SACRAMENTO, CA
January 10, 1997

DowElanco

Mr. Rick Woodard
Water Quality Program Manager
CALFED Bay-Delta Program
1418 9th Street, Suite 1155
Sacramento, California 95814

CALFED WATER QUALITY ACCEPTABLE RANGES FOR PARAMETERS OF CONCERN RELATIVE TO CHLORPYRIFOS

Thank you for the opportunity to review the CALFED Water Quality Acceptable Ranges (WQAR) for Parameters of Concern draft document of November 19, 1996. As the stated goal of the CALFED Water Quality Team is to create a water quality program that is acceptable to all stakeholders, it is critical that a process be developed that meets the long term needs of the State. Such a mechanism should be flexible and allow for improvements in both the data base employed to assess water quality concerns as well as new science regarding exposure and availability. Acceptance of interim water quality standards, even those characterized as "targets", without a flexible mechanism to further assess and update such values creates final water quality criterion by default.

The CALFED Water Quality Team appears to have chosen the interim freshwater Water Quality Criteria developed by the California Department of Fish and Game (DFG) as proposed in *"Hazard Assessment of the Insecticide Chlorpyrifos to Aquatic Organisms in the Sacramento - San Joaquin River System"* (1994, Administrative Report 94-1) to define the proposed acceptable range for chlorpyrifos. The DFG report evaluated one hundred and twenty tests based on methodology developed by USEPA in *"Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and their Uses"* by Stephan et al., USEPA, 1985. Although these guidelines provide a method for the determination of both acute and chronic criterion, DFG developed an interim chronic value only; this value was described as interim because of insufficient data. While the short half-life of chlorpyrifos (>90% degradation within 48 hours) and sporadic pattern of detection in the Sacramento and San Joaquin Rivers may support an acute criterion, the establishment of a chronic value, in the absence of exposure information, is not supportable.

I would like to point out that the above mentioned USEPA methodology has been further defined since the DFG 1994 report. These refinements are developed in the *"Final Water Quality Standards for the Great Lakes System"* (Federal Registrar, 23 Mar 1995), this mechanism is now commonly referred to as GLI Tier I methodology. The California Department of Pesticide Regulation has proposed to develop Quantitative Response Limits (QRL's), derived from the Acute Criterion, that are analogous to the GLI Tier I CMC (Criterion Maximum Concentrations).

DowElanco ecotoxicologists have been following the development of water quality criteria quite closely as it relates to chlorpyrifos, both in California and the Nation. We do note some differences between the USEPA Tier I methodology and the DFG methodology, as USEPA methodology currently describes a hierarchy for data selection [Sections E (pages

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158 to 160) and I (pages 161 to 163)]. We find that the data base for chlorpyrifos is sufficiently developed that default criteria (such as, saltwater species, static systems) are unnecessary to complete an acute data grid. In our analysis (attached), and per the USEPA Tier 1 hierarchy for data selection, we have selected toxicological endpoints developed in flow-thorough systems with measured concentrations over those derived in static systems with nominal concentrations.

Data selection for calculation of Final Acute Value. Our calculations (attached) result in a significantly higher Final Acute Value (FAV) for chlorpyrifos (0.129 $\mu g\ L^{-1}$) than that developed by DFG (0.07 $\mu g\ L^{-1}$). DFG indicates that 109 aquatic ecotoxicity studies were considered and approximately 70 were found to be acceptable. We found only 29 of >200 acute toxicity studies in the data base of Barron and Woodburn (*Rev. Environ. Contam. Toxicol.* 1995. Vol 144. pp. 1—93) to be acceptable based on strict interpretation of the USEPA Tier I methodology (see attachment). As mentioned above, the data base on chlorpyrifos is very deep, therefore, it is possible to assemble required data for FAV computation using the most stringent criteria outlined in the methodology (section IV of Appendix A to Part 132 of the Final Rule). For example, we used only tests conducted with freshwater species using flow-through systems; static systems with nominal (as opposed to measured) chlorpyrifos concentrations were not selected.

