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SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF INTEGRATIVE BIOLOGY

BERKELEY, CALIFORNIA 94720-3140

May 3, 2002

CALFED ERP Selection Panel  
c/o Mr. Dan Ray  
CALFED Bay-Delta Program  
1416 9<sup>th</sup> St, Suite 630  
Sacramento, CA 95814

Dear Selection Panel:

Thank you for the opportunity to respond to the initial funding recommendations in the ERP and to clarify a significant misunderstanding of the Technical Panel regarding our proposal, "Water quality effects of pesticides used in orchard agriculture - Part 2: Aquatic fate and effects of particle-sorbed pyrethroids " which was not recommended for funding at the Technical Panel level. The Technical Panel based its decision entirely on a single erroneous assumption, and by doing so, is jeopardizing the collection of much needed information on environmental fate and effects of an emerging pesticide class. The Technical Panel's decision was based on the single premise that no one has the analytical capability to detect pyrethroids at concentrations low enough to be environmentally relevant. Using information from our proposal, the review comments, and information available in the literature that a reviewer knowledgeable in the subject area should have been familiar with, we will show that.

1. The Technical Panel disregarded the fact that all five external reviewers recommended funding;
2. The Technical Panel's concern is unfounded and based on overly pessimistic assumptions of the needs of the project, unsupported by the project design as described in the proposal;
3. Our analytical capabilities are more than adequate to measure toxicologically relevant concentrations;
4. Not only are the proposed analytical methods feasible, but they have been successfully used in about a dozen previous investigations in situations similar to those we will encounter;
5. Our proposed approach is supported by the leading national authorities in the subject, all of whom believe we can meet the analytical needs of the project, and thus the basis for the Technical Panel not recommending funding is groundless.

Our proposal received 5 external reviews. Three reviewers (#2,4,5) rated the proposal "excellent", with no substantive criticisms. The remaining two reviewers (#1,3) rated it "good" with their principal concern being whether current analytical techniques were sufficiently sensitive. Even those two reviewers rating it "good" viewed the proposal very positively and suggested partial funding to demonstrate analytical feasibility. The Technical Panel took a view much more negative than that of any of the five external reviewers and did not recommend it for any funding. The Technical Panel's concern as to whether current state-of-the-art analytical

techniques are adequate for the work proposed was the sole basis for their decision. All other issues identified by the Panel were minor and were copied verbatim from External Reviewer #2 who had rated the proposal "excellent". We can show that the Technical Panel's analytical concerns were exaggerated and in error, and thus that there is no substantive reason in the comments from the Technical Panel or from the external reviewers that warrant funding being denied.

We should emphasize that while there is a chemistry component to our proposed study, its focus is on pyrethroid toxicology. In the information provided below we will address analytical chemistry issues because they were the sole significant concern of the Technical Panel. However, it should be recognized that in our proposal the analytical work was largely a "means to an end", in that it supported our research objectives pertaining to bioaccumulation and toxicity. Neither the external reviewers nor the Technical Panel raised any major issues with the ecotoxicological elements which were the primary focus of the proposal, so we have not given these aspects much emphasis in the discussion below.

#### Reason for the Panel's misinterpretation

We believe the Technical Panel and the 2 reviewers who expressed analytical concerns misunderstood the project's analytical needs and erroneously concluded that current techniques are inadequate. The reviewers believed we intended to measure pyrethroids at low ng/l (ppt) levels (Reviewer #1 - "I doubt strongly that ECD will be sensitive enough to analyze for these compounds in the low part per trillion range"; Reviewer #3 was not as specific but used terms like "lower level of analyses" and "detect low levels"). We agree that low ng/l levels (<10 ng/l) are pushing the limits of science, but in the proposal we said we could achieve detection limits in the range of 10-50 ng/l. The limits originally stated within the proposal are adequate and achievable within current capabilities as documented further below.

In the proposal we noted pyrethroids can be acutely toxic to very sensitive species at low ppt levels, and while this is true, most species that have been tested are not nearly so sensitive. Figure 1, drawn from information in EPA's AQUIRE (ECOTOX) database, shows the acute LC50 values for all species for which toxicity testing data are available for the two most widely used agricultural pyrethroids in California, permethrin and esfenvalerate. Of the 69 species that have been tested with permethrin, only 0-2 species have LC50s at levels that are potentially below our detection limit. Of the 37 species that have been tested with esfenvalerate, only 1-4 have LC50s at levels that are potentially below our detection limit. It is likely that chronically toxic levels to sensitive species are beyond current analytical limits. The concern of the Technical Panel that we can not get to levels low enough to protect extremely sensitive species ignores the fact that we can reach levels that protect about 95% of aquatic species. This concern was the entire basis for the Technical Panel's rejection of our proposal, but it seems ridiculous to us to halt research on pyrethroids that is relevant to and could potentially protect 95% of the species, until analytical methods are developed to protect the last 5%.

