COMPREHENSIVE RESEARCH ON RICE

ANNUAL REPORT

January 1, 1982 - December 31, 1982

PROJECT TITLE: The Environmental Fate of Pesticides Important to Rice Culture.

PROJECT LEADER AND PRINCIPLE UC INVESTIGATORS:

Project Leader: D. G. Crosby, Environmental Toxicology Dept., UCD.

Principal Investigators:

J. B. Bowers (Staff Research Associate)
Mark Freiberg (Student Assistant)
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Richard Higashi (Postgraduate Research Chemist).

LEVEL OF 1982 FUNDING: $24,960.

OBJECTIVES AND EXPERIMENTS CONDUCTED BY LOCATION TO ACCOMPLISH OBJECTIVES:

A. Objective I. To identify, investigate, and model environmental factors which govern movement and chemical fate of rice pesticides.

1. Biomethylation of tin compounds (UC-Davis).
2. Duter degradation in rice soil (UC-Davis).
3. Degradation of tin sulfides (UC-Davis).
4. MCPA and 2,4-D degradation (UC-Davis).
5. New methods for MCPA analysis (UC-Davis).
6. Pesticide residue confirmation (UC-Davis).
7. Pendimethalin degradation (UC-Davis).
8. Rice field microcosm design and construction (UC-Davis).
9. Molinate/Ordram volatilization in the microcosm (UC-Davis).
10. IUPAC meeting (Hakone, Japan).
11. International Congress of Pesticide Chemistry (Kyoto, Japan).

B. Objective II. To estimate the relative importance of such factors to the practical use of specific rice pesticides.

1. DuTer degradation pathways (UC-Davis).
2. MCPA degradation pathways (UC-Davis).

C. Objective III. To apply research results toward meeting regulatory requirements and improved management of rice pesticides.

1. Thiobencarb degradation in drinking water (UC-Davis; Sacramento).

2. Accumulation and retrieval of rice-pesticide information (UC-Davis).

3. Relations with CDFA and SWRCB (UC-Davis; Sacramento) .

SUMMARY OF 1982 RESEARCH (MAJOR ACCOMPLISHMENTS BY OBJECTIVE)

A. Objective I.

1. <u>Duter (triphenyltin hydroxide, TPTH)</u>. We reported previously on the photochemical breakdown of TPTH in water. However, the formulated Duter sinks soon after application, and so its possible breakdown in rice field sediment becomes important. A number of other types of organometallic compounds now are recognized to be biomethylated in flooded soil. Our preliminary results were mentioned in our 1981 report.

Rice field mud slurries (UCD) were supplemented with sucrose and bactopeptone to promote microbial growth; TPTH in ethanol was added to provide levels of 7 to 7,000 μg/L (ppb). The sealed bottles were incubated, samples were removed at intervals and extracted with hexane, and the hexane extracts were analyzed by gas chromatography using a flame-photometric detector equipped with a tin-specific filter. Alternatively, samples were cleaned up by steam distillation before extraction. Microbially-rich primary sewage sludge, often used in experiments with other metals, was treated in the same way.

In no instance was the expected triphenylmethyltin detected, although major interferences sometimes made interpretation difficult. At best, biomethylation was not a major pathway, although the presence of other volatile organotin products is not precluded by the chromatograms. However, when rice field soil or sewage sludge were treated with trimethyltin hydroxide instead of TPTH, a methylated product--tetramethyltin--was detectable in the headspace above the slurry, indicating that the methylating organisms were available and active, and the amount increased with time (Fig. 1). Untreated controls were negative, but sterilized controls still generated a low level of tetramethyltin.

While the headspace above the TPTH-treated samples did not contain triphenylmethyltin, benzene was detectable, increased with time, and was not present in untreated controls (Table I). Although yields were low, they were consistent with CO_2 evolution from ^{14}C-TPTH reported in the literature. In this case, too, sterilized controls provided TPTH degradation (to benzene), suggesting that breakdown is largely nonbiological; benzene also was produced from TPTH at room temperature by baked soil, vermiculite, and even distilled water, while untreated controls produced none.

Table I. Formation of Benzene from TPTH in Sediment.[a]

TPTH (mg)	Benzene (ng/mL)	Total Benzene (μg)	Yield (%)
0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0
0.1	1.4	1.2	2.0
0.1	1.4	1.2	2.0
0.5	4.0	3.4	1.0
0.5	6.6	5.6	1.8
1.0	9.4	8	1.3
1.0	10.6	9	1.4
5.0	42	36	1.1
5.0	50	43	1.4

[a] Recovery from headspace after 7 days.

