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REVIEW PAPER

COMPARISON OF THE PROPOSED ECOSYSTEM PROTECTION GUIDELINE VALUES FOR DIURON IN FRESH AND MARINE ECOSYSTEMS WITH EXISTING TRIGGER AND PROTECTIVE CONCENTRATION VALUES

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ABSTRACT

Currently, there are eight different sets of protective concentration values, trigger values and guideline values for ecosystem protection for diuron in Australian waters. Included among these are the guideline values that we are proposing for diuron in freshwaters and marine waters that were generated as part of the revision of the Australian and New Zealand Guidelines for Fresh and Marine Water Quality. These proposed guideline values will be submitted for national endorsement and incorporation into the Guidelines and the Great Barrier Reef Water Quality Guidelines. The various sets of guideline values differ substantially from each other. This paper was prepared with three primary aims: 1) to examine the various sets of protective concentration values, current trigger values, and the proposed guideline values for freshwater and for marine waters; 2) to explain how the different values were derived; and 3) to explain the purpose of each set of values. This study provides a comprehensive evaluation of the various sets of ecosystem protection values for diuron, and presents arguments for why the proposed guideline values should be adopted and used in preference to existing trigger values or protective concentration values derived prior to 2017.

Key words: Guideline Value; Trigger Value; Australian and New Zealand Guidelines; Water quality.

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BACKGROUND

In Australia, water quality is managed using the National Water Quality Management Strategy (NWQMS), and outlined in over 25 documents. These documents aim to protect the nation's water resources by improving water quality while at the same time supporting businesses, industry, the environment and communities that depend on water for their continued development. With respect to chemical contaminants, water quality in Australia is managed in accordance with the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC and ARMCANZ 2000), henceforth called the 2000 guidelines. The 2000 guidelines provide both qualitative and quantitative (numerical) limits for chemicals in water. The numerical limits for chemicals in the 2000 guidelines were termed trigger values, because measured concentrations greater than the trigger value at a site triggered further action (e.g. site-specific investigation, management action or clean-up procedures).

The 2000 guidelines are currently being revised to provide new limits that are to be referred to as guideline values (GVs) (Batley et al. 2014; Warne et al. 2015). Many of the new GVs will be for chemicals with existing trigger values (henceforth also referred to as 'guideline values' for ease of discussion), including diuron, and for chemicals without existing GVs. Guideline values can be derived using one of two methods: a species sensitivity distribution (SSD) method (the preferred method) or an assessment factor (AF) method (ANZECC and ARMCANZ 2000; Warne et al. 2015). The AF method derives a single limit for each chemical by dividing the single lowest toxicity value for the chemical by an assessment factor. The SSD method uses all of the available, suitable ecotoxicity data to derive a series of protective concentration values. The protective concentrations offer four default levels of protection: 99, 95, 90 and 80 per cent of species in the ecosystem being considered. These levels of protection are referred to as PC99, PC95, PC90 and PC80, respectively.

When protective concentration values are generated and endorsed at a national level as part of a revision of the Australian and New Zealand Guidelines for Fresh and Marine Water Quality, they become GVs (Warne et al. 2015). In contrast, researchers and other organisations can derive protective concentration values for their own purposes such as conducting risk assessments (e.g. Pathiratne and Kroon 2016) and/or determining and reviewing label conditions for the use of pesticides (e.g. APVMA 2011). Such protective concentration values are not GVs as they: may have been derived for a different purpose; may not have been derived using the methods approved for guideline derivation; or, have not undergone the necessary review and endorsement processes. Nevertheless, they may be suitable for adoption as GVs if they are deemed appropriate through the review and endorsement process.

Having multiple sets of protective concentration values and guideline values in the scientific literature for a single chemical is likely to create confusion about which is most appropriate to use in particular situations.

Partly to address this issue, the current revision of the 2000 guidelines (ANZECC and ARMCANZ 2000) permits third parties (e.g. consultants, government departments or industry groups) to derive and submit protective concentration values for review and consideration as GVs.

