W-45 Technical Meeting Minutes

Riverside, California, USDA-ARS, Salinity Laboratory, June 9-11, 2002

Attendance: Kevin Armbrust, Steve Aust, J. Gan, Cathleen Hapeman, Jeff Jenkins, Robert Krieger, Linda Lee, Ann Lemley, Qing Li, Glenn Miller, Sharon Papiernik, Ron Pardini, Chris Pritsos, Josef Seifert, Tracy Sterling, Barry Wilson.

Guests: Staci Simonich

Welcome and introduction: Pritsos welcomed the group, and thanked Sharon for hosting the meeting.

Administrative Advisor, Ron Pardini, spoke about new resources for research such as the farm bill and homeland security issues. USDA has the homeland security grants available for food security work. Each State is supposed to have facilities for security.

Pardini talked about the Impact Report. The Western group has the report as "Best of the West". He encouraged having a collective impact report from this committee. The group discussed the support from the w-45 allocation in different States. Each representative shares the arrangement of grant uses in their institute.

The websites are:

National Impacts: www.reeusda.gov/success/impact.htm
Best of the West Impacts: www.ag.unr.edu/wri
W45 Web page: www.ag.unr.edu/w45
Western Regional page: www.colostate.edu/orgs/waaesd
Natl. Information Management System – web based reporting for multi-state research projects: www.lgu.umd.edu/login.cfm

Jenkins updated the joint meeting with W-82. We need to have a clear goal to have a joint meeting with W-82. The group discussed the issues for discussion when we meet with W-82. Many objectives of W-45 and W-82 are overlapped. The meeting can help to clarify the objectives of the two projects. Pardini suggested having a liaison(s) to meet. The date (January) is a problem for some members, conflicting with teaching. Jenkins will contact with W-82 and inform W-82 that arranging a formal meeting with W-82 cannot work out at this time due to many conflicts. The group will select several liaisons from W-45 to attend W-82 meeting to present W-45 projects which are interests to W-82. This will be stated in the minutes. This is approved by consensus.

Report review and critique:

The group presented and critiqued technical reports as per usual.

Simonich gave a nice presentation of her past, current and future research.

Old and new business:

New members:

The group had a brief discussion and unanimously approved Staci Simonich's (OR) request to join W-45. The group welcomed Staci as a new member.

Collaborations:

A discussion regarding ongoing and potential collaborations between W45 members was initiated at the suggestion of Ron Pardini. It was suggested that we go around the table and very briefly discuss ongoing and potential collaborations within the group. These included:

Kreiger (Riverside, CA): Potential interactions with Simonich (OR) on his interactions with Proctor and Gamble (Mr. Fit project). Also potential interactions with member on his various Turf projects particularly as they relate to runoff issues.

Simonich (OR): Potential interactions with Jenkins (OR) on his Hood River projects and Miller (NV) on gas phase hydroxyl radical generation.

Jenkins (OR): Ongoing interactions with Wilson (Davis, CA) on cholinesterase activity in steelhead.

Wilson (Davis, CA): Ongoing interactions with Seifert (HI) looking at delayed neuropathy from pesticide exposure. Potential interactions with Kreiger (Riverside, CA) on Turf studies.

Seifert (HI): Ongoing interactions with Wilson (Davis, CA) as previously mentioned.

Lemley (NY): Potential interaction with Kreiger (Riverside, CA) to disseminate Mr. Fit information throughout the Northeast. Potential interactions with Jenkins (OR).

Papiernik (USDA-ARS, Riverside, CA): Ongoing work with Hapeman (USDA-ARS, Beltsville, MD) on transport of agricultural pollutants.

Hapeman (USDA-ARS, Beltsville, MD): Ongoing work with Papiernik (USDA-ARS, Riverside, CA) as previously mentioned and potential interactions with Armbrust on pesticide fate and runoff.

Aust (UT): Potential interactions with several W45 members in using his wood chip filler technology to control pesticide runoff. Other potential interactions with Li (HI) on his bioremediation project.

Gan (Riverside, CA): Potential interactions with Aust (UT) and Armbrust (MS) on runoff projects and pyrethoids with Kreiger (Riverside, CA).

Armbrust (MS): Potential interactions with Sterling (NM) on weed science issues dealing with the efficacy and environmental fate of agrochemicals for weed control. Potential interaction with Hapeman (USDA-ARS, Beltsville, MD) on pesticide fate in seawater.

Sterling (NM): Potential interaction with Li (HI) on the development of high affinity binding assay for picloram.