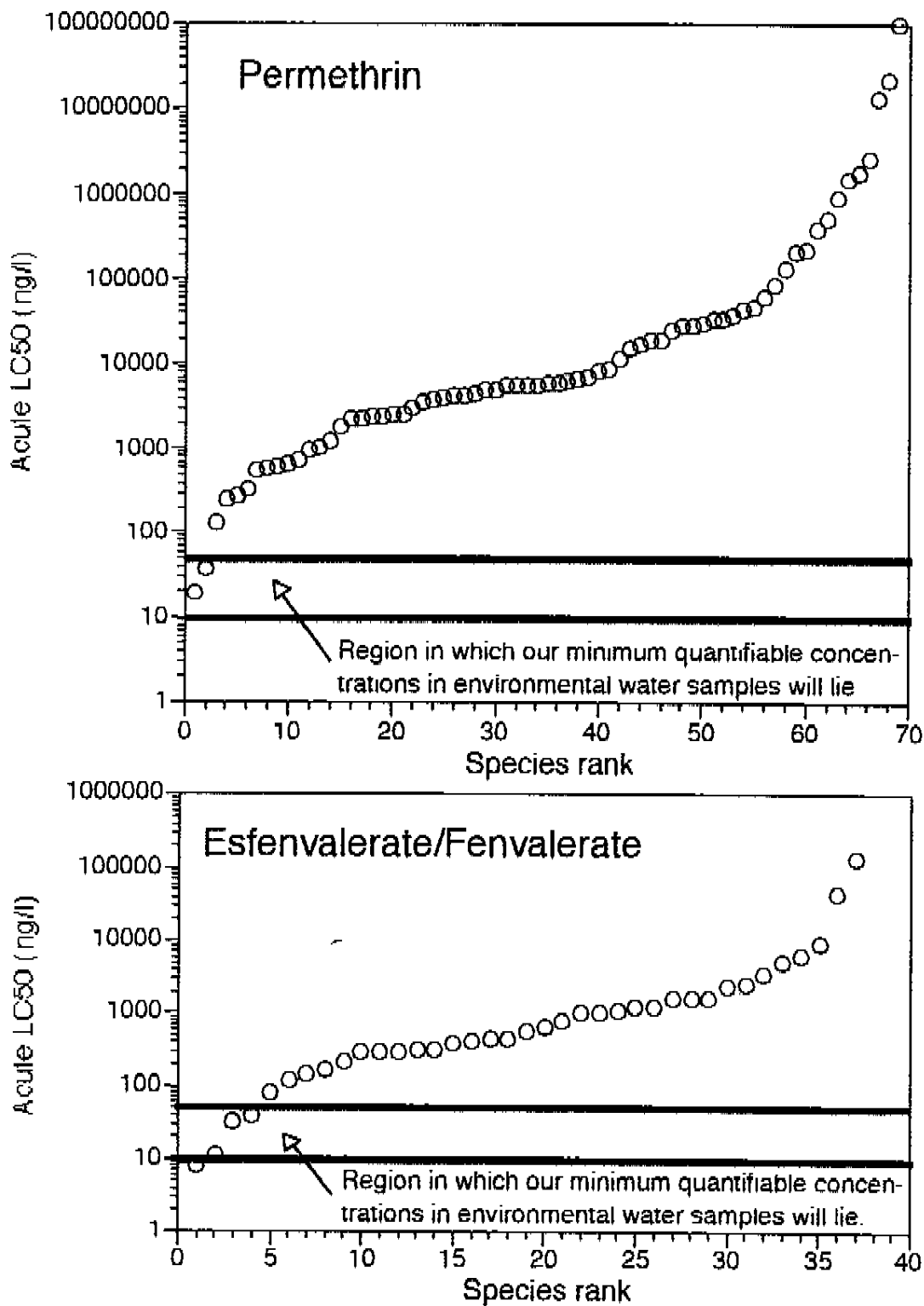


Figure 1. Our aqueous quantification limits for pyrethroid compounds in comparison to the distribution of pyrethroid sensitivities for all aquatic species in the EPA AQUIRE database.