Another means of reducing confusion - particularly with respect to pesticides - is to align the methods used to derive the Australian and New Zealand GVs (Warne et al. 2015) with those of the Australian Pesticides and Veterinary Medicines Authority (APVMA) review process (APVMA 2011). By doing this, the two methods would inform one another and protective concentration values developed by one process could be adopted by the other.

Currently, there are eight different sets of protective concentration values and GVs for ecosystem protection for diuron in Australian waters. These are: (1) the current freshwater GVs in the 2000

guidelines (ANZECC and ARMCANZ 2000); (2) the current marine GVs in the 2000 guidelines (ANZECC and ARMCANZ 2000); (3) the PC95 and PC99 values derived by the Australian Pesticides and Veterinary Medicines Authority (APVMA 2011); (4) the marine GVs (PC99, PC95 and PC90) derived by the Great Barrier Reef Marine Park Authority (GBRMPA 2010) for tropical species; (5) the marine high sensitivity protective concentrations (the PC99, PC95, PC90) derived by the Great Barrier Reef Marine Park Authority (GBRMPA 2010) that included toxicity data on photosynthetic inhibition; (6) the PC99, PC95, PC90 and PC80 values derived by Pathiratne and Kroon (2016) for tropical freshwater species; (7) the proposed new freshwater GVs (PC99, PC95, PC90 and PC80) (King et al. 2017a); and (8) the proposed new marine GVs (PC99, PC95, PC90 and PC80) (King et al. 2017b). All of these values are presented in Table 1. The last two sets will be submitted for national endorsement as part of the revision of the Australian and New Zealand Guidelines for Fresh and Marine Water Quality. However, this process is likely to take some time and until this happens, there is uncertainty over which set of values should be used.

The purpose of this document is to examine the various sets of protective concentration values (APVMA 2011; Pathiratne and Kroon 2016), current GVs (ANZECC and ARMCANZ 2000; GBRMPA 2010), and the proposed GVs (King et al. 2017a; 2017b) for freshwater and for marine waters, explain how the different values were derived, their purpose and which is the most appropriate to use.

FRESHWATER VALUES

Current Diuron Freshwater Trigger Value

The current diuron GV for ecosystem protection of freshwaters is 0.2 µg/L (ANZECC and ARMCANZ 2000).

For diuron, the ANZECC and ARMCANZ (2000) document included chronic toxicity data for only one fish species and acute toxicity data for 23 species of fish, crustaceans, and insects (Warne 2000). The available ecotoxicity data did not meet the minimum data requirements to use the SSD method to derive GVs for diuron. Therefore, the GV was calculated by dividing the lowest chronic toxicity value of 33.4 µg/L by an assessment factor of 200 (Warne 2000). The resulting GV was categorised as *low reliability* (using the ANZECC and ARMCANZ 2000 reliability scheme). Under the new method for deriving GVs (Warne et al. 2015) this GV would be classified as having a *very low reliability*.

Proposed Diuron Freshwater Guideline Values

The new method for GV derivation (Warne et al. 2015) was used to derive the proposed diuron GVs (Table 1). These values will be submitted for consideration for national endorsement and inclusion into the Australian and New Zealand Water Quality Guidelines and the Great Barrier Reef Water Quality Guidelines.

There are now considerably more ecotoxicity data available for diuron than when the current GV was derived in 2000. In total, there were toxicity data that passed the screening and quality assessment processes for 59 freshwater species that belonged to eight phyla and 14 classes of organisms. The represented phyla were Annelida, Arthropoda, Bacillariophyta, Chlorophyta, Chordata, Cyanobacteria, Mollusca and Tracheophyta.

The distribution of freshwater species sensitivity to diuron is bimodal with phototrophs (organisms that photosynthesise; e.g. algae, macrophytes, plants) being significantly ($p \leq 0.05$) more sensitive (toxicity occurs at lower concentrations) than other organisms (non-phototrophs that do not photosynthesise) (King et al. 2017a). This is not surprising as diuron is a herbicide that exerts its

Table 1. Summary of published protective concentrations and proposed guideline values for diuron.