Pritsos (NV): Ongoing interactions with Wilson (Davis, CA) on developing pigeon model for migratory bird exposure to agrochemicals and with Miller (NV) on assays for determination of oxidative stress in biological samples.

Other ongoing interactions include the participation of Gan, Aust, Hapeman, Papiernik and Lemley in an upcoming ACS Div. of Environmental Chemistry Symposium.

It was discussed and agreed that collaborations between Aust and other W45ers interested in pesticide runoff issues should be a priority for the group.

Collective impact report:

It was agreed that each individual should formulate a brief impact statement for inclusion in the annual report and E-mail it to Chris Pritsos and Qing Li.

Extension: Extension is represented in the group through Kreiger, Jenkins, Lemley and Gan.

Next meeting:

Potential sites for next year's meeting were discussed. It was suggested that with the Pan Pacific Conference on Pesticide Science being scheduled for June 1-4 in Honolulu, HI that it might be a good idea to piggyback the W-45 meeting with this conference. Some discussion regarding the potential long distance travel for East Coast members was discussed however it was decided to go forward with trying to set up the meeting in HI either immediately before or after the Pan Pacific Conference. Should this not be possible, it was agreed upon that Reno, NV could serve as a back-up site.

Pritsos gave a final note of thanks to Sharon Papiernik for hosting a wonderful dinner for the group the night before and to Sharon Papiernik and Bob Kreiger for hosting the meeting.

The meeting was adjourned at 11:45 AM, June 12, 2002.

Respectfully submitted,

Qing X. Li
W-45 Secretary

Subcommittee Assignments and Reviews

Each subcommittee will review their assigned projects on Sunday evening. The underlined person is responsible for leading the discussion on Sunday and for writing and presenting the subcommittee's project review on Monday. On Monday, each project leader will be allotted 5 minutes for a verbal introduction of the research being reported, the review subcommittee will be allotted 15 minutes for questions and critique. Ten minutes will then be allotted for open discussion and questions about each project. Please be sure to provide you written review on disk to Qing Li before you depart.

As previously discussed, the Reports and Reviews should reflect a high regard for Clarity, Scientific Merit/Quality and Collaboration with other W-45 members. The summary of principle accomplishments must be understandable to the lay community and useful to administrators and policy makers.

Group	Reviewers	Reports to Review
A	Pritsos, Papiernik, Li, Simonich	Sterling, Aust, Lee
B	Seifert, Lemley, Miller, Sterling	Pritsos, Gan, Papiernik, Wilson
C	Jenkins, Hapeman, Gan, Armbrust	Lemley, Li, Krieger, Seifert
D	Aust, Krieger, Wilson, Pardini	Hapeman, Armbrust, Jenkins

Please Note: First person listed as reviewer is responsible for first report to be reviewed by review team, second person listed as reviewer is responsible for second report to be reviewed and so on.

Project Review and Critique:

State: Maryland - USDA/ARS-Beltsville
Project Leader: C.J. Hapeman
Reviewer Team: Aust, Krieger, Wilson and Pardini

The project is a continuation of studies on methods to reduce runoff, soil loss, pesticide load and toxicity from vegetable cultivation practices utilizing plastic mulch. Vegetative buffer strips of cereal rye between rows of plastic mulch were investigated. Cereal rye was chosen as it establishes quickly, withstands traffic, and dies off in summer heat, before it competes with the crop for moisture. Vegetable producers prefer plastic mulch even though it results in higher runoff with pesticide loads that are 3 to 25 times greater than with a vegetative mulch. Soil erosion with associated copper hydroxide, suspected to be toxic to the ecosystem, is 2 times greater with no vegetative buffer zone.

In this study, metribuzin, esfenvalerate, endosulfan, chlorothalonil and copper, at 42, 3, 56, 190 and 129 mg/m2, respectively, were applied. Trickle irrigation, containing urea, was used during dry conditions. Runoff resulting from rain was monitored every 5 minutes as flow rate and total flow. Runoff from bare soil between tomato rows was 2-10 fold that from cereal rye furrows. Soil loss was nearly 10X higher. Total load loss for particulate phase copper was 2-4 times greater. Dissolved copper load was 2-10 times that of the particulate phase. Runoff data were extremely variable, due to rain events. Some rain events seem drastic as almost 2 tons of soil were lost per hectare due to two rain events, only 6 days apart. Soil loss was 10 fold less for the cereal rye cover. Copper load was much less with the cereal rye cover but not significantly when runoff was extreme. The concentration of copper in the runoff was thus much higher in runoff from the rye cover when runoff was high.