DFG associates the four lowest Genus Mean Acute Values (GMAV) with acute values for the *four most sensitive species* identified in their data base (Table 4). This is not consistent with USEPA Tier I methodology. In our computations we selected the *four lowest GMAV* computed from the 29 sets of species-level data evaluated. If calculations result in fewer than 59 GMAV, then the four lowest GMAV are used; otherwise, the four GMAV closest to P=0.05 are selected (section IV.N of Appendix A to Part 132 of the Final Rule).

DFG does not indicate the probability of occurrence of the four selected GMAV. These probabilities are necessary to calculate the FAV. In the case of our analysis, the probability of occurrence associated with the four lowest GMAV ranged from 0.0625 to 0.25.

Final Acute Equation. The USEPA Tier I methodology makes provision for normalization of the FAV if there is a demonstrated relationship of toxicological response and water quality characteristics. DowElanco believes this an appropriate consideration for chlorpyrifos, since organic carbon (and perhaps other water quality characteristics) may well attenuate the observed toxicological response. We are currently reviewing the published literature and supporting independent external inquiry to determine if this is the case and whether the final acute equation should therefore account for covariance in a significant water characteristic. In light of this, CALFED should recognize that any WQAR for chlorpyrifos developed at this point in time is provisional and may need adjustment as the data base is clarified.

Criterion Maximum Concentration. The USEPA Tier I methodology divides the FAV by two to develop the CMC. This approach has also been taken by DFG in the proposed WQAR. This divisor is a generic factor used in the USEPA algorithm to represent the slope of the dose-response curve for a non-specific pesticide and is not relevant to the activity of chlorpyrifos. Organophosphate insecticides, such as chlorpyrifos, have an extremely steep dose-response curve. The activity of this material is usually reduced from 100% to zero within a single 1/2X reduction in dose. The use of a generic factor of conservatism requiring a 1/2X reduction from a fifty percent effect value greatly over-estimates the impact of this rapidly degrading material in the aquatic ecosystem. Without a

rationale for this generic adjustment factor, it may be viewed as arbitrary and should not applied in development of the WQAR.

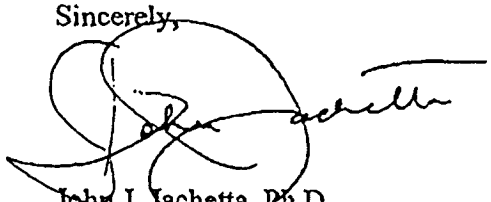
Final Chronic Value. DFG evaluated 11 chronic toxicity tests and accepted seven; as discussed in their report, there was insufficient data to directly calculate a chronic criterion, nor were there enough data to derive a final acute-to-chronic ratio for freshwater species. To calculate a final chronic value for freshwater species, DFG varied from USEPA guidelines by using the saltwater acute-to-chronic ratio for *Mysidopsis bahia*. *Mysidopsis* is an ocean-dwelling species which is not generally used to derive freshwater water quality criteria.

DFG's Recommendation for Criteria. Because of limited data, the DFG process did not conform to USEPA guidelines. However, DFG did recommended an interim water quality criterion in their 1994 hazard assessment for chlorpyrifos. Rather than express the criterion in terms of both acute and chronic criteria, DFG appears to have selected the lowest of the final acute value, final chronic value and final plant value as a single water quality criterion for freshwater. In this case the lowest of these values was the final chronic, 0.02 $\mu g\ L^{-1}$. DFG did qualify this assessment by noting that this criteria should be considered interim, as it was not derived from an acute-to-chronic ratio representative of freshwater species. An acute criterion was not proposed for chlorpyrifos, though such values exist for similar crop protection products.

Chlorpyrifos is subject to rapid dissipation in the aquatic environment. The half-life for dissipation of this crop protection product is 16 hours in surface water, ninety percent of this molecule degrades within 46 hours. True toxicity in ambient water is a function of concentration, toxicity and the likelihood of exposure. In the case of chlorpyrifos, the short half-life and sporadic pattern of detection in the Sacramento and San Joaquin Rivers may support an acute criterion; however, the establishment of interim chronic values, in the absence of freshwater data or exposure information, is not supportable.