Freshwater values		Marine values	
Level of protection provided	**Diuron limits (µg/L)**	**Level of protection provided**	**Diuron limits (µg/L)**
Current trigger value (ANZECC and ARMCANZ 2000)		**Current trigger value (ANZECC and ARMCANZ 2000)**	
No specific level of protection	0.2	No specific level of protection	1.8
Proposed guideline values (King et al. 2017a)		**Proposed guideline values (King et al. 2017b)**	
99% species protection – PC99	0.08	PC99	0.43
95% species protection – PC95	0.23	PC95	0.67
90% species protection – PC90	0.42	PC90	0.86
80% species protection – PC80	0.9	PC80	1.2
APVMA protective concentration values (APVMA 2011)		**Great Barrier Reef trigger values (GBRMPA 2010)**	
PC99	1.19	PC99	0.9
PC95	1.56	PC95	1.6
Pathiratne and Kroon (2016) protective concentration values		PC90	2.3
PC99	0.4	**Great Barrier Reef protective concentration values (GBRMPA 2010) – these include photosynthetic inhibition data**	
PC95	1.3	PC99	0.01
PC90	2.7	PC95	0.06
PC80	7.2	PC90	0.1

toxicity by inhibiting photosynthesis. For this reason, as recommended in Warne et al. (2015), the proposed GVs were derived using only phototroph toxicity data.

Proposed GVs for diuron in freshwaters were derived based on chronic NOEC/NOEL/EC5/EC10 toxicity data and chronic LOEC/EC50 toxicity data that had been converted to estimates of chronic NOEC/EC10 data. Such data were available for 26 freshwater phototrophic species that belonged to four phyla and seven classes. These met the minimum data requirements to use the SSD method to derive default GVs for diuron (Warne et al. 2015). There was a good fit of the statistical distribution to the ecotoxicity data. Given the above, the proposed GVs were classed as being *very high reliability* using the new reliability scheme (Warne et al. 2015). It should be noted that the default GVs presented here are expressed in terms of the active ingredient (diuron) rather than commercial formulations.

The SSD of the 26 phototrophic freshwater species that were used to derive the proposed GVs is presented below (Figure 1).

Australian Pesticide and Veterinary Medicine Authority Freshwater Protective Concentration Values

In July 2011, the APVMA published the environmental risk assessment for diuron that included the derivation of protective concentration values that should protect 99 and 95 per cent of freshwater species (APVMA 2011). The APVMA stated that there are uncertainties about the protective

concentrations derived because the available data were not ideal in terms of toxicity endpoints, reliance on acute ecotoxicity data and the consequent use of acute to chronic ratios, and the use of ecotoxicity data for formulations containing diuron rather than the technical material (active ingredient).

The APVMA report (APVMA 2011) states that the, 'sensitivities of primary producers (algae and aquatic plants) is generally much higher than that for primary consumers (aquatic invertebrates) and secondary consumers (fish) sensitivity' (APVMA 2011). Therefore, separate sets of protective concentration values were derived for primary producers and for consumers.

The protective concentration values for primary producers were based on a mixture of chronic NOEC values and acute EC50 data converted to chronic NOEC data using a default conversion factor of five or 10. The APVMA (2011) report also included formulated products in the SSD where ecotoxicity data using the active constituent were not available. The ecotoxicity data were a mixture of values for 12 freshwater and 16 marine species.

A PC95 value of 1.56 µg/L was determined using toxicity data for primary producers (algae and aquatic plants) only, as it was recognised that the sensitivities of these species are much higher than that for primary consumers (aquatic invertebrates) and secondary consumers (fish) (APVMA 2011).