### Analytical requirements of the work proposed

A careful review of our proposal provides the following data on the types of samples we will have for pyrethroid quantification and we can roughly approximate the sample numbers:

- 1) Analyzing pyrethroid mass in water samples: 100 samples, all collected in ditches and streams adjacent to treated fields.
- 2) Analyzing pyrethroid mass in sediment samples: 200 samples, both surficial and suspended sediments collected from both near-farm water bodies and mainstem rivers.
- 3) Analyzing pyrethroid mass in tissue or fish feed samples: 100 samples, all from laboratory exposures of splittail.
- 4) Analyzing pyrethroid in water, sediment or tissue based on radioactivity of  $^{14}\text{C}$ -labelled compounds: 2500 samples, all from laboratory invertebrate exposures.

Clearly the vast majority of the samples we proposed to analyze utilize radiolabelled pyrethroids, for which the analytical concerns identified by the Panel are moot. Quantifying environmentally relevant concentrations of pyrethroids in sediments and tissues is not nearly as difficult as in water, since with  $\log K_{ow}$ 's of about 6, concentrations in sediment and tissue are many orders-of-magnitude higher than in water. Although there is very little information in the literature on sediment concentrations that would be potentially toxic (we had proposed to collect much more information to address this data gap), the few reported levels are in the high ppb to low ppm range (70  $\mu\text{g}/\text{kg}$  to grass shrimp (McKenney et al., 1998), 1,300 to nematodes (Chandler et al., 1994), 2,100  $\mu\text{g}/\text{kg}$  to a chironomid (Conrad et al., 1999), 2,800-3400 to copepods (Chandler et al., 1994)). The analytical concerns of the Technical Panel are relevant only to our water samples, all of which are being collected adjacent to treated fields and shortly after treatment. Concentrations in these water samples should be relatively high and have been found to be measurable by many previous investigators (discussed below). Even so, the Panel's concern applies to only 100 water samples out of our total of 2900 samples (~3% of the samples). Even if the analytical concerns of the Technical Panel were warranted, it seems far more reasonable and prudent to suggest modification of the study design, and totally unjustifiable to reject the proposal in its entirety because of analytical concerns regarding 3% of the samples.

### Success of similar past efforts

The Technical Panel's no-funding recommendation was based on the claim that no one can measure environmentally relevant levels of pyrethroids. Although there has been no work in the ERP region on aquatic field assessment of pyrethroid residues, many other investigators elsewhere in the country have tested for residues using procedures similar to those we proposed and have successfully quantified pyrethroids in water and sediment. Given the successes of previous investigations, it is apparent that the analytical work we had proposed is quite feasible. When sampling water near treated areas (Table 1), as we had proposed to do, concentrations shortly after treatment are generally well above the low ppt levels that the Panel felt we could not attain. All 12 studies we have reviewed were able to successfully quantify water concentrations of pyrethroids, and in only 5 of the studies did concentrations drop below detection limits in even some of the samples. All 12 of these studies quantified pyrethroids by gas chromatography with

Table 1. Compilation of studies in which water samples were analyzed for pyrethroid residues following either agricultural or experimental application to outdoor systems.

Reference	Scenario	Measured conc. (ng/l)
Schulz and Liess, 2001 Environ. Tox. Chem. 20:185	Fenvalerate application to stream	100-1,000
Tanner and Knuth, 1996 Arch Env Con Tox 31:244-251	Esfenvalerate application to ponds	<50-6,300
Shires and Bennett, 1985 Ecotox. Environ. Safety 9:145	Ditches near cypermethrin-treated fields	50-2,500
Lutnicka et al. 1999 Wat. Res. 33 3441	Ponds near deltamethrin-treated fields	~0-15,700
Conrad et al., 1999 Wat Res 33 1603	Waterbodies near permethrin-treated fields	Up to 2,600
Helliwell and Stevens, 2000 Field Crops Res. 67:263	Cypermethrin applied to rice fields	<1-410
Woin, 1998 Ecotox. Environ. Safety 41:137	Fenvalerate application to ponds	7-1,000
Drener et al., 1993 Environ. Tox. Chem. 12:1297	Bifenthrin application to outdoor tanks	~10-7,800
Webber et al., 1992 Environ. Tox. Chem. 11:87	Esfenvalerate application to ponds	10-690
Fairchild et al., 1992 Environ. Tox. Chem. 11:115	Esfenvalerate application to ponds	270-2,790
Materna et al., 1995 Environ. Tox. Chem. 14:613	Esfenvalerate application to ponds	1,200-20,600
Giddings et al., 2001 Environ. Tox. Chem. 20:660-668	Cypermethrin and esfenvalerate applic. in several pond studies	~0-6,900

Table 2. Compilation of studies in which sediment samples were analyzed for pyrethoid residues following either agricultural or experimental application to outdoor systems.