Mercuric sulfide has been reported to be converted to methylmercury derivatives by light in the presence of methyl donors such as acetic acid. However, attempts to observe a similar conversion of bis(triphenyltin) sulfide to triphenylmethyltin were unsuccessful.

2. MCPA. Our 1981 Report provided evidence for the environmental degradation of MCPA to a series of unstable products including 5-chlorosalicylaldehyde (VI). This year's work has expanded and confirmed those findings (Fig. 2). In sunlight, the aldehyde was converted rapidly in aqueous solution to 5-chlorosalicylic acid (VII) and gentisic aldehyde (VIII), as shown by high-pressure liquid chromatographic and gas chromatographic analysis. These products then were further degraded in sequence to IX, X, XI, and XII; XII was very unstable environmentally and decomposed with a half-life of only a few minutes to a mixture of fatty acid fragments.

Our previous report also mentioned the formation of 4-chloro-2-methylanisole (III). Continued work this year confirmed the rapid volatilization of III and its stability in both aqueous solution and the atmosphere. Repeated attempts to locate a source of ^{14}C-MCPA in the US, Germany, England, and Japan were unsuccessful, but we found that the close MCPA relative, 2,4-D, also generated the corresponding 2,4-dichloroanisole in sunlight, although in low yield (Table II). When ^{14}C-2,4-D labelled in the sidechain CH_2 (* on Fig. 2) was irradiated and the products collected and subjected to radio-chromatography, the radioactivity appeared to remain with the resulting dichloroanisole; we conclude that the anisoles are formed by loss of CO_2 from the parent herbicide, and therefore, their environmental generation is limited but inevitable.

Table II. Formation of 2,4-Dichloroanisole from 2,4-D.

Days	% 2,4-D Remaining	Anisole Yield (%)
0	100	0
1	67	0.01
2	45	0.06
3	40	0.08
6	37	0.06

It is our experience that the most satisfactory method of MCPA analysis presently is by gas chromatography of its methyl ester with a microcoulometric (Cl-specific) detector. However, this method is not particularly sensitive, and the detector is rather unusual and expensive. Repeated attempts were made to generate a simple gas-chromatographable derivative which could be measured by the common electron-capture detector, in particular the cyclic derivative 5-chloro-7-methylbenzofuran-3-one, but they so far are unsuccessful. Residues of molinate can be confirmed by strong-acid hydrolysis to hexamethylenimine and formation of a characteristic electron-capturing product with 4-chloro-3-nitrobenzotifluoride, and the characteristic mass spectra of MCPA, molinate, and thiobencarb have been measured and cataloged.

3. Pendimethalin. Dr. Bayer proposed to investigate the utility of pendimethalin [N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitroaniline, Prowl[R]] as a rice herbicide. In order to get an early estimate of pendimethalin's persistence in the rice field environment, a few preliminary sunlight irradiation experiments were carried out in water, organic carrier (hexane), and on a solid surface (glass). Gas chromatographic analysis indicates very rapid breakdown in an organic solvent simulating leaf (half-life 1.5 days) and on the glass surface simulating soil (half-life 2 days), but degradation in water was slow and uncertain. A more thorough investigation is warranted if efficacy trials are continued.

4. Rice Field Microcosm. Our previously reported experiments on the environmental fate of rice pesticides has confirmed the difficulty and expense of making accurate comparisons and predictions based on field experiments and the frequent inadequacy of purely laboratory measurements. A prototype rice field microcosm has been designed and tested this year. It is based on a 20 gallon all-glass aquarium (Fig. 3) equipped with airtight cover, thermostatically-controlled heating, and measurement devices. Filtered air from an intake manifold is pulled through the headspace and vented through a system which allows for trapping of vapor. A 15 cm (6 inch) layer of water can be held at ± 0.8° C over long time periods.

As an initial test of the microcosm, technical molinate was introduced into the water (28° C) to give an initial concentration (2.43 ppm) similar to that found after a field application, and the volatilization loss was measured by sampling, extraction, and gas chromatographic analysis. The results (Fig. 4) show comparatively limited statistical error (r = 0.94) in relation to a computer-derived curve, and the half-life was 2.17 days. Next, Ordram 10G was introduced at a rate of 3.48 kg/ha 3.1 lbs/acre), which generated a peak residue in the water at 43 hrs (1.55 ppm), again quite similar to those reported from field application (typically 1.8 ppm at about 30 hrs). The dissipation curve (Fig. 5) at 28° C corresponded well to that measured with field samples and gave a half-life of 2.03 days compared to a field value of roughly 2 days (average field-water temperature 28° C).