Comments: Unfortunately no statistics were provided, and some results were difficult to analyze, such as toxicity to newly hatched grass shrimp larvae. But the report contained very extensive vegetable production data. Better production was observed on some days but not others but totals were identical. The toxicity data don't lend themselves very well to analysis. The data are variable and confusing as toxicity decreases and then increases with increasing dilution. But the conclusion was that toxicity was less for runoff from cereal rye buffers. This is difficult to see and no statistical analyses were provided.

A review of the literature on the effect of vegetative buffer zones would be helpful as these have been studied rather extensively. A statement as to the need for further research on this subject as applicable to vegetable growers that use plastic mulch would help demonstrate the need or significance of the research. The figure legends were sometimes incomplete or otherwise difficult to analyze. The species used in toxicity studies needs to be included in the abstract. The work planned for next year seems very appropriate because significant runoff into estuaries seems very evident. Otherwise the report reflects excellent work on a significant potential problem for which a practical and effective solution is suggested.

State: Oregon
Project Leader: J. Jenkins
Reviewer Team: Wilson, Aust, Krieger and Pardini

Summary: Methods of sampling, storage and analysis of runoff from agricultrual spraying of Guthion (azinphos-methyl) are reported presumably as a preclude to studies of the toxicity of the residues to wild salmonid populations.

Clarity: The report is claearly and simply written. One criticism is that the lengthy discussion of methodology and its improvement is not accompanied by data demonstrating their statements. The data presented are probably sub-toxic levels found in the field tests.

Scientific Merit: The project is of high quality and seems of high quality, even in the absence of data germane to the methodology development.

Collaborations: Although many collaborators are mentioned, work with members of W45 are not.

Laymans Summary: The summary (III) is more of a background presentation, the results of the study and their significance are not presented.

Useful Findings for Administrators: The improvement in analytical techniques, replacing non-detects with numerical values and variances, will be of important to risk assessment of runoff and realistic setting of pesticide residue levels.

A cautionary note: Underlying this study (and others too) is the idea that pesticide runoff levels contribute to the decline in numbers of fish, in this case salmonids. But, the pesticide levels presented in the report are low, perhaps too low to adversely affect the fish. Other possibilities to keep in mind are that there may be high levels of the pesticide in streams where reproduction occurs and the fish hatch, there may be chronic accumulated effects of the pesticide, or that more than one agent may be involved.

State: California - USDA/ARS-Riverside
Project Leader: Sharon Papiernik
Reviewer Team: Miller (Primary), Lemley, Sterling and Seifert

The USDA Riverside project was well written, technically well done and, most important, interesting and useful. The review committee was particularly impressed with the productivity of the P.I. in terms of publications on a variety of areas important to W-45 members. We suggest a small formatting change for the report - use page numbers.

Specific comments:

1. The committee noted the substantial differences in the chemical profiles between the radish and soil concentrations. This suggests that residual soil on the radishes was *not* the source of the observed con concentrations of DDT residues.
2. The substantial profile differences between soil and radish is particularly prevalent for DDT - it is present in soils as the predominant contaminant, although in radishes, it is almost non-existent. This suggests that either DDT is either largely unavailable to be taken up by the radish, or is efficiently metabolized by radish.
3. A table of octanol water partition coefficients and water solubilities would have been useful.
4. A discussion of how these results compared with previous studies on uptake would have been helpful.
5. The committee recognizes the difficulty in providing all of the specific concentrations of all of the chemicals, although we also felt that summing of the DDT residues can leave out very important information on which compounds are preferentially taken up.

Overall, this was a very useful piece of research and the committee commends the USDA Riverside group for the report.

State: California – UC Davis
Project Leader: B. Wilson
Reviewer Team: A. Lemley (Primary), G. Miller, T. Sterling, J. Seifert

The Davis Project is to be commended for a very thorough comparison of methods for ACHE determination. There were a few questions we would like to be clarified. When using the Sigma products for the standardization, what is left of the kit contents. How was normalization accomplished? Results showed the kits were not consistent over temperature. How were the different temperatures achieved. How could the kits be improved? What is the future of ACHE testing and the application of this product?

State: California – UC Riverside
Project Leader: J. Gan
Reviewer Team: A. Lemley (Primary), G. Miller, T. Sterling, J. Seifert

The team would like to compliment the researcher on the choice of an important topic and the development of well-designed experiments. The runoff from nurseries is an potential source of water contamination, and the study of distribution of pesticides between soil particles and water in this venue is an appropriate and useful approach.