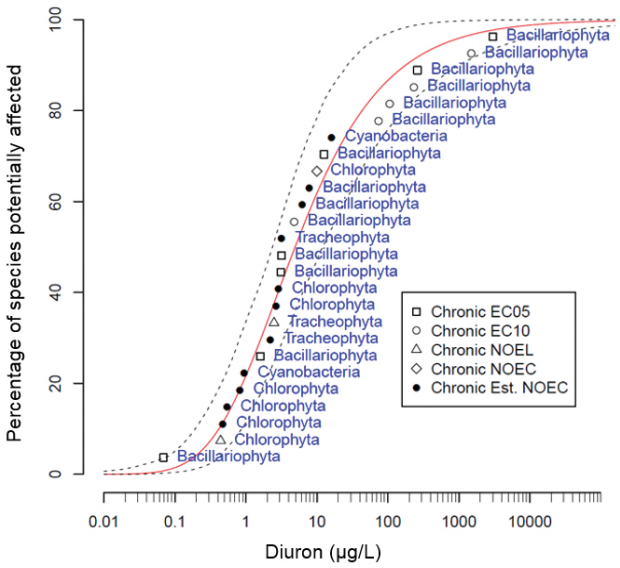

Figure 1. The species sensitivity distribution of the chronic toxicity of diuron to freshwater species. This was used to derive the proposed freshwater diuron guideline values (King et al. 2017a).

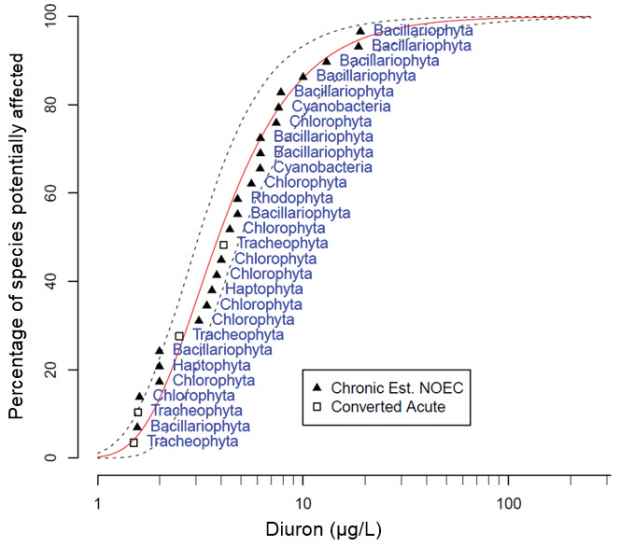

Figure 2. The species sensitivity distribution of the chronic toxicity and chronic estimates of toxicity of diuron to freshwater and marine species used by the Australian Pesticide and Veterinary Medicine Authority (APVMA 2011) to derive protective concentration values (PC99 and PC95). Regraphed using the data from APVMA (2011) and Burrlioz V2 (2016).

The SSD for diuron in the APVMA (2011) report is presented in Figure 2.

Pathiratne and Kroon Freshwater Protective Concentration Values

Pathiratne and Kroon (2016) developed protective concentration values for eight commonly detected pesticides, including diuron in tropical freshwater ecosystems adjacent to the Great Barrier Reef. They had a mixture of acute and chronic ecotoxicity data for diuron to 11 freshwater species – three microalgae, one macroalga, two cladocerans, one amphipod, one crustacean, one fish and an amphibian (Pathiratne and Kroon 2016). This met the minimum data requirements to use the SSD method to derive GVs for diuron (Warne et al. 2015). An important difference in the method used by Pathiratne and Kroon (2016), compared to Warne et al. (2015), was that they did not test whether the distribution of species sensitivity was uni- or multi-modal. This is important as diuron is a photosystem II inhibiting herbicide, and therefore, there should theoretically be a bimodal distribution in species sensitivity with phototrophs being more sensitive. A bimodal distribution was observed in King et al. (2017a) for freshwater diuron ecotoxicity data. It is also apparent from the SSD in Pathiratne and Kroon (2016) that the distribution is bimodal (Figure 3).

COMPARISON OF THE FRESHWATER LIMITS

Comparison of the Current Trigger Value and Proposed Guideline Values for Diuron in Freshwater Ecosystems

The default position is that a GV derived in the 2017 revision automatically supersedes and replaces any GV in the 2000 guidelines. Therefore, provided that the proposed freshwater GVs are nationally endorsed, they will automatically replace the current GV of 0.2 µg/L. In addition, this is warranted because:

- The revised method for deriving GVs includes the most recent science, whereas the 2000 guideline derivation method was developed in the late 1990s;
- The proposed GV is based on all the available data of appropriate quality, including new data that has been released since the current trigger value was derived in 2000;
- There are considerably more chronic toxicity data available for a larger number of species and taxa than in the 2000 guidelines;
- The proposed GVs are derived using the species sensitivity distribution (SSD) method (the preferred method for deriving GVs) whereas the 2000 trigger value was derived using the assessment factor method; and
- The proposed GVs have a *very high reliability*, using the Warne et al. (2015) method whereas the 2000 guidelines GV would now be classified as having *very low reliability*.