Reference	Scenario	Measured conc. ( $\mu\text{g}/\text{kg}$ )
Muir et al., 1985 J. Agric. Food Chem.	Ponds near deltamethrin-treated fields	3000-5000
Conrad et al., 1999 Wat. Res. 33:1603	Permethrin application to ponds	4-200
Helliwell and Stevens, 2000 Field Crops Res. 67:263	Cypermethrin applied to rice fields	6-57
Chandler et al., 1994 Mar. Envir. Res. 37:313	Creeks near fenvalerate-treated fields	~0-100
Webber et al., 1992 Environ Tox. Chem. 11:87-105	Esfenvalerate application to ponds	6-56
Clark et al., 1989 Environ Tox. Chem. 8:393-401	Fenvalerate and cypermethrin application to sediments	Fen. 97-13000 Cyp. 5-100

electron capture detection, just as we had proposed to do (not mass spec. as Reviewer #1 suggested we use).

For sediment sampling, we have summarized the results of 6 studies (Table 2). All were successful in measuring pyrethroids in the sediments, and concentrations were consistently above detection levels in 5 of the 6 studies.

#### Our analytical capabilities

In our proposal we had given expected detection limits in water samples of 10-50 ng/l. To demonstrate that these values are indeed feasible, we provide Table 3 that gives data on the recovery of pyrethroids from lab water and pond water, both spiked with 50 ng/l. The pond water contained no detectable amounts of pesticides prior to the spiking procedure. Extracting one liter of water, we obtained recoveries ranged from 82 to 108% for spiked lab water and 78 to 87% for spiked pond water. Our reporting limit using pyrethroid standards (permethrin and cypermethrin reported as total isomeric mixture) is 5 ng/l, which suggests that by processing multiple liters of water and doing further sample cleanup, the signal to noise ratio will improve, the standard deviations will be lower, and we will be able to measure concentrations even below the 50 ng/l example used for determining recovery efficiency in Table 3.

In addition to the water studies, we have also extracted esfenvalerate and  $^{14}\text{C}$ -labelled permethrin from sediments. Recoveries from sediment spiked with 5  $\mu\text{g}/\text{kg}$  of compound were  $118 \pm 15\%$  ( $n=5$ ) for esfenvalerate and  $100 \pm 3\%$  for  $^{14}\text{C}$ -labelled permethrin (sediment contained 2.1% organic carbon). The reporting limit for these compounds from sediment is 5  $\mu\text{g}/\text{kg}$  (esfenvalerate) and 0.5  $\mu\text{g}/\text{kg}$  ( $^{14}\text{C}$ -labelled permethrin) using 2-5 g of sediment. As we noted above, reported toxic concentrations of pyrethroids in sediment commonly exceed 1000  $\mu\text{g}/\text{kg}$ , more than two orders-of-magnitude above the levels we can quantify. Using HPLC-UV, we were also able to separate parent  $^{14}\text{C}$ -labelled permethrin from polar metabolites spiked into sediment.

Finally, we have extracted esfenvalerate from earthworm tissues (1-2 g ww of worm) and found recoveries of  $105 \pm 13\%$  ( $n = 5$ ). The worms (*Eisenia foetida*) had a lipid content of  $10.4 \pm 1.8\%$  and were spiked with 0.16 – 5.6  $\mu\text{g}/\text{g}$  dw of esfenvalerate.

Overall, the reporting limits and % recovery data from water, sediment and tissues are adequate at this time to conduct the proposed research.

Table 3. Percent recoveries (mean  $\pm$  SD) for permethrin, cypermethrin, bifenthrin, and esfenvalerate from 1L of spiked (50 ng/l) laboratory and pond water.