These results, preliminary as they are, show promise of allowing us to estimate the effect of temperature, air velocity, and application rate on molinate residues quickly and with considerable precision. A quantity of rice field soil has been collected, air-dried, sieved, and homogenized in preparation for its introduction as another microcosm component, and a cover transparent to the UV portion of sunlight has been obtained for later photodegradation experiments.

5. International Pesticide Activities. Participation in the meeting of the Pesticide Chemistry Commission of the International Union of Pare and Applied Chemistry (Hakone, Japan) resulted in finalizing an extensive international survey on the environmental chemistry of organotin compounds (including DuTer). The Fifth International Congress of Pesticide Chemistry (Kyoto, Japan) included an international symposium on rice herbicides (Program listed as Appendix A) and many technical papers on rice herbicides. Several important leads, which are being followed up, include:

a. A rice field microcosm developed at Taiwan National University (Prof. S.-J. Chen). Although its purpose of measuring the distribution of pesticides among animals and plants is quite different from ours, and it suffers a number of technical problems; our own microcosm can benefit from its mistakes and successes.

b. Field difficulties with thiobencarb. The dechlorinated degradation product, formed post-application by soil microorganisms and by sunlight, has proven to be quite toxic to rice sedlings and could present an insurmountable obstacle to benthiocarb use (Prof. S. Kuwatsuka, Nagoya University).

c. Extensive toxicological experimentation with rice pesticides, especially molinate and thiobencarb, in fish (Dr. Y. Hashimoto, Tokai Regional Fisheries Research Lab). Dr. Hashimoto has supplied an extensive collection of reprints (largely in Japanese).

d. Development of 3-hydroxy-5-methylisoxazole (HMI, Tachigaren^{R}) as a rice fungicide, growth promoter, and protectant agaist herbicide toxicity in rice (Dr. Y. Ota, National Institute of Agricultural Sciences).

The manufacturer (Sankyo Co., Ltd.) has provided a sample of HMI for our evaluation and is interested in collaboration, although HMI is not registered for rice in the U.S.

B. Objective II.

1. DuTer Fate. Although biological deactivation of TPTH by methylation does not seem to occur, degradation to the reportedly inactive diphenyltin oxide starts immediately upon contact with soil and proceeds even in the absence of microbial action. One one hand, this suggests a limited environmental persistence for DuTer; on the other, it also suggests that both the period for initiation of fungicidal action and the effectiveness under field conditions (that is, in the presence of soil) must be much more limited than previous *in vitro* tests (without soil) have indicated. It raises the interesting possibility that the principal breakdown product, diphenyltin oxide, is the actual fungicide.

2. MCPA Fate. We believe that the pathway and relative rates of MCPA degradation in water and atmospheric drift are now satisfatorily established. Following aerial application to a flooded rice field, photolysis of MCPA will occur in airborne droplets as well as on the field; part of the principal degradation product--chlorocresol--will volatilize and be photolyzed as vapor to nontoxic products, while the remainder will be degraded similarly but more slowly in water. A very small proportion will be converted to the volatile and stable 4-chloro-2-methylanisole and be dispersed in the atmosphere, but at any given time, the level is too small to measure by present methods. However, the MCPA half-life in water is long enough (3 days after a peak at 5 days) that the herbicide is likely to be released from treated fields in readily-detectable concentrations.

C. Objective III.

1. Thiobencarb degradation in drinking water. Assistance has been provided to the Division of Water and Sewage, City of Sacramento, to determine the cause of off-flavor problems in drinking water. The problem presently appears to result from incomplete oxidation of thiobencarb during water-treatment. Collaboration is continuing.

2. Information on Rice Pesticides. A pilot program has been established in collaboration with Dr. M.-Y. Li, UCD Department of Environmental Toxicology with MCPA as the model. The goal is to make available to University rice researchers, Extension personnel, the rice industry, and others, the most complete, organized, and up-to-date information on rice pesticides. Development steps are as follows: a) extensive search of past literature and establishment of a card file segregated by interest categories which contains literature citations and abstracts, b) continuing addition of current references, c) establishment of a collection of the articles cited, starting at 1981 and eventually working back as well as staying current, d) summary of current articles for distribution to farm advisors by Dr. Hill, and 3) availability of the file to answer industry questions through Dr. Hill. Much of the MCPA card index now is complete, and its basic collection of articles established. Computer-searching for recent scientific articles also is available now and has been used in establishing the card file.