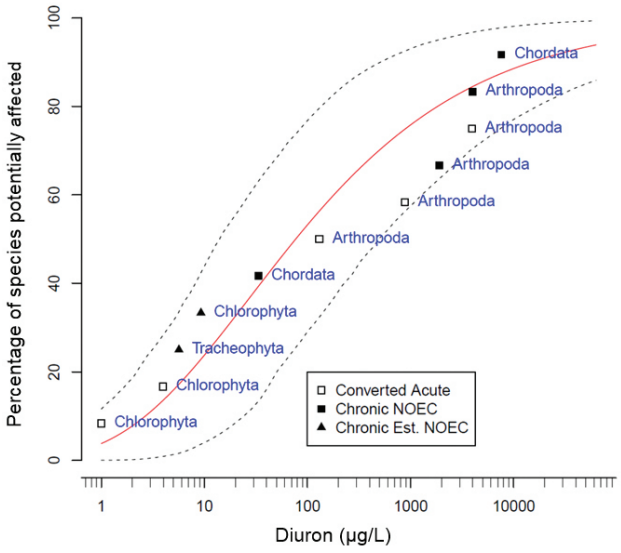

Figure 3. The species sensitivity distribution of the chronic and chronic estimates of toxicity of diuron to freshwater species used by Pathiratne and Kroon (2016) to derive protective concentration values (PC99, PC95, PC90 and PC80). Regraphed using the data from Pathiratne and Kroon (2016) and Burrlioz V2 (2016).

Comparison of the APVMA Protective Concentration Values and the Proposed Guideline Values for Freshwater Ecosystems

Although the protective concentration values derived by the APVMA (2011) were derived using a method based on the 2000 guidelines (ANZECC and ARMCANZ 2000) there are a number of important differences, as well as a number of important updates to those methods that have since been adopted:

- The APVMA combined fresh and marine species into the same SSD method to derive protective concentrations for freshwater ecosystems. This was not supported in the 2000 guidelines but is allowable in the revision of the guidelines (Warne et al. 2015) when there are insufficient data for freshwater species. There are now sufficient ecotoxicity data for freshwater species to derive a freshwater GV (King et al. 2017a).
- The APVMA combined chronic estimates and converted acute data (i.e. divided by assessment factors). This was not permitted in the 2000 guidelines but is allowable in the revision of the guidelines (Warne et al. 2015) if there are insufficient chronic toxicity data. There are now sufficient chronic toxicity data for freshwater species to derive a freshwater GV without resorting to the use of acute toxicity data (King et al. 2017a).

The proposed GVs should be used in preference to the APVMA protective concentration values because:

- They are based on chronic toxicity data for 26 freshwater phototrophic species rather than a mixture of chronic estimates and converted acute toxicity data for 28 phototrophic species.
- They are calculated in accordance with the revised method for deriving Australian and New Zealand water quality guidelines for toxicants.
- The default position is that any new GV for a chemical will automatically replace a current GV. The same logic should apply in this case – the more recent value should replace an older value.

The reason that the proposed GVs (King et al. 2017a) are considerably smaller than the APVMA protective concentration values (APVMA 2011) is that the former includes toxicity data that are markedly lower (i.e. they include species or values that are markedly more sensitive) than those used in the APVMA derivation. The lowest toxicity value used in the APVMA study was a value of 1.56 µg/L, whereas the proposed GVs include data for six species with toxicity values lower than 1.56 µg/L (i.e. ranging from 0.069 to 0.94 µg/L).

Comparison of the Pathiratne and Kroon Protective Concentration Values and the Proposed Guideline Values for Freshwater Ecosystems

The protective concentration values of Pathiratne and Kroon (2016) were derived specifically for tropical freshwater species. Therefore, only toxicity data for tropical species or species tested under tropical conditions (i.e. water test temperature was at least 24°C) were used to derive the protective concentration values.

