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DuPont Crop Protection

December 5, 2009

Mr. Daniel McClure, P. E.
California Regional Water Quality Control Board
Central Valley Region
11020 Sun Center Drive #200
Rancho Cordova, CA 95670

DuPont comments on the Draft Diuron Criteria Derivation

Dear Mr. McClure:

DuPont Crop Protection appreciates the opportunity to comment on the draft Diuron Criteria Derivation document authored by Tessa L. Fojut, Amanda J. Palumbo and Ronald S. Tjeerdema. DuPont is the lead registrant of diuron in the United States, and we have an interest in the application of the water quality criterion method of Tenbrook *et al.*, 2009 to diuron specifically and as a precedent for other herbicides.

We recommend that data used in regulatory decision-making processes be conducted in accordance with Good Laboratory Practice (GLP) and in accordance with internationally accepted test guidelines. We support the effort by Fojut *et al.* to use data with high relevance and high reliability and recognize the significant effort undertaken by the authors to evaluate the many reports and literature references available for diuron. We note that the studies selected for derivation of the acute and chronic criteria were studies submitted by DuPont to support registration actions of the US EPA and the State of California. As study designs and data quality requirements have changed, DuPont has continued to update the database of ecological effects tests, and we are preparing to submit to the US EPA several studies that are relevant to establishing water quality criteria. These studies will be available to you through a Freedom of Information Act request after EPA has assigned an MRID. The new studies include data on three algal species (Table 1). A recently conducted study (Ferrell, 2006) on *Lemna gibba* has already been submitted to the EPA (MRID 46996701). Many of the data reports detailed in the Fojut *et al* diuron review are useful, scientifically valid reports, but these studies typically are not conducted in compliance with GLP standards or internationally accepted test guidelines and do not meet US EPA and OECD standards for data used in regulatory decision-making processes.

Diuron is algistatic/phytostatic to algae and aquatic plants. That is, after being placed into fresh, diuron-free medium, algae and aquatic plants were found to recover. This was observed in regulatory guideline studies with two sensitive species, *Selenastrum capricornutum* and *Lemna gibba*. In one of the tests with *Selenastrum capricornutum* (Douglas and Handley, 1988), a recovery phase determined that diuron was algistatic at test concentrations up to 0.16 mg/L, the highest concentration tested. In a test with *Lemna gibba* (Ferrell, 2006), a 14-day recovery period followed by a 7-day exposure period determined that recovery (i.e., growth and reproduction) occurred at test concentrations up to 0.0791 mg/L, the highest concentration tested. These recovery values can therefore be identified as the No Observed Adverse Effect Concentrations (NOAEC) for algae and Lemna. Because both algae and aquatic plants were able to recover after an episodic exposure, the recovery should be taken into consideration when determining the chronic water quality criterion.

The data summaries for the bioaccumulation studies conducted by Isensee (1976) and Call et al (1987) should be included in the appendix. The work by Isensee should not be considered relevant for the diuron criteria derivation and should be removed from Table 1 and Section 13 (Bioaccumulation). Our conclusion is based on the screening level study design as shown by the static test systems, low replication of the test, low number of fish (two), and the determination of the bioconcentration factor based on total radioactive residues rather than residues of diuron. The work by Call *et al* is more representative of a regulatory guideline study design than the Isensee study. Fish were exposed to the test material in a flow-through design (not explicitly indicated in the paper, but a static test system is not possible), ensuring exposure to constant levels of the test material. Residues of diuron in fish were determined during the periods of uptake and depuration. The authors determined that 1.3% of the total tissue radioactivity was diuron, resulting in a mean bioconcentration factor of 2, not log 2. This should be changed in Table 1 and in Section 13. Using a BCF value of 2, the calculations for the mallard and human NOEC_{water} values will change to 2,500,000 µg/L and 1000 µg/L, respectively. These values exceed the proposed chronic criterion by factors of 2,000,000 and 800, respectively.

The authors selected data for two taxa as reliable and relevant for establishing an acute water quality criterion. Following the method for an acute criterion, the authors used an assessment factor of 36 to divide the lowest EC₅₀ and produce the acute value. The authors discussed the uncertainties in applying an assessment factor based on neurotoxic insecticides to a herbicide, but made no other effort to justify applying the same assessment factor to diuron. A sound rationale for this decision is desirable and should be developed before applying the method to diuron or other herbicides. There are data for 15 species in tables 4 and 5, of which data for 3 species are considered reliable and relevant. The acute value of 333 µg/L calculated through the use of the assessment factor (section 7, page 6) is less than the LC/EC₅₀ for all species with one exception, *Gammarus lacustris* (Sanders, 1969) which the authors categorized as less reliable/less relevant (LL). It is not appropriate to increase the assessment factor when the existing data is not considered adequate for construction of a species sensitivity distribution.