3. Other Activities. During the year, the Project Leader has participated as an advisor to both the Toxic Substances Branch of the State Water Resources Control Board and the Herbicide Task Force of the California Department of Food and Agriculture.

PUBICATIONS OR REPORTS:

W. M. Draper and D. G. Crosby. Sensitive enzyme-catalyzed chromogenic reagent for hydrogen peroxide and other peroxygen compounds on thin-layer chromatographic plates. J. Chromatog. **216**, 413 (1981).

D. G. Crosby. Atmospheric reactions of pesticides. Presented at the Fifth International Congress of Pesticide Chemistry, Kyoto, Japan, August 31, 1982.

D. G. Crosby. Environmental fate of herbicides used in California rice culture. Presented at the Fifth International Congress of Pesticide Chemistry, Kyoto, Japan, September 4, 1982.

D. G. Crosby. Environmental Toxicology of rice pesticides. Presented at Rice Field Day, Biggs, Calif., September 15, 1982.

CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS:

The persistence, movement, and breakdown of rice pesticides under California conditions is becoming a major public and industry issue, and accurate prediction and accounting of their residues is increasingly important to successful pesticide management. Last year's preliminary finding of DuTer's stability to microbial methylation in ricefield soil was confirmed in detail, but the soil unexpectedly was found to cause non-biological degradation (to benzene), meaning that breakdown to nontoxic products is inevitable. Work on aquatic and atmospheric degradation of MCPA is largely complete and explains the lack of detection of MCPA breakdown products in water; all but one are much less stable than MCPA to degradation and dissipate rapidly. Formation of that one--4-chloro-2-methylanisole-- has proven to be unavoidable, but the rate is insignificant and the product so far undetectable in the field.

Prediction of rice field movement and persistence of pesticides often has been difficult to extrapolate from laboratory to field. A closed glass laboratory microcosm--a "model rice field"-- is under development, initially to attempt the prediction of volatilization rates of rice herbicides under a variety of simulated field conditions. Experiments with both molinate and its granular formulation, Ordram 10G, at an average water temperature 28° C and application rate of 3.1 lbs/acre resulted in dissipation curves and half-lives (persistence) closely conforming to those measured under the same conditions in the field. This opens the way toward measuring the effect of changing these and other variables on residues in rice field and river water.

A rice-pesticide information system is under development which is designed to provide a readily-accessible file of scientific reports and articles for rice-researchers, searched directly or by means of a catalog; a current awareness ability for new scientific and regulatory information to be transmitted to the researchers and to industry via the Rice Extension Specialists; and an information resource available via local UC farm advisors. MCPA has been the trial subject, and several hundred abstracts and articles already have been accumulated.