In conclusion, DowElanco ecotoxicologists, using a comprehensive data base and stringent interpretation of USEPA Tier I guidance, have developed a chlorpyrifos FAV of 0.129 $\mu g\ L^{-1}$. We do believe that the development of water quality standards using the probabilistic approach outlined by the Aquatic Risk and Mitigation Dialogue Group is more consistent with current science and may be considered as an alternative goal for the CALFED Water Quality Team. Such an approach develops a more realistic risk assessment by looking at probable exposure in addition to potential effect. In addition, the development of a more proactive plan, such as that proposed by the Western Crop Protection Association for a University of California system-wide Best Management Practice research, education, and outreach program may be a more productive use of CALFED resources. If, however, CALFED chooses to use a USEPA Tier I standard, we suggest that the 0.129 $\mu g\ L^{-1}$ value be adopted as the interim WQAR for chlorpyrifos.

Sincerely,



John J. Iachetta, Ph.D.
State Regulatory Affairs Manager

Attachment 1: Chlorpyrifos Water Quality Guideline Setting by USEPA Tier I Methodology Acute Criterion

cc: John Sanders, Ph.D. Branch chief, Environmental Monitoring and Pest Management Branch

Brian Finlayson, Ph.D., Environmental Services Supervisor, Department of Fish and Game, Pesticide Investigation Unit

Bryan Stuart, Ph.D., DowElanco Sacramento
Nick Poletika, Ph.D., DowElanco, 306/A2
California State Action File

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ATTACHMENT 1

Chlorpyrifos Water Quality Guideline Setting by USEPA Tier I Methodology
Acute Criterion

Source for methodology:
USEPA. 1995. Final Water Quality Guidance for the Great Lakes System. CFR Parts 9, 122, 123, 131, & 132. Final rule. Appendix A to Part 132 -- Great Lakes Water Quality Initiative Methodologies for Development of Aquatic life Criteria and Values. Methodology for Deriving Aquatic Life Criteria: Tier I.

I. A. Material of concern: CHLORPYRIFOS

II. Collection of data: Data on toxicity to aquatic animals and plants comes from the review of Barron and Woodburn (*Rev. Environ. Contam. Toxicol.* 1995. Vol 144. pp. 1—93).

III. B. Required data:

1. Results of acceptable acute (or chronic tests) for
   a. class Osteichtyes, the family Salmonidae
   b. class Osteichtyes, other than Salmonidae, preferably an important warm water species
   c. a third representative of the phylum Chordata (an aquatic vertebrate)
   d. a planctonic crustacean
   e. a benthic crustacean
   f. an insect
   g. a representative of a phylum other than Chordata or Arthropoda
   h. a representative in any order of insect or any phylum not already represented.
2. Acute-chronic ratios with data for at least
   a. one fish
   b. one invertebrate
   c. one freshwater species
3. Data for at least one freshwater algae or vascular plant

These data are present in the compilation of Barron and Woodburn (*Rev. Environ. Contam. Toxicol.* 1995. Vol 144. pp. 1—93)

IV. Final Acute Value

The following hierarchy was used for data selection criteria to fill the requisite categories for the Tier 1 acute value computation:

freshwater species
  flow-through test
    measured concentration
    nominal concentration
      EC_{50}
      LC_{50}

The data base for chlorpyrifos is sufficiently rich that default criteria (such as, saltwater species, static systems) were unnecessary to complete the acute data grid. The resulting tabulation of GMAV is shown in Table 1. From Table 1, the relevant GMAV and resulting FAV calculation are:

Sensitive genus	GMAV, µg/L	P
Amphipod, *Grammarus* sp.	0.14069599	0.0625
Cladoceran, *Daphnia* sp.	0.21	0.125
Mayfly, *Cloen* sp.	0.25	0.1875
Mayfly, *Emphemerella* sp.	0.34641016	0.25

$$S^2 = (((\ln GMAV)^2)-((((\ln GMAV))^2)/4))/((P)-((((\sqrt{P}))^2)/4)) = 12.2$$

$$L = ((\ln GMAV)-S((\sqrt{P})))/4 = -2.8$$

$$A = S(\sqrt{(0.05)})+L = -2.05$$

$$FAV = [EXP](A) = 0.129\ \mu g\ L^{-1}$$

V. Final Acute Equation

FAV may be normalized by taking into account the effect of water quality parameters as covariates that influence the expression of acute aquatic toxicity. For chlorpyrifos it is reasonable to assume that organic carbon (and perhaps pH) have an influence on acute toxicity. On-going evaluation of the existing data as well as development of new data will clarify this effect and may result in a revised FAV. As such the currently derived FAV should be judged interim at present.