The recommended acute criterion (Section 7) according to the method of Tenbrook *et al.*, 2009 should be 168 µg/L. The addition of another assessment factor of two based on a study identified as unreliable by the authors is not appropriate. The study by Sanders (1969) should not be considered in this assessment since there is no data for the controls. Without this data, it is impossible to determine the overall health of the test organisms used in the study. Table 6 clearly identifies this study as 'LL' because the study design was not based on a standard study design and a control response was not reported. Applying an additional safety factor so that the final acute criterion was below all endpoints reported for all taxa appears to negate the value of the data review for identifying data that is reliable for establishing a water quality criterion. The final criterion, using the additional, arbitrary assessment factor was coincidentally equal to the US EPA benchmark value of 80 µg/L and was accepted because of the similarity to the EPA value rather than as a result of the criteria outlined in Tenbrook *et al.* 2009. The revision of the acute criterion to 168 µg/L should be reflected in the appropriate portion of Section 18, Final criteria statement.

In Tenbrook *et al.*, 2009, Chapter 2 (Evaluation and Selection Methods), Section 2-2.1.2 (Hypothesis tests vs. regression analysis) "...the MATC is the value used in the new methodology to calculate the chronic criterion." Following this guidance, the chronic criterion (Section 8) should be 1.8 µg/L, the MATC from Blasberg et al. 1991.

Data is available in Blasberg *et al.* to calculate the EC₅₀, and Tenbrook *et al.* state in Chapter 3, Section 2.1.1.2 that an EC_x may be used for criteria development. Aquatic plant studies are designed to allow determination of the EC₅₀, which is a conservative, robust endpoint. The endpoints measured in aquatic

plant studies are sublethal (effects on growth), and the effects are generally reversible. Because algal and aquatic plant studies are based on effects such as population growth rate and not on individual effects such as mortality, the EC₅₀ is an appropriate endpoint for establishing a water quality criterion. The NOEC is not an appropriate endpoint, since it is dependent on dose-selection and cannot be compared among species.

Aquatic plant endpoints should be based on measurements of growth or growth rate as recommended by OECD and should consider the potential for recovery. We recommend that the Central Valley Water Quality Control Board select the EC₅₀ based on growth rate instead of the NOEC to take account of the type of effects measured in aquatic plant studies. The potential for recovery was not considered by Fojut *et al.*, but should be the basis for determining a chronic water quality criterion since the exposures to diuron will be episodic. This change should be reflected in Section 18, Final criteria statement.

Thank you for the opportunity to comment on the Draft Diuron Criteria Derivation document. We look forward to continued interactions with you and with the researchers at University of California – Davis as you further develop the methodology for establishing water quality criteria.

Sincerely,

A handwritten signature in black ink that reads "Aldos C. Barefoot". The signature is written in a cursive style with a large, stylized initial 'A'.

Aldos C. Barefoot, Ph. D.
Research Fellow
Environmental Safety Assessment

Table 1
Algal and Aquatic Plant Studies

Study	Organism	Code/Lab	Report Date	Biomass Endpoint(s)	Growth Rate Endpoint(s)	GLP
Algal Toxicity	<i>Selenastrum capricornutum</i>	Douglas & Handley DPT 171	1988	72 hr EC ₅₀ – 0.018 mg/L 120 hr NOEC – ~0.01 mg/L	0.022 mg/L (120 hrs) 120 hr NOEC – ~0.08 mg/L	Yes
Algal Toxicity	<i>Synechococcus leopoliensis</i>	D. Dengler, DuPont-19438	2006a	0.026 mg/L (72 hr) NOEC – 0.0037 mg/L	0.380 mg/L (72 hr) NOEC – 0.011 mg/L	Yes
Algal Toxicity	<i>Navicula pelliculosa</i>	D. Dengler, DuPont-19440	2006b	0.022 mg/L (72 hr) NOEC – 0.011 mg/L	0.065 mg/L (72 hr) NOEC – 0.011 mg/L	Yes
Aquatic Plant	<i>Lemna gibba</i> G3	B. Ferrell DuPont-20775 MRID 46996701	2006	0.0144 mg/L (7 day EC ₅₀) Based on Biomass Yield NOEC – 0.00247 mg/L	0.0203 mg/L (7 day EC ₅₀) Based on Biomass NOEC – 0.00247 mg/L	Yes

References

Dengler, D. (2006a). Testing of Toxic Effects of Diuron Technical on the Blue-Green Alga *Synechococcus leopoliensis*; DuPont 19438, DuPont de Nemours France, S.A.

Dengler, D. (2006b). Testing of Toxic Effects of Diuron Technical on the Diatom *Navicula pelliculosa*; DuPont 19440, DuPont de Nemours France, S.A.

Douglas, M.T. and Handley, J. W. (1988). The algistatic activity of diuron technical, DPT 171; DuPont de Nemours France, S. A.

Ferrell, B.D. (2006). Diuron (DPX-14740) Technical: Static, 7-Day Growth Inhibition Toxicity Test with *Lemna gibba* G3; DuPont 20775; E.I. du Pont de Nemours and Company, HaskellSM Laboratory for Health and Environmental Sciences. MRID 46996701.

Fojut, T. L., Palumbo, A. J. and Tjeerdema, R. S. 2009. Diuron Criteria Derivation Draft, Environmental Toxicology Department, University of California – Davis.

Tenbrook, P. L., Palumbo, A. J., Fojut, T. L., Tjeerdema, R. S.; Hann, P.; Karkoski, J. (2009). Methodology for Derivation of Pesticide Water Quality Criteria for the Protection of Aquatic Life in the Sacramento and San Joaquin River Basins. Phase II: Methodology Development and Derivation of Chlorpyrifos Criteria.