However, these protective concentration values do have a number of limitations:

- Pathiratne and Kroon (2016) did not test whether the species, for which they had ecotoxicity data, had a uni- or bi-modal distribution. As stated previously, King et al. (2017a) found that there was a bi-modal distribution with the phototrophs being markedly more sensitive than the non-phototrophs, which was apparent in the Pathiratne and Kroon (2016) SSD for diuron. Fitting a single uni-modal distribution to a bi- or multi-modal dataset will result in a poor fit of the distribution to the data, and therefore, a poor estimate of the protective concentration values.

- With the focus being on deriving protective concentration values for tropical freshwater ecosystems, the number of species and organism types used to calculate the protective concentration values (11 species and four phyla) was markedly lower than for the proposed GVs (in total, data were available for 59 freshwater species that belonged to eight phyla; or, with the exclusion of the non-phototrophs there were data for 26 freshwater phototrophic species that belonged to four phyla).

MARINE VALUES

Current Diuron Marine Trigger Value

The current diuron GV for ecosystem protection of marine waters is 1.8 µg/L (ANZECC and ARMCANZ 2000). For the 2000 guidelines no chronic toxicity data were available for marine species, and only acute data for two species that belonged to two different taxonomic groups (fish and molluscs) were available (ANZECC and ARMCANZ 2000). The available ecotoxicity data did not meet the minimum data requirements to use the SSD method. Therefore, in accordance with the methods at that time, the GV was calculated by dividing the lowest chronic toxicity value of 1800 µg/L by an assessment factor of 1000 (Warne 2000). The resulting GV had a *low reliability* (using the ANZECC and ARMCANZ 2000 reliability scheme). Under the new method for deriving GVs (Warne et al. 2015) this value would be classified as having a *very low reliability*.

Great Barrier Reef Marine Park Authority Marine Trigger Values

The GVs for diuron (GBRMPA 2010) in marine waters of the Great Barrier Reef are presented in Table 1. They were calculated using the SSD method and included ecotoxicity data for a total of 18 species that consisted of fish (three species), invertebrates (three species) and algae (12 species). The data were a mixture of acute (for the fish and invertebrates) and chronic (for the algae) toxicity values, and as a result the GVs were classed as having moderate reliability using the 2000 guidelines reliability scheme. Using the new reliability classification (Warne et al. 2015) the GVs would have a high or moderate reliability, depending on the fit of the distribution to the data.

The Great Barrier Reef Marine Park Authority also derived protective concentration values that included data measuring sub-lethal effects for non-traditional endpoints (e.g. particularly photosynthesis inhibition). The Authority stated that these values were not proposed to be adopted as guidelines. They published these values to provide concentrations to compare with ongoing monitoring data as identified potential levels of concern. The resulting PC99, PC95 and PC90 values were 0.01, 0.06 and 0.1 µg/L, respectively.

Proposed Diuron Marine Guideline Values

The new method for GV derivation (Warne et al. 2015) was used to derive the proposed diuron marine GVs (Table 1). These values will be submitted for consideration, national endorsement and inclusion into the Australian and New Zealand water quality guidelines. If they are endorsed they will supersede the Water Quality Guidelines for the Great Barrier Reef Marine Park (GBRMPA 2016).

There are now considerably more marine ecotoxicity data available for diuron than when the existing national marine GV was derived (ANZECC and ARMCANZ 2000). In total, there were toxicity data that passed the screening and quality assessment processes for 45 marine species that belonged to 12 phyla. The represented phyla were Annelida, Arthropoda, Bacillariophyta, Chlorophyta, Chordata, Cnidaria, Echinodermata, Haptophyta, Mollusca, Ochrophyta, Rhodophyta and Tracheophyta.

The distribution of marine species sensitivity to diuron is bimodal with phototrophs (organisms that photosynthesise; e.g. algae, macrophytes, plants) being significantly ($p \leq 0.05$) more sensitive (toxicity occurs at lower concentrations) than non-phototrophs (organisms that do not

photosynthesise) (King et al. 2017b). This is not surprising as diuron is a herbicide that exerts its toxicity by inhibiting photosynthesis (King et al. 2017b). For this reason, as recommended in Warne et al. (2015), the proposed GVs were derived using only phototroph toxicity data.