Compound	% recovery lab water	n	% recovery pond water	n
Permethrin	$99 \pm 14$	4	$78 \pm 24$	4
Cypermethrin	$92 \pm 6$	4	$86 \pm 15$	4
Bifenthrin	$82 \pm 11$	4	$86 \pm 21$	4
Esfenvalerate	$108 \pm 9$	4	$87 \pm 5$	4

### Views of independent authorities on our analytical needs and capabilities

Our proposal was not recommended for funding because of the erroneous assumption that we need to quantify pyrethroids at extremely low levels that are unattainable with current technology. We have provided information to show this assumption is false. However, to provide the Selection Panel even more evidence, we have consulted with 4 individuals who have extensive experience in the environmental chemistry and toxicology of pyrethroid pesticides. These individuals include some of the most published authorities on pyrethroids. We provided them copies of our proposal, the reviews, and this letter, and asked their views on analytical feasibility of our proposed research, the issue that was the Technical Panel's grounds for rejection. The individuals whom we contacted are listed below and the letters they provided are attached. In reviewing these letters you will see that all these authorities on pyrethroid chemistry or toxicology found the Technical Panel's concern to be groundless and our research objectives achievable.

Dr. Kyle Hoagland – Professor of Limnology at the University of Nebraska. His research focuses on aquatic ecology. He has published over 50 papers and book chapters, with 13 papers and book chapters on ecotoxicology, and 4 papers specifically addressing the effects of pyrethroid insecticides on aquatic ecosystems. Dr. Hoagland is currently Director of the Water Center at the University of Nebraska and Acting Director of the School of Natural Resource Sciences.

Dr. Todd Anderson – Associate professor in the Department of Environmental Toxicology and The Institute of Environmental and Human Health (TIEHH) at Texas Tech University. He is an analytical chemist whose research focuses on the movement of organic chemical contaminants in the environment in order to evaluate and better characterize potential exposure of organisms to contaminants.

Dr. Blair Siegfried – Professor of Entomology at the University of Nebraska. A component of his research focuses on physiological/biochemical basis of selective pesticide toxicity among aquatic organisms, and he has published 5 papers specifically on differential uptake and metabolism of pyrethroid insecticides in aquatic insects.

Dr. Thomas LaPoint - Professor in Biological Sciences and Director of the Institute of Applied Sciences at the University of North Texas, Denton. His expertise is in aquatic ecotoxicology, with particular emphasis in the fate, distribution and effects of pesticides and metals in experimental ecosystems. He has published 30 papers and several book chapters, including several papers specifically on pyrethroid toxicology.

### Summary

All of the external reviewers recommended funding in whole or in part. As a result of the analytical misunderstandings, we feel that the Technical Panel ignored overwhelmingly positive comments from all of the reviewers and overreacted by rejecting the proposal in its entirety. It is true that neither we nor anyone else can measure pyrethroids in water at levels necessary to protect the most sensitive species from chronic, and for a very few species, acute toxicity. However, all pyrethroid research should not be halted until these analytical capabilities exist,



particularly when our existing capabilities allow us to measure concentrations low enough to protect the vast majority of aquatic species. Pyrethroid use has increased rapidly in the ERP geographic area in the past 5-10 years. The agricultural industry and residential users are not waiting for development of ultra-sensitive analytical techniques. Research like ours that is analytically feasible needs to proceed, so that the research community does not fall even further behind in addressing environmental issues associated with the rapidly increasing use of pyrethroids.

Contrary to the Technical Panel's assertions, we can measure pyrethroids at environmentally relevant levels. We proposed to use the analytical techniques that many other investigators have already used successfully. We agree that further development of pyrethroid analytical chemistry is needed, but the current state of the science is adequate for the research we proposed. By focusing on sediment and tissue analyses, utilizing radiolabelled compounds, and taking water samples only in areas where the potential for pyrethroid presence is greatest, we believe that the project we have proposed will make substantial contributions to environmental science and CALFED's ecosystem restoration needs.

While this letter has focused on analytical issues associated with pyrethroids, the Selection Panel should not lose sight of the fact that our proposal is fundamentally for toxicological studies. The Technical Panel's sole concern related to analytical capabilities; they had no substantive problems with the ecotoxicological studies that are the core of the research (e.g., bioavailability, bioaccumulation, toxicity to invertebrates and fish). Pyrethroid use is rapidly growing in the ERP region, but there is little toxicological information that can be used to evaluate and manage environmental risks, and there is virtually no information specific to the ERP region. We proposed a study that will provide much needed information which we can obtain using existing analytical technologies that are adequate for the project's needs. CALFED is funding no other toxicological work on pyrethroids, and without the data generated by our proposed studies environmental management and restoration decisions will continue to be made with little or no information on the environmental effects of these compounds. We have clearly shown that the Technical Panel was in error with respect to the reason they gave for their decision not to forward our proposal to the Selection Panel for consideration. Given the critical need for the data that we have demonstrated we can provide, we request that the Selection Panel allow the work to proceed.