The review team has several questions and comments to clarify the work for others.

1. It would have been very helpful to have a diagram of the sampling points. For example, on Figure 1, what is PAM1 and PAM2 and SP1 and SP2. What is the reference to PAM in the first paragraph of the Results and Discussion. What does this mean?

2. In Figure 1, there are high values of permethrin at 135 m. Is this real? Did you do statistics on these data? If it is real, how do you explain it?

3. In Table I, do you have a hypothesis as to why there is no change in the K_d values for trans permethrin?

4. Based on your results, should there be a modification of TMDLs based on sediment loading?

5. Did you have a list of publications?

State: New Mexico – NMSU
Project Leader: T.M. Sterling
Reviewer Team: Li, Papiernik, Pritsos

This report describes the experimental determination of the genetic mechanisms of the resistance to the auxinic herbicides picloram and clopyralid by yellow starthistle weed (*Centaurea solstitialis* L.). The resistant phenotype is recessive and conferred by a single nuclear gene. The review group recognized that it is important to identify the mechanisms of herbicide resistance. The information will have direct implementation value to the best management practices of herbicide application and weed control. The experimental design was clear. This is an interesting project. However, the review group has the following comments and questions.

1. Show the chemical structures of picloram and clopyralid.
2. Explain why "these data confirm that the gene conferring resistance is nuclear rather than cytoplasmic in location." (Page 4)
3. Give some background information of the susceptible and resistant seeds. How are they known pure RR and rr strains?
4. Isolation of the auxinic-herbicide binding proteins was optimized by using picloram affinity chromatography column. Then, why it cannot be consistently detected. (Page 5)

5. Are there any differences in picloram recognition (Page 5)?
6. Explain the differential expression of genes under picloram pressure. (Page 6)
7. There were very limited numbers of plants in some tests. (Table 3)

Page 2: Is the statement of "BAH is a stable product because of its extremely slow reaction rate with BIC" correct?

Table 1: Is the soil series information in Table1 available?

Figure 1: It is suggested to draw chemical structures.

Figure 4: There were not legends for the 4 figures in Figure 4.

State: Indiana – Purdue University
Project Leader: L.S. Lee
Reviewer Team: Li, Papiernik, Pritsos

This report presents degradation and formation of N,N'-dibutylurea, a conversion product from the fungicide Benomyl breakdown, in soils. The formation experiments were conducted by applying n-butyl isocyanate to soil. However, the formation of N,N'-dibutylurea from n-butyl isocyanate was not observed under the experimental conditions. Therefore, if N,N'-dibutylurea is found in soils, it is most liely from application of N,N'-dibutylurea-containing Benomyl formulation. N,N'-Dibutylurea degradation was primarily microbial and relatively fast (90% degraded in 6 weeks) The degradation was affected by a combination of at least two of the following factors: high clay content (>40%), dry condition, high pH, and high temperature.

Specific comments and questions:

Page 2: Explain the statement of "BAH is a stable product because of its extremely slow reaction rate with BIC."

Table 1: Is the soil series information in Table1 available?

Figure 1: It is suggested to draw chemical structures.

Figure 4: There were not legends for the 4 figures in Figure 4.

State: Utah – Utah State University
Project Leader: Steve Aust
Reviewer Team: Sharon Papiernik (Primary), Chris Pritsos, Qing Li

The review committee commends Dr. Aust on his excellent report, which was clear and concise. The committee particularly noted that the experiments, which had a relatively simple design, provided very important information for the understanding of the mechanism of degradation of recalcitrant organic compounds by wood-rotting fungi. The committee has several questions for clarification and further information:

1. Structures of pentachlorophenol (PCP), pentachloroanisole (PCA), and other proposed degradation products would be appreciated.
2. What is the difference between archtypical and typical organisms?

3. It is our understanding that the observed degradation of PCP (production of metabolites) does not match previously-known enzyme activities. Does the inclusion of the proposed methylation mechanism explain the observed degradation pattern?
4. What are the enzymes involved in the transformation of methylated phenols?
5. In Figure 1, you report 10% mineralization of PCP in ~1 month: Is this rate of degradation significant for environmental applications and remediation?
6. In Figure 2, the variation in measured PCA concentrations is high, and the maximum PCA occurs at 6-14 days (largest mean PCA at 10 d). This is inconsistent with your report of maximum PCA at 15 d on page 5.
7. Thus far, it appears that degradation of these compounds by wood-rotting fungi has only been measured in liquid culture. How is this proposed to be used for mycoremediation? How would you expect PCP to be degraded in soil or another matrix?
8. Any ideas as to why white- and brown-rot fungi can methylate PCP and soft-rot cannot?
9. In the work planned for next year, you say you will use differential display to identify the enzymes involved in the degradation. How will this be done? If you use differential display, why do you need to do sequencing to identify the enzymes?
10. How do you envision the engineering process to control the rate-limiting step in this transformation?