X. Criterion

B. Criterion Maximum Concentration (CMC)

CMC = FAV/2 = 0.0645 µg L^{-1}

DowElanco at present does not support the CMC as a regulatory criterion based on the limited information in the USEPA Tier I methodology concerning reduction of the FAV by a factor of two.

Table 1: Data Required for FAV Determination:

LC_{50}/EC_{50} µg/L	SMAV	GMAV	Reference	Rank (R)	Probability (P)
a. class Osteichtyes, the family Salmonidae					
Rainbow trout, *Oncorhynchus mykiss*					
8.0			Holcombe et al., 1982		
9.0			Philips and Holcombe, 1985		
	8.48528				
		8.48528		8	0.5
b. class Osteichtyes, other than Salmonidae					
Bluegill, *Lepomis macrochirus*					
10			Philips and Holcombe, 1985		
	10				
		10		9	0.5625
Channel catfish, *Ictalurus punctatus*					
806			Philips and Holcombe, 1985		
	806				
		806		14	0.875
c. a third representative of the phylum Chordata					
Fathead minnow, *Pimephales promelas*					
203			Holcombe et al., 1982		
140			Jarvinen and Tanner, 1982		
120			Jarvinen and Tanner, 1982		
542			Philips and Holcombe, 1985		
	207.349				
		207.349		13	0.8125
d. a planctonic crustacean					
Cladoceran, *Daphnia pulex*					
0.21			van Wijngaarden and Leeuwangh, 1993		
	0.21				
		0.21		2	0.125
Amphipod *Grammarus fasciatus*					
0.18			USEPA, 1986		

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0.18				
Grammarus pseudolimnaeus				
0.18		USEPA, 1986		
0.3		Siefert, 1984		
0.2		Siefert, 1984		
0.22104				
Grammarus pulex				
0.07				
0.07		van Wijngaarden and Leeuwangh, 1993		
0.1407			1	0.0625
e. a bentihic crustatcian				
Crayfish, *Orconecetes immunis*				
6		Philips and Holcombe, 1985		
6				
6			7	0.4375
f. an insect				
Diptera, *Chaborus obscuripes*				
6.6		van Wijngaarden et al, 1993		
Mayfly, *Caenis horaria*				
>3				
3		van Wijngaarden et al, 1993	6	0.375
3				
Mayfly, *Cloen dipterum*				
0.25		van Wijngaarden and Leeuwangh, 1993		
0.3		van Wijngaarden et al, 1993		
0.25				
0.25			3	0.1875
Mayfly, *Emphemerella* sp.				
0.4		Siefert, 1984		
0.3		Siefert, 1984		
0.34641				
0.34641			4	0.25
Water strider, *Corixa puctata*				
2.0		van Wijngaarden et al, 1993		
2.0				
2.0			5	0.3125
g. a rcprcsentative of a phylum other than Chordata or Arthropoda				
Mollusca, snail				
Anius vortex				

> 94		van Wijngaarden and Leeuwangh, 1993		
> 94		van Wijngaarden et al, 1993		
	94			
		94	10	0.625
Aplexa hypnorum				
> 806		Philips and Holcombe, 1985		
	806			
		806	15	0.9375
Bithynia tentuculata				
> 94		van Wijngaarden and Leeuwangh, 1993		
> 94		van Wijngaarden et al, 1993		
	94			
		94	11	0.6875
Lymnaea stagnalis				
> 94		van Wijngaarden and Leeuwangh, 1993		
> 94		van Wijngaarden et al, 1993		
	94			
		94	12	0.75

h. a representative in any order of insect or any phylum not already represented reflected in the forgoing tabulation

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