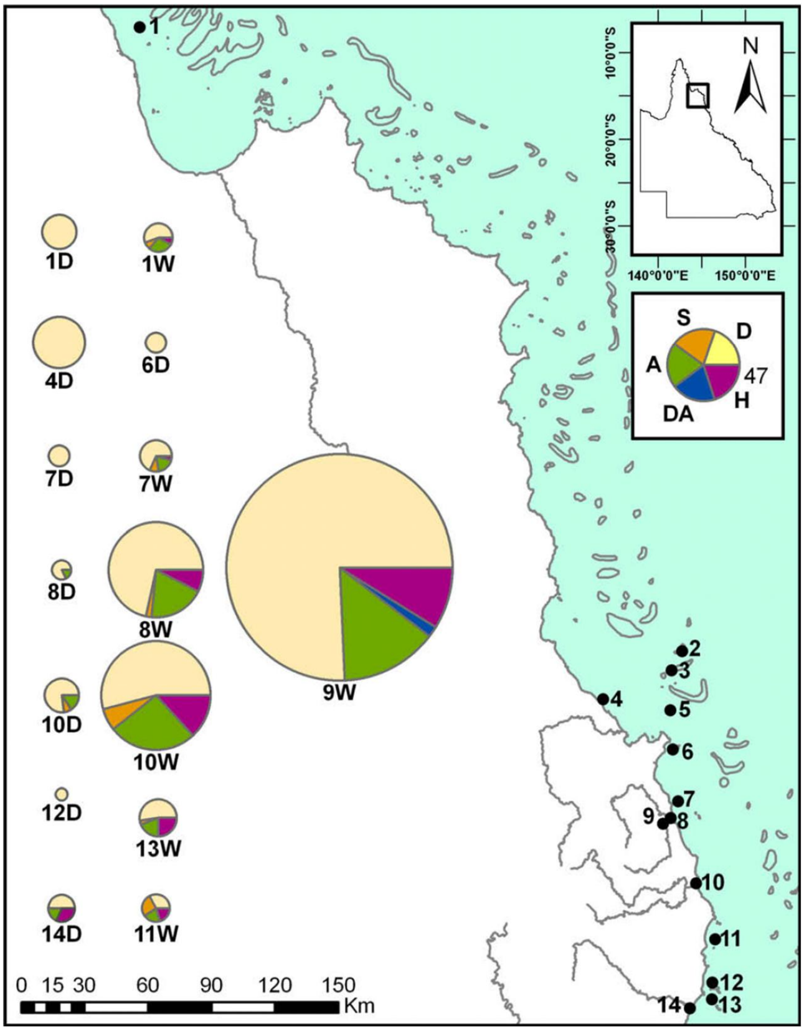

Figure 1: Sampling locations in the Great Barrier Reef, Australia (1 = Hannah Island; 2 = Hastings Reef; 3 = Michelmas Reef; 4 = Double Island; 5 = Green Island; 6 = Fitzroy Island; 7 = High Island; 8 = Russell–Mulgrave River Mouth; 9 = Russell River upstream; 10 = Johnstone River; 11 = South Barnard Islands; 12 = Dunk Island; 13 = Bedarra Island; 14 = Tully River). Calculated water concentrations of commonly detected herbicides in the dry (D) (October 2004) and wet (W) (January 2005) season are shown as pie charts. The relative size of each pie chart represents the total concentration of detectable herbicides at a site (A = atrazine, D = diuron, DA = desethylatrazine, H = hexazinone and S = simazine) .(Taken from (Shaw, Furnas et al. 2010))

Current application rates in Queensland are ineffective at protecting aquatic ecosystems

The current application rates for diuron in Queensland limit cane growers (the dominant users) to 1.8 kg/ha annually under the QLD reef protection legislation although the APVMA label rates are up to 3.6kg/ha (APVMA 2011). The current cane growing application rates of 0.9-1.8 kg/ha (APVMA 2011) are not effective at preventing diuron from escaping to the surrounding aquatic environment as monitoring data has demonstrated (Kennedy, Schroeder et al. 2012) and water quality guidelines are frequently exceeded (see below). The most recent environmental assessment by the APVMA (APVMA 2011) states that "the lowest application rate that was deemed to result in an acceptable risk to algae and aquatic plants in primary streams was 160 g/ha", more than ten times lower than the current usage rates. The APVMA report also states that "the contribution of diuron and its main toxic metabolites (particularly DCPMU) in sediments to algae and aquatic plants indicated an unacceptable risk to these organisms when exposed through the pore water based on measured sediment levels in irrigation ditches, streams and estuaries in Australia." Even if it were to be used at rates near 160 g/ha, it is unlikely diuron will be effective on the weeds of concern in sugarcane thus producing the combined problem of continuing use leading to aquatic contamination as well as ineffective weed control.