State: California – UC Riverside
Project Leader: R. Krieger
Reviewer Team: Simonich, Jenkins,Gan, Armbrust

Reported is an analysis of products for pesticide cleaning products for fruits and vegetables compared to water rinse.

Were companies approached to explain their claims and how they were substantiated? Such as claims made in P&G brochure?

Part 1: time between treatment and washing is unknown. Is there an aging effect? Water rinse procedures are unclear. Conditions simulated typical homemaker, was there much variation in consumer habits? What are the properties of the water, such as hardness and other subtle differences (such as water temperature) that may effect the extraction capability of the water?

Part 2: treatment/wash interview is known. What is a "typical consumer"?

Results and Discussion, 5th paragraph: water and Fit are not significantly different, but Fit residues were lower? This seems conflicting. What are the standard deviations of the measurements?

What are the US EPA tolerances? This would be useful in data interpretation.

Knowledge of crops used in the study would be useful for data interpretation and evaluation of the potential for extrapolation to other crops. What is the ability of different crops to "trap" pesticides – ie waxed apples and cucumbers vs. lettuce.

As a limited number of pesticides were evaluated (2), can the results be compared to the 10 compounds used in P&G study. Were Captan and Methomyl used in the P&G study? What crop does P&G base its claim on and is it the same as yours?

Is it bad if consumers feel that they are able to eat "non-organic" foods if they are "cleaned"? Is it significant that Fit removes more wax than water rinse?

State: New York – Cornell University
Project Leader: A. Lemley
Reviewer Team: Jenkins, Simonich, Gan, Armbrust, Hapeman

Reported is the contin uation of research on the feasibility of ion exchange anodic Fenton treatment (membrane AFT) for the treatment of pesticide wastewater. Reported here is further refinement of methods reported in previous W-45 reports. Method development using 2,4 D as the substrate is further validated in this report using the insecticide carbaryl. The research goal is to improve the laboratory method's applicability to use in the field.

We commend Ann on her determination to move closer a practical application of the Fenton treatment for remediation of pesticides.

We would like to see a brief discussion of model.

The purpose of HPLC and GC/MS analysis is unclear.

Should consider treatment efficiency per unit energy input, as well as Fenton reagent used.

Pg 4 second paragraph, what about the gradient?

Pg 4, third paragraph, "Because it is advisable" is unclear as a for optimal NaCl concentrations.

Degradation products, need chromatogram proportion of products. Is what is generated better than the starting material. How will it be disposed of.

How were peaks ID, spectral library, standards.

Figure 3. What curve fit used for each data set?

Carbaryl stable at acidic pH. But will

Catylase may be a better quench agent than methanol because degrades residual peroxide.

What about scale up. Competitive reactions with pesticide formulation and spray tank additives.

Have you considered collaboration with W-45 microbiologist?

State: Hawaii – University of Hawaii
Project Leader: Q. Li
Reviewer Team: Gan, Simonich, Jenkins, Armbrust

Reports on new immunoassay for imidacloprid. Do other methods exist?

The report is standalone and concise.

Need compare analysis and cost with existing HPLC and GC methods.

What is sensitivity of detection compared to existing HPLC and GC methods.

Matrix interference with coffee appears to be a significant limitation. Need to characterize magnitude of interference by statistical analysis comparing dilutions.

How does IC50 of 0.4 ppb value compare to other compounds.

Has method been applied to real (aged) samples?

Has immunoassay method sensitivity and selectivity been compared to existing (LC-MS) methods.

Barry: ACh receptors?

State: Hawaii – University of Hawaii
Project Leader: J. Seifert
Reviewer Team: Armbrust, Gan, Simonich, Jenkins

Reported is a teratogenicity study of imidacloprid using chicken embryo. The premise is solid based on data available on organophosphates. The study is also timely.

Generally the study is straightforward, however brief and lacking in detail. For example, results and discussion is only one paragraph. Comparison with OPs would be useful.

Would be interesting to test Imidacloprid degradation product 4-chloronicotinic acid this procedure.

Is there registrant data on teratogenicity in rats or mice?