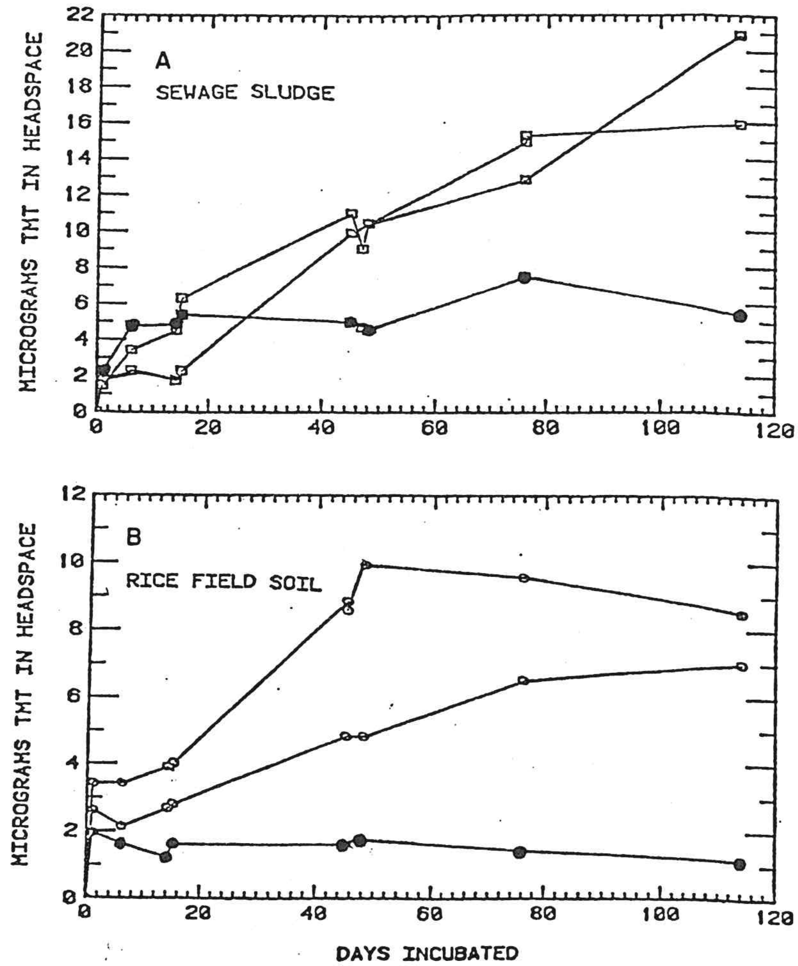

Fig. 1. Tetramethyltin formation in headspace over sewage sludge (A) and ricefield soil (B) treated with trimethyltin hydroxide (replicate curves). ● Denotes autoclaved samples.

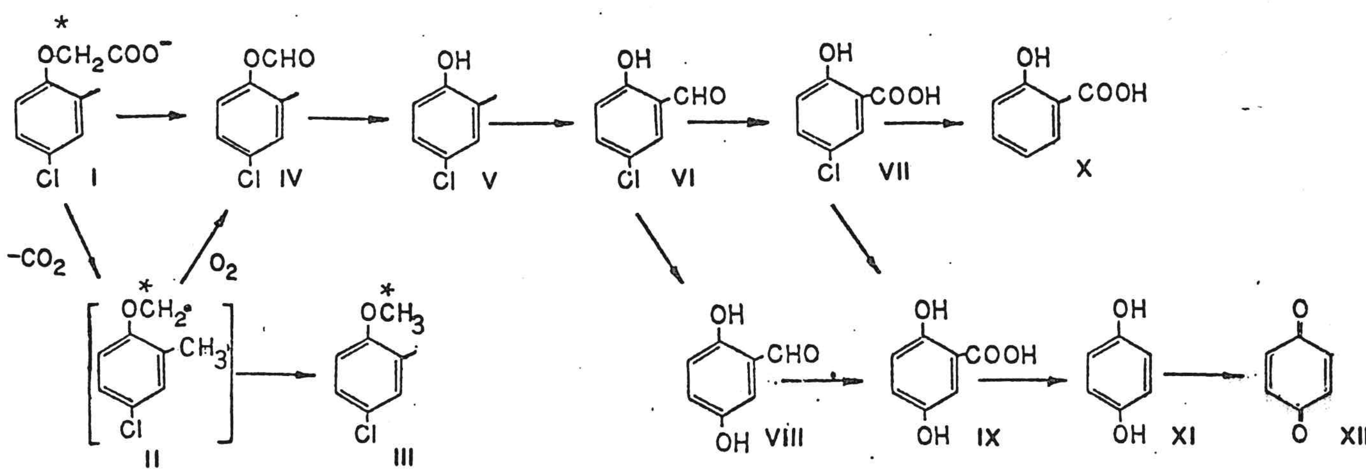

Fig. 2. Photolysis pathway of MCPA (DMA salt) in water and airborne droplets.

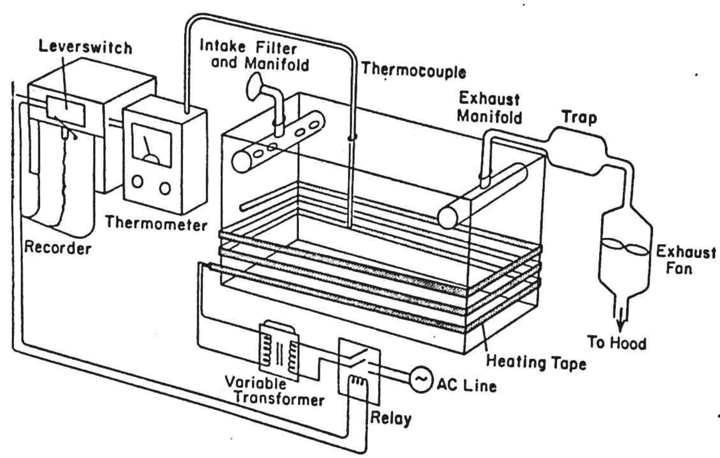

Fig. 3. Schematic diagram of the ricefield microcosm.