Sincerely,



Donald P. Weston  
Adj. Assoc. Professor  
UC Berkeley



Michael J. Lydy  
Assoc. Professor  
Southern Illinois University

# UNIVERSITY *of* NORTH TEXAS

*Department of Biological Sciences  
Environmental Science Program  
Institute of Applied Sciences*

May 1, 2002

Selection Panel, Ecosystem Restoration Program  
C/o Mr. Dan Ray  
CALFED Bay/Delta Program  
1416 9<sup>th</sup> Street, Ste 630  
Sacramento, CA 95814

Dear Mr. Ray.

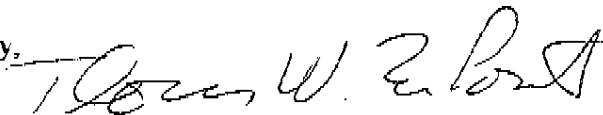
Drs. Mike Lydy and Don Weston have asked me to respond to you concerning two aspects of the proposal (No 188) they had submitted to CALFED to determine the fate and effects of particulate-sorbed pyrethroids. One aspect concerns the analytical procedures to measure environmental concentrations of effect and, secondarily, if the analytical capabilities in Dr. Lydy's laboratory are sufficient to measure environmentally-realistic concentrations. The second aspect concerns the need for ecological risk assessment of pyrethroids, linking laboratory measures of toxicity to responses of aquatic organisms in the field.

There should be no question but that the detection limits of circa 5 ng/L with standards, and 10 - 50 ng/L in environmental samples, are sufficient to measure the potential for uptake and bioaccumulation, and to look for *in-situ* toxic effects. I have no doubt that the quantitation level necessary for the pyrethroids of interest will be achieved by Dr. Lydy and crew. Further, the need for understanding the pyrethroid-sediment interactions and linkages with dietary uptake is critical. This research will aid substantially in understanding the cumulative effects of multiple pesticides

The second aspect concerns the need for this type of study (as proposed by Lydy and Weston). Without understanding the role multiple pesticides have, along with the nature of outdoor systems (with suspended and deposited sediments, the organic materials, etc), we cannot fully understand the bioavailability of pesticide residues in aquatic ecosystems.

Based on my experience with pesticide fate and effects (pyrethroids in particular), I do not think the grounds the Technical Panel gave for rejecting the proposal are scientifically valid. Hence, my full support goes for this proposal and I hope you will re-evaluate this proposal and consider it for full funding.

Sincerely,



Thomas W. La Point, Ph.D.  
Professor & Director

# UNIVERSITY of NORTH TEXAS

Department of Biological Sciences  
Environmental Science Program  
Institute of Applied Sciences

April 30, 2002

Selection Panel, Ecosystem Restoration Program  
C/o Mr. Dan Ray  
CALFED Bay/Delta Program  
1416 9<sup>th</sup> Street, Ste 630  
Sacramento, CA 95814

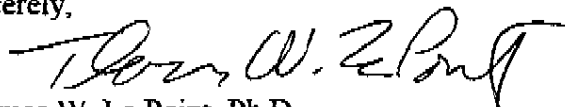
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Sincerely,



Thomas W. La Point, Ph.D.  
Professor & Director



School of Natural Resource Sciences  
Administrative Office  
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1 May 2002

Selection Panel, Ecosystem Restoration Program  
c/o Mr. Dan Ray  
CALFED Bay/Delta Program  
1416 9<sup>th</sup> St., Suite 630  
Sacramento, CA 95814

Dear Mr. Ray:

I am writing to address a methodological concern raised regarding the proposal, "Water quality effects of pesticides used in orchard agriculture - Part 2: Aquatic fate and effects of particle-sorbed pyrethroids" (proposal 188, University of California, Berkeley), specifically whether the principal investigators' analytical techniques are adequate for the work proposed. In other words, is the analytical approach proposed in this study sufficient for environmental sampling of pyrethroid insecticides. The specific concern is that, "the trace analysis proposed is very risky, has not been successfully demonstrated, and in my view will likely be inadequate."