Proposed GVs for diuron in marine waters were derived based on chronic NOEC/EC10 toxicity data and chronic LOEC/EC50 toxicity data that had been converted to estimates of chronic NOEC/EC10 data. Such data were available for 20 marine phototrophic species that belonged to six phyla and 11 classes. This met the minimum data requirements to use the SSD method (Warne et al. 2015). There was a good fit of the statistical distribution to the ecotoxicity data. Given the above, the proposed GVs were classed as being of *very high reliability* using the new reliability scheme (Warne et al. 2015). As with the proposed freshwater diuron GVs, the proposed marine GVs are expressed in terms of the active ingredient (diuron) rather than as commercial formulations.

The SSD of the 20 phototrophic marine species that were used to derive the proposed GVs is presented below (Figure 4).

COMPARISON OF THE MARINE LIMITS

Comparison of the Current Trigger Value and Proposed Guideline Values for Marine Ecosystems

The default position is that a GV derived in the 2017 revision automatically supersedes and replaces any GV in the 2000 guidelines. Therefore, providing the proposed marine GVs are nationally endorsed, they will automatically replace the current GV for of 1.8 µg/L.

In addition, the adoption of the proposed GVs is warranted because:

- The revised method for deriving GVs includes the most recent science, whereas the 2000 guideline derivation method was developed in the late 1990s;
- The proposed GVs are based on all the available data of appropriate quality, including new data that have been released since the current GV was derived in 2000;
- There is considerably more chronic toxicity data available for a larger number of species and taxa than in the 2000 guidelines;
- The proposed GVs are derived using the SSD method (the preferred method for deriving GVs), whereas the 2000 GV was derived using the assessment factor method; and
- The proposed GVs have a *very high reliability*, using the Warne et al. (2015) method whereas the 2000 GV would be classified as having *very low reliability*.

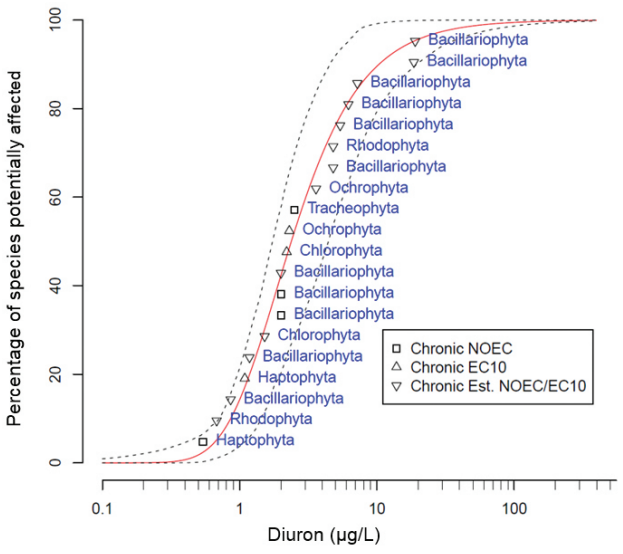

Figure 4. The species sensitivity distribution of chronic diuron toxicity data to marine species. This was used to derive the proposed marine diuron guideline values (King et al. 2017b).

Comparison of the Great Barrier Reef Trigger Values and Proposed Guideline Values for Marine Ecosystems

Although the GBRMPA GVs (GBRMPA 2010) were derived using a method based on the 2000 guidelines (ANZECC and ARMCANZ 2000) there is an important difference:

- The GBRMPA combined chronic, chronic estimates (divided by an assessment factor of 5) and converted acute data (divided by an assessment factor of 10). This was not permitted in the 2000 guidelines, but is allowable in the revision of the guidelines (Warne et al. 2015) when there are insufficient chronic toxicity data. There are now sufficient chronic toxicity data for marine species to derive a marine GV without resorting to the use of acute toxicity data (King et al. 2017b).

Providing the proposed marine GVs are nationally endorsed they will automatically replace the 2010 GBRMPA GVs (GBRMPA 2016).

