A PROPOSAL

SUBMITTED BY

UNIVERSITY OF HAWAII

TO:	State of Hawaii Department of Agriculture
PROJECT TITLE:	"Evaluation of leaching potential of agricultural chemicals for the Hawaii Department of Agriculture"
PRINCIPAL INVESTIGATOR:	Philip Moravcik
DEPARTMENT:	Water Resources Research Center
PROJECT PERIOD:	January 1, 2017 – December 31, 2018
AMOUNT REQUESTED:	$403,199.00

AUTHORIZING UNIVERSITY OFFICIAL: [signature] DATE: 1/17/17
Kyle Koza
Contracts & Grants Specialist

ADDRESS: University of Hawaii
Office of Research Services
2440 Campus Rd, Box 368
Honolulu, HI 96822

This proposal has been approved for submission by the University of Hawaii Office of Research Services. The University of Hawaii reserves the right to negotiate terms and conditions prior to acceptance of any award. Please ensure that all correspondence regarding this application and project are addressed to the Office of Research Services.

WORKPLAN

Leaching of Selected Pesticides in Hawaii Soils as Influenced by Soil Properties and Hydrologic Conditions

Prepared For:
Hawaii Department of Agriculture
Pesticides Branch

Prepared by
Philip Moravcik
Water Resources Research Center
University of Hawaii at Manoa
with
Dr. Richard E. Green, Consultant
and Dr. Chittaranjan Ray, Consultant

September 2016

1.0 Purpose

The purpose of this investigation is to:

1) To monitor the transport of selected herbicides, insecticides and fungicides in soil profiles at three test sites on Oahu, Maui, and Kauai as a function of time,
2) To evaluate the sorption potential and aerobic degradation half-life values for the selected chemicals under laboratory conditions, and
3) To conduct modeling exercises to evaluate the impact of soil and pesticide properties and management on leaching.

2.0 Description of the Problem

Ground water is the primary source of drinking water for the population in the State of Hawaii. Dibromochloropropane (DBCP) and ethylene dibromide (EDB) were used on pineapple plantations for slightly over 20 years (starting with DBCP in 1959) for plant parasitic nematode control. Unfortunately, these chemicals appeared in drinking water wells in Central Oahu 15 to 17 years following their application on the land surface. Although the use of DBCP and EDB was banned following their detection in ground water, they continue to be the major contaminants in Oahu's ground water today. Herbicides used on pineapple and sugarcane have also appeared in ground water samples from production wells. In a 1997-98 sampling by the Hawaii Department of Agriculture (HDOA) involving 40 ground water samples from Hawaii, Maui, and Oahu, the herbicides bromacil and hexazinone were detected in three and eight samples, respectively. Two wells on Oahu contained bromacil at concentrations as high as 2.24 and 2.45 μg/L and a well on Maui had a concentration of 0.82 μg/L. Hexazinone contaminated wells were located on all three islands. Another herbicide - atrazine has also been found in well water samples collected by the HDOA and the Hawaii Department of Health (DOH). Unsaturated soils in agricultural areas also show the presence of pesticide residues.

Most agricultural areas in Hawaii overlie potable water aquifers. Depth to ground water varies from a few feet in coastal areas to over 1,000 ft in the interior part of the islands. Travel time of a contaminant from land surface to ground water can range from less than one year to over several decades depending upon topography, rainfall, and irrigation practices. Once a pesticide moves below the root zone, there is little loss due to photodegradation and microbial activity. Furthermore, the organic carbon content of soils declines with depth, thus reducing the potential for sorption of applied chemicals. The implication is that leaching of pesticides below the root zone of crops should be minimized to protect underlying ground water.

Subsequent to the discovery of DBCP and EDB in ground water on Oahu, HDOA has taken an aggressive approach to pesticide registration and management. For new pesticide registration, a computerized leaching model along with a GIS interface (Rao et al., 1985; Li et al., 1998) is used in which the leachability of the new compound is compared against two reference chemicals; one being a known leacher and the other being a non-leacher under Hawaiian conditions. This approach has the ability to predict the leaching behavior of chemicals using soil, hydrologic, and pesticide property data. If the calculated leaching index of a compound shows a risk of leaching to ground water, assignment of a "restricted use status", or initiation of a state management plan may be considered. Li et al. (1998) considered 40 chemicals in their leaching evaluation using this approach developed by researchers at the University of Hawaii.

The log-transformed attenuation factor model (AFR), the model currently used for registration in Hawaii, examines the mean and variances of AFR values for individual compounds. The