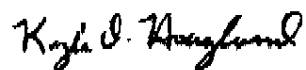
Let me begin by stating that the general and specific concerns raised by the reviewer and echoed by the Panel are not supported by studies already published in the primary ecotoxicological literature. Research conducted in my laboratory on several pyrethroid insecticides (including permethrin and four other second generation pyrethroids) to examine their effects in both single species (on aquatic invertebrates) and in community-level bioassays (including phytoplankton, zooplankton, fish, and water pumped directly from a nearby pond) included detailed analyses of pyrethroid concentrations. All analyses were conducted using hexane extracts and a GC with an ECD (detection limit of 5 ng/L; recovery rates of  $80 \pm 15\%$ ). For our community-level studies (Hoagland et al., 1993. *Environ. Toxicol. Chem.* 12:627-637; Drenner et al., 1993. *Environ. Toxicol. Chem.* 12:1297-1306), we added bifenthrin to trays of soil which were dried in the sun for three days, rewetted, and introduced into outdoor mesocosms (2.2 m high, 1.8 m diameter, with constant circulation) to simulate a turbid runoff event. Mesocosms were sampled at 1, 8, 24, 48, 72, 96 and 168 hours after addition, resulting in a rapid decay curve of bifenthrin in the water column as the insecticide settled out sorbed to the heavier sediment particles. Clearly, we were able to track this sediment-bound pyrethroid without any difficulty in a typical environmental setting with all of its inherent potential interferences.

The results of these studies also demonstrated that the rates of recovery and limits of detection (see above) were well below the effective or lethal concentrations for even some of the most sensitive organisms in aquatic ecosystems (e.g., the invertebrate *Ceriodaphnia dubia*; Moky and Hoagland, 1990. *Environ. Toxicol. Chem.* 9:1045-1051), consequently demonstrated analytical methods which are very similar to those proposed are adequate to address environmental levels of these insecticides to assess their realistic ecological impacts.

Mr. Dan Ray cont'  
pg 2

In brief, although thoughtful and reasonable concerns were raised regarding the methods proposed in this important research, the PIs are correct in asserting that these concerns are unwarranted. Therefore, this research should not be denied funding on these grounds, on the contrary, their proposal is compelling, well justified, and certainly should be funded. Thank you for your consideration

Sincerely,



Kyle D. Hoagland, Acting Director  
School of Natural Resource Sciences  
and  
Director, UNI Water Center

## TEXAS TECH UNIVERSITY

## TEXAS TECH UNIVERSITY HEALTH SCIENCES CENTER

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May 2, 2002

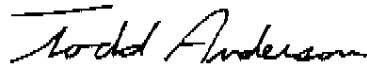
Selection Panel, Ecosystem Restoration Program  
c/o Mr. Dan Ray  
CALFED Bay/Delta Program  
1416 9th Street, Suite 630  
Sacramento, CA 95814

Dear Selection Panel

Drs. Mike Lydy and Donald Weston have asked to me to provide an evaluation of their proposed research with pyrethroid insecticides that was submitted to CALFED, reviewed, and subsequently not recommended for funding due to analytical concerns. It is my professional opinion that the Technical Review Panel is mistaken with regards to the feasibility of measuring pyrethroids at low levels in environmental matrices. GC/ECD will provide superior detection in environmental matrices compared to MS. As is pointed out by Drs. Lydy and Weston, various researchers have measured pyrethroids at ppt levels in the sample matrices and with the analytical techniques being proposed. Dr. Lydy has produced preliminary data supporting the proposed efforts/methods and the ability to detect ppt levels of pyrethroids. In addition, radiotracer studies in the laboratory are an ideal way (perhaps the only way) for addressing metabolites. I would conclude that the analytical portion of the proposed studies is on very solid ground and overall, the work is deserving of support.

While it may be true that all of these details (recent literature, methods, preliminary analytical data) were not included in the original proposal, the investigators have sufficiently addressed the concerns of the Technical Review Panel. Given the excellent reviews of the original proposal, I can see no logical reason to reject this critical environmental work.