In a study just released, flood plumes in the GBR were shown to inhibit photosynthesis in zooxanthellae due to the presence of PSII herbicides (of which diuron has previously been shown to dominate) (Shaw, Brodie et al. 2012).

Alternatives to diuron do exist for use on the weeds of concern for cane growing. A number of these are already being trialled by cane farmers including products such as Stomp (active pendimethalin), Balance (active isoxaflutole), Flame (active imazapic) and Soccer (active metribuzin) . .Current research is examining the effectiveness of these options (with good results so far) as well as the water quality implications of their use (e.g. (Fillols and Callow 2010; Fillols and Callow 2010)). In addition, the possibility of largely replacing residual herbicides like diuron with knock-downs such as glyphosate using shielded sprayer technology is also under investigation, also with positive results (Milla, Whitten et al. 2011).

Water quality guideline criteria are frequently exceeded under current application rates.

The Qld water quality guidelines (DERM 2009) developed to provide region specific criteria have set event flow diuron levels at 0.75 µg/L for the Pioneer River and Sandy Creek in the Mackay-Whitsunday region. Both of these were exceeded in monitoring conducted during the 2009-10 wet season (3.4 and 4.7 µg/L respectively) (Smith, Middlebrook et al. 2012). For other areas within the GBR catchment where there are no region specific criteria, the ANZECC guideline level of 0.2 µg/L applies (ANZECC and ARMCANZ 2000). This guideline level was exceeded in the Tully River (0.58 µg/L) and by more than a factor of 25 in Baratta Creek (5.63-5.78 µg/L) during the same monitoring campaign (Smith, Middlebrook et al. 2012). In Barratta Creek the guidelines have been exceeded every year from 2005-10 with concentrations as high as 8.5µg/L measured in 2008-09 (Davis, Lewis et al. 2012). ANZECC levels were also exceeded in the Dawson River (0.68 µg/L) in a 2002 monitoring campaign (Packett, Dougall et al. 2009) while Haughton River levels also regularly exceed guideline levels between 2005 and 2010 (Davis, Lewis et al. 2012).

Sub-lethal effects not included in trigger values

In marine waters, the GBRMPA water quality 99% protection trigger value of 0.9 µg/L is also often exceeded (Lewis, Brodie et al. 2009; Lewis, Schaffelke et al. 2012). The GBRMPA trigger values for diuron are however far from conservative as the GBRMPA have not incorporated the sub-lethal effects of the herbicide on marine organisms (GBRMPA 2010). Diuron has been shown to be detrimental to a range of essential ecosystem components at sub-lethal concentrations such as corals and their symbiotic algae, crustose coralline algae (CCA), benthic microalgae, seagrasses, mangroves and forminifera (Haynes, Ralph et al. 2000; Duke, Bell et al. 2005; Harrington, Fabricius et al. 2005; Negri, Flores et al. 2011; Magnusson, Heimann et al. 2012; van Dam, Negri et al. 2012). Most of these studies demonstrate that diuron reduced photosynthesis (using PAM fluorometry) and it has been recently shown that this effect is directly proportional to reductions in growth and biomass of microalgae (Magnusson, Heimann et al. 2008) which are used to develop water quality guidelines.

The GBRMPA documentation does however state that, "*Additional consideration of the potential sub-lethal ecosystem effects of suppressed photosynthesis is recommended*" (GBRMPA 2010). Table 1 lists toxicology studies identified by the GBRMPA showing toxic impacts on organisms at concentrations below the current trigger levels. Figure 2 provides an example illustration of the area exposed to detrimental levels of diuron within the GBR in the Mission Beach region.