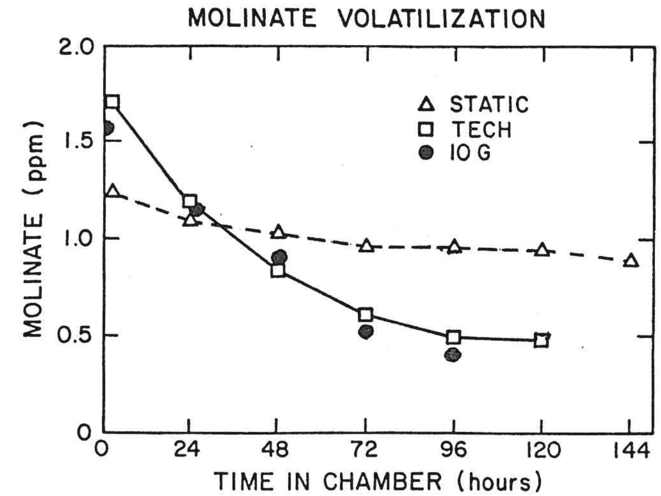

Fig. 4.

Volatilization rate at 28°C of technical molinate at 0 (static) or 0.3 cm/sec air flow compared to that of formulated Ordram 10 G (3.48 kg/ha, 3.1 lbs/acre) at 0.3 cm/sec airflow.

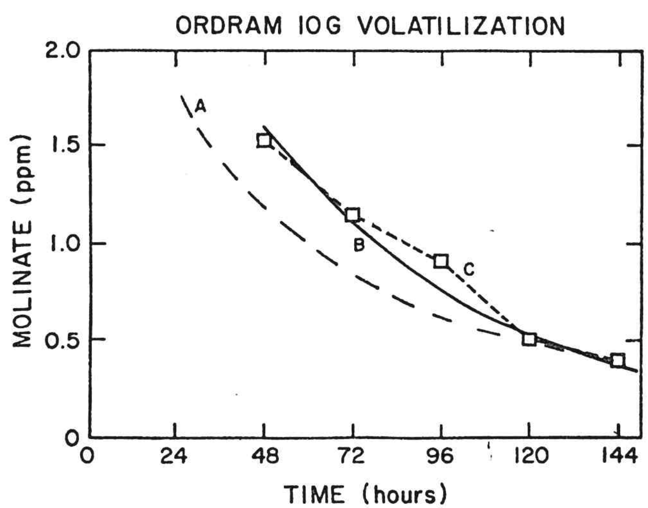

Fig. 5.

Comparison of Ordram 10 G volatilization in a ricefield (A) at 3.36 kg/ha with that in the microcosm (B) at 3.48 kg/ha. C represents microcosm data points (C).

APPENDIX A

The Fifth International Congress
of Pesticide Chemistry (IUPAC)

Kyoto, Aug. 29 – Sept. 4, 1982

SYMPOSIUM

" Herbicides for Rice Culture "

1. K. Ueki, M. Ito, Yuji Yamasue*, and Y. Kobayashi (Kyoto University):
   Weed succession by long-term application of herbicides in Japan

2. Shooichi Matsunaka (Kobe University):
   Essential characteristics of herbicides for rice culture

3. Donald G. Crosby (University of California, Davis):
   Environmental fate of herbicides during US rice culture

4. Shozo Kuwatsuka (Nagoya University):
   Fate of herbicides in flooded paddy fields in Japan

5. Yasushi Hashimoto and Yasuhiro Nishiuchi (Fishery Research Institute in Tokai Area and Agricultural Chemicals Inspection Station):
   Effects of herbicides on aquatic animals

6. S.K. De Datta (International Rice Research Institute):
   Ecconomic assessment of herbicide utilization in rice culture

Progress Report
November, 1982

Also Submitted to
Comprehensive Research on Rice
as an Annual Report

Title: Improving the Efficiency of Pesticide Application Methods to Increase Pesticide Effectiveness and Decrease Environmental Problems.

Principal Investigators: Norman B. Akesson and Wesley E. Yates, Department of Agricultural Engineering, University of California, Davis, CA. 95616.