In addition, the proposed GVs should be used rather than the GBRMPA GVs because:

- They are calculated in accordance with the revised method for deriving Australian and New Zealand water quality guidelines for toxicants (Warne et al. 2015).
- They are based on chronic toxicity data rather than a combination of acute and chronic data.

The reason that the proposed GVs (King et al. 2017b) are considerably smaller than the GBRMPA GVs (GBRMPA 2010) is that the former includes toxicity data which are markedly lower (i.e. they include species or values that are more sensitive) than those used in the GBRMPA derivation. The lowest toxicity value used in the GBRMPA study was a value of 10 µg/L. However, 18 of the 20 toxicity values used to derive the proposed GVs (King et al. 2017b) were less than 10 µg/L (Figure 4). These were, in descending order of toxicity, *Emiliania huxleyi* (0.54 µg/L), *Ceramium tenuicorne* (0.68 µg/L), *Thalassiosira pseudonana* (0.86 µg/L), *Isochrysis galbana* (1.09 µg/L), *Skeletonema costatum* (1.18 µg/L), *Dunaliella tertiolecta* (1.5 µg/L), *Entomoneis punctulata* (2 µg/L), *Nitzschia closterium* (2 µg/L), *Phaeodactylum tricornutum* (2 µg/L), *Nephroselmis pyriformis* (2.2 µg/L), *Saccharina japonica* (2.3 µg/L), *Zostera marina* (2.5 µg/L), *Monochrysis lutheri* (3.6 µg/L), *Achnanthes brevipes* (4.8 µg/L), *Porphyridium cruentum* (4.8 µg/L), *Navicula forcipata* (5.4 µg/L), *Amphora exigua* (6.2 µg/L), and finally *Chaetoceros gracilis* (7.2 µg/L).

Comparison of the Great Barrier Reef Protective Concentration Values and Proposed Guideline Values for Marine Ecosystems

The GBRMPA (2010) also derived high sensitivity protective concentration values (PC99, PC95 and PC90) for marine ecosystem protection. As stated earlier these values were not proposed to be adopted as guidelines, but rather were published to provide concentrations to compare with ongoing monitoring data as identified potential levels of concern. These protective concentration values were calculated using the same method as the GBRMPA GVs except that they included toxicity data that measured sub-lethal effects for non-traditional endpoints, predominantly photosynthetic inhibition following exposure of less than 24 hours (GBRMPA 2010).

Such data are not used to derive Australian and New Zealand GVs because:

- The minimum exposure duration that is acceptable is 24 hours (Warne 2000; Warne et al. 2015). The logic behind this minimum exposure duration is the assumption that short-term exposure will lead to short-term harmful effects that the organism will recover from rapidly. For example, the suppression of photosynthesis after a 15 minute exposure is likely to be short-lived, and therefore, unlikely to be ecologically relevant (see the next dot point for definition of ecologically relevant). The effect would be similar to the reduction in photosynthesis when

a cloud passes in front of the sun or during a very cloudy day – neither of which would be considered ecologically harmful. This is certainly the case for PSII herbicides where the effects are reversible. Therefore, unless a short-term exposure leads to a long-term significant reduction in photosynthesis, it is unlikely to be ecologically relevant.

- Non-traditional endpoints, including photosynthesis inhibition "*that have not had their ecological relevance unambiguously demonstrated, should only be used as an additional line of evidence in weight-of-evidence (WOE) based risk assessments*" (Warne et al. 2015). Ecological relevance of an endpoint is defined based on whether or not it has "*negative effects on the ecological competitiveness of an organism (i.e. its ability to increase the frequency of its genes in subsequent generations)*" (Warne et al. 2015). The endpoints considered to be ecologically relevant will be both, species and toxicant specific.

Therefore, as recognised by GBRMPA (2010) these GBRMPA protective concentration (high sensitivity) values should not be adopted as the national GVs for diuron in marine waters.

CONCLUSION

It is recommended that the proposed GVs for diuron in freshwater (King et al. 2017a) and marine water (King et al. 2017b) be used in preference to any of the GVs or protective concentration values derived prior to 2017.

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