More recent studies include the sensitivity of *Acropora millepora* from 0.48 µg/L (Negri, Flores et al. 2011); benthic microalgae (Ochrophytes) 0.63 µg/L (Magnusson, Heimann et al. 2012), *Navicula sp.* (0.78 µg/L) *Nephroselmis pyriformis* (0.32 µg/L) *Phaeodactylum tricornutum* (0.42 µg/L) and *Cylindrotheca closterium* (0.63 µg/L) (Magnusson, Heimann et al. 2010); diatoms in the foraminifera *H. depressa macro* (0.8 µg/L) and *O. ammonoides* (0.9 µg/L) (van Dam, Negri et al. 2012).

If the sub-lethal effects were to be included, the GBRMPA trigger values would reduce by orders of magnitude from 0.9 to 0.01 µg/L for 99% protection and from 2.3 to 0.1 µg/L for 90% protection.

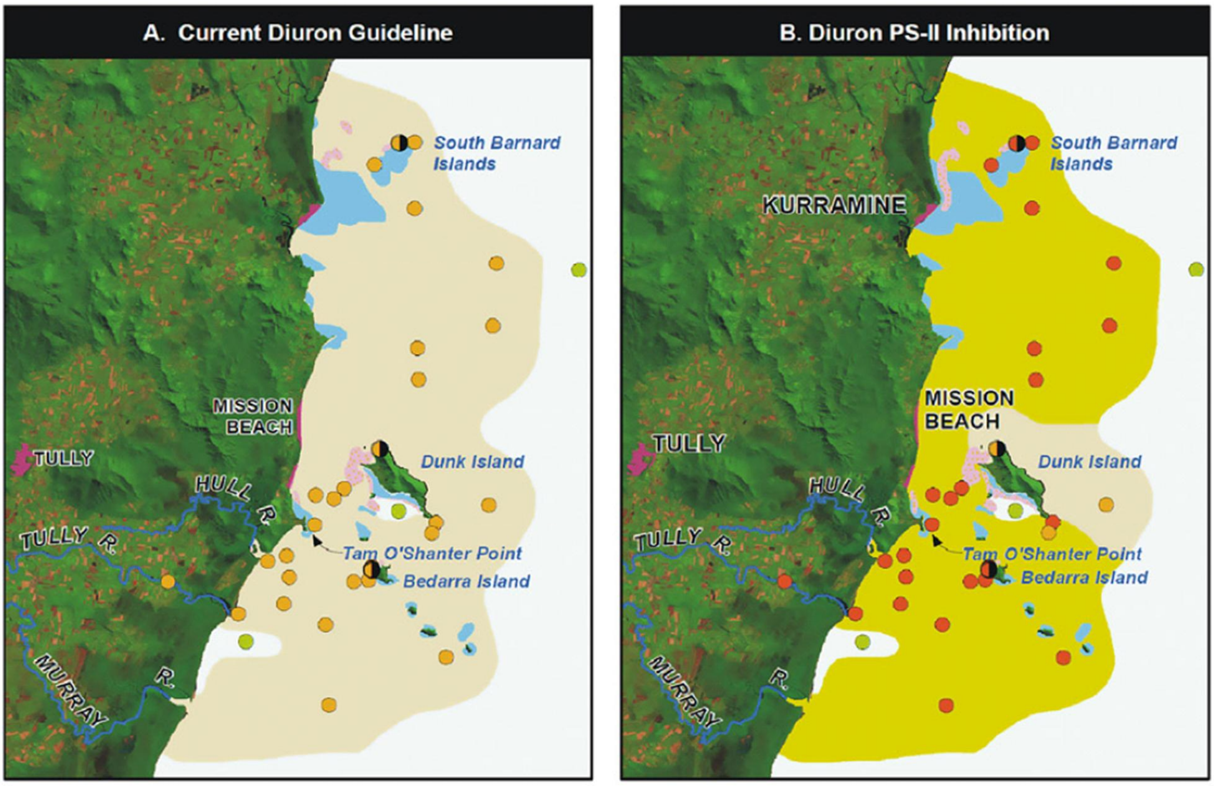

Figure 2: Example of trigger value exceedences for diuron in the Mission Beach region taken from (Lewis, Schaffelke et al. 2012)

Table 1: Studies cited by GBRMPA (GBRMPA 2010) that demonstrate the negative effects of diuron at concentrations less than the current water quality guidelines:

Species	Effects concentration (µg/L)	Endpoint Toxicity
Seagrass		
H. ovalis	0.1	↓ photosynthesis
Z. capricorni	0.1	↓ photosynthesis
Corals		
S. pistillata (Zooxanthellae)	0.25	↓ photosynthesis
A. formosa	0.3	↓ photosynthesis
S. histrix	0.3	↓ photosynthesis
Diatoms		
D. tertiolecta	0.05	↓ photosynthesis
N. closterium	0.1-0.19	Sensitivity
N. closterium	0.05	Sensitivity
P. tricornutum	0.1-0.19	Sensitivity
D. tertiolecta	0.11	↓ photosynthesis

Diuron poses a direct threat to the dugong and turtle

One of the most sensitive seagrasses to diuron exposure is *Halophila ovalis.* This seagrass experiences reduced photosynthesis at exposure concentrations nine times lower than the current GBRMPA trigger value of.0.9 µg/L (Haynes, Ralph et al. 2000). This seagrass is a favoured food of the dugong and green turtle (Aragones, Lawler et al. 2006). Diuron therefore poses a direct threat to one of the dugong's main food sources. Seagrass and dugong populations are already in decline due to chronic water quality degradation combined with the acute effects of the 2010/11 massive floods and Cyclone Yasi (Bell and Ariel 2011; Brodie and Waterhouse 2012). The continued chronic stress to seagrass posed by the continuing use of diuron (and other stressors) will likely restrict seagrass recovery and hence impinge further on dugong populations.

Diuron adds to the effects of other herbicides and environmental stressors

Diuron is rarely detected in the aquatic environment in isolation. For example, more than 15 pesticides have been detected in Barratta Creek (Smith, Middlebrook et al. 2012) and the effects (particularly of PSII herbicides) is often additive (Magnusson, Heimann et al. 2010). Diuron is both the most dominant PSII herbicide detected within the GBR (Kennedy, Schroeder et al. 2012; Smith, Middlebrook et al. 2012) and the most potent (Lewis, Schaffelke et al. 2012; Kennedy, Bentley et al. 2010). When assessing the combined impacts of PSII herbicides in four regions of the GBR there was a fivefold increase in the number of water quality samples that exceeded comparable guideline criteria (Lewis, Schaffelke et al. 2012). Removal of diuron from the environment will therefore greatly reduce the stress on aquatic ecosystems from PSII herbicides.

PSII herbicides are however not the only environmental stressor on the GBR ecosystem. To effectively protect against multiple stressors such as pesticides, sedimentation, ocean acidification and climate change, the potential impacts of multiple stressors must be assessed. Diuron has been shown to increase the susceptibility of corals, crustose coralline algae (CCA) (Negri, Flores et al. 2011) and foraminifera (van Dam, Negri et al. 2012) to elevated sea surface temperature and also the impacts of sedimentation on CCA (Harrington, Fabricius et al. 2005). Prevention of diuron entering the GBR ecosystem will therefore contribute to the resilience of the ecosystem to other environmental stressors.

Diuron poses a direct threat to internationally important ecosystems

As the weight of scientific evidence illustrates, diuron poses a direct threat to the resilience of the World Heritage listed Great Barrier Reef. It also represents a threat to both nationally and internationally significant wetlands such as those that exist in the lower Burdekin floodplain, a Ramsar listed site. These floodplains are fed by Barratta Creek and the Haughton River among others. These waterways have consistently recorded high levels of diuron (Davis, Lewis et al.

2012) which has been reported as being responsible for the death of important wetland species such as mangroves (Duke, Bell et al. 2005).

Current passive monitoring of Diuron is likely to underestimate actual levels in the environment

Much of the current monitoring for pesticides such as diruon is conducted with passive monitors (rather than measurements taken from discreet samples collected at specific times) that measure average concentrations over a period of time (days to weeks) (Kennedy, Bentley et al. 2010). These samplers generally sample only the dissolved concentrations. Unlike other PSII herbicides however, diuron has affinity with particulate matter and so can remain bound to suspended sediment. On average about 33% of total diuron is bound to particulates (Davis, Lewis et al. 2012). This means that results from passive samplers are very likely to be underestimating concentrations by as much as 50%.

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