This project was funded for fiscal year 1980-81, by combined contribution from 20 marketing order groups including rice. Two progress reports and a final report January 26, 1981, were forwarded to the Contributors. No further funding was received in 1981 and 1982 and this progress report is in effect reporting on continuing work that was funded from the 1980-81 budget and in part, as well as from other sources such as the West Side Rice Growers.

A new proposal for 1981-1982 funding was forwarded in October, 1981, and the rice growers (MORSC) contributed $1500 in early 1982.

The work we have accomplished to date relates to basic ground and aircraft spray applications with primary effort being directed to spray drop size control methods. This includes work performed on presently available hydraulic pressure and spinning type nozzles, both in a static (no air motion) mode and operated in our new wind tunnel, as well as directly on the Department's Dehavelland Beaver aircraft. The latter is equipped with wing mounting for the Particle Measuring System Co. laser beam drop size frequency counter and a single nozzle is tested by placing it and the PMS on the aircraft wing with the spray fed and controlled from the airplane cabin. The commodity group funds (MORSC) contributed approximately $12,000 to the purchase of this $55,000 drop size equipment.

We have been able to finance construction of a wind tunnel for study on effects of air flow on atomization and again have done considerable work examining the characteristic drop size distributions from hydraulic pressure nozzles. The tunnel has a 2 foot square throat and can be operated upto 150 mi/hr air speed which would cover the range of commonly used aircraft and air carrier sprayers.

Of particular interest to specific pesticides and crops such as rice is the work we have done with various herbicide formulations which has resulted in a better understanding of the effects of various spray additives and adjuvants such as emulsifiers, deposit and coverage enhancing materials and drift reduction (or large drop size producing) materials such as the water soluable polymers, Target and NalcoTrol. Our test work is aiding us to more clearly define the role that these materials play in the spray mixtures with specific chemicals and on specific weeds.

Other work has been on various Pyrethroid materials to determine coverage capability with both oil base formulations and normal emulsions. Data on drift-losses and recovery of spray in swath patterns has been obtained, which is pertinent to all oil base reduced volume spraying.

Also considerable test work was done on various formulations of Bacillus thuringiensis for certain insect control and including field tests on rice field mosquitoes where the BT was very successful.

A considerable portion of time and funds has been directed to weed control in rice. Work has been continued for basic aerial application improvement for weed control using propanil and 2,4-D. This work relates to studies made to determine better application methods and aircraft equipment including helicopters that could reduce drift-loss and still maintain weed control in rice. Studies on atomization, evaporation and effects of these factors on deposit in the aircraft swath as well as drift-losses have been made. A propanil application study was made in June 1981 to 83 acres of rice and careful monitoring of drift loss and spotting of sensitive test plants (prunes) was made.

In 1982 this study was expanded with propanil being applied (by helicopter) to approximately 1500 acres as small area applications of 15 to 100 acres. This was done over a period of about 2 weeks and monitored with air (22 ft^3/min) filter samplers which were operated during and following the applications. Although "yellow spot" symptoms were found on various trees and shrubs in the area, the levels were below any identifiable "damage" potential. These studies, 1981 and 1982, were supported largely through grants from the West Side Rice Growers Group in Colusa and Glenn counties.

Formulation and drop size studies have been initiated to establish basic response to formulation changes by various atomizers, hydraulic nozzles, spinning atomizers and various new types such as aerodynamic monodisperse and electro-static atomization. The latter is primarily designed for atomization and not for deposit enhancement. This is a totally new concept we have recently received from England through the Weed Research Organization at Oxford University and I.C.I. Chemical Company. Our work in narrowing drop size range, which we feel is a fundamental requirement to any significant breakthrough in spray application control, has progressed to a 3rd generation of atomizers incorporating an airfoil (wing like) boom with simple orifice design capable of 200 to 400 microns diameter drop release. By shielding the orifices in the airfoil the drops can be accelerated and released in any airstream of 100 mi/hr without the customary fracture and consequent production of airborne (drift capable) small drops.

In summary we have developed a new laboratory and field test capability for (1) basic study of physical properties of pesticide formulations for evaporation, atomization and drift potential, (2) spray drops analysis with the PMS (Particle Measuring Systems) instrument with which we are now able to identify atomization constants we could not establish with past techniques, and (3) test capability for new atomizers such as spinner and electro-static types as well as customary hydraulic types.

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December 2, 1982