Sincerely,



Todd A. Anderson, Ph.D.  
Associate Professor of Environmental Toxicology



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May 1, 2002

Selection Panel, Ecosystem Restoration Program  
c/o Mr. Dan Ray  
CALFED Bay/Delta Program  
1416 9<sup>th</sup> St. Suite 630  
Sacramento, CA 95814

Dear Selection Panel:

I am writing to express my views regarding the feasibility of analytical techniques described in CALFED proposal entitled "Water quality Effects of Pesticides used in Orchard Agriculture—Part 2: Aquatic Fate and Effects of Particle-sorbed Pyrethroids" (PI Weston). I believe that the proposal addresses important issues related to the potential ecological toxicity of this class of insecticides and assembles a unique group of scientists to examine this complex issue. I have read the proposal and disagree on a number of levels with the decision not to fund the project on the basis of inadequate analytical methodologies for detection of pyrethroid residues.

The main objection I have with this decision is in regard to the relatively insignificant role that analytical techniques play relative to the ecotoxicological focus of this project. Of the five different tasks outlined in the approach section, only the first seems to be somewhat dependent on analytical detection of pyrethroid concentrations at concentration <10 ng/L. Even if the analytical techniques proposed were completely inappropriate, the vast majority of the objectives of the proposed research would be unaffected. Even so, I consider the approaches the investigators proposed to analyze pesticide residues to be appropriate, and consistent with the approaches other investigators have successfully employed in studying the environmental fate of pyrethroids. The combination of in vivo techniques and focus on quantification of sediment residues which are likely to be much higher, enhances the likelihood of accurate and precise detection.

I believe that the agricultural use of pyrethroid insecticides represents a potentially significant threat to aquatic ecosystems, and the proposed research is an important step in attempting to quantify the risks associated with these compounds. Pyrethroids are exceptionally active against a wide range of insect pests yet are relatively safe to vertebrates. Perhaps the biggest hindrance to a wider role of pyrethroids in agriculture is their extreme toxicity to aquatic organisms. Understanding the potential for ecological effects from these compounds will undoubtedly result in a more rational approach to regulating the use of these compounds, and I believe the proposed research represents an important step toward such understanding.

Please contact me if you have questions regarding my comments.

Sincerely,

A handwritten signature in black ink that reads "Blair Siegfried".

Blair Siegfried  
Professor

# UNIVERSITY *of* NORTH TEXAS

*Department of Biological Sciences  
Environmental Science Program  
Institute of Applied Sciences*

May 1, 2002

Selection Panel, Ecosystem Restoration Program  
C/o Mr. Dan Ray  
CALFED Bay/Delta Program  
1416 9<sup>th</sup> Street, Ste 630  
Sacramento, CA 95814

Dear Mr. Ray:

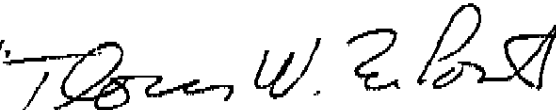
Drs. Mike Lydy and Don Weston have asked me to respond to you concerning two aspects of the proposal (No. 188) they had submitted to CALFED to determine the fate and effects of particulate-sorbed pyrethroids. One aspect concerns the analytical procedures to measure environmental concentrations of effect and, secondarily, if the analytical capabilities in Dr. Lydy's laboratory are sufficient to measure environmentally-realistic concentrations. The second aspect concerns the need for ecological risk assessment of pyrethroids, linking laboratory measures of toxicity to responses of aquatic organisms in the field.

There should be no question but that the detection limits of circa 5 ng/L with standards, and 10 – 50 ng/L in environmental samples, are sufficient to measure the potential for uptake and bioaccumulation, and to look for *in-situ* toxic effects. I have no doubt that the quantitation level necessary for the pyrethroids of interest will be achieved by Dr. Lydy and crew. Further, the need for understanding the pyrethroid-sediment interactions and linkages with dietary uptake is critical. This research will aid substantially in understanding the cumulative effects of multiple pesticides.

The second aspect concerns the need for this type of study (as proposed by Lydy and Weston). Without understanding the role multiple pesticides have, along with the nature of outdoor systems (with suspended and deposited sediments, the organic materials, etc), we cannot fully understand the bioavailability of pesticide residues in aquatic ecosystems.

Based on my experience with pesticide fate and effects (pyrethroids in particular), I do not think the grounds the Technical Panel gave for rejecting the proposal are scientifically valid. Hence, my full support goes for this proposal and I hope you will re-evaluate this proposal and consider it for full funding.

Sincerely,



Thomas W. LaPoint, Ph.D.  
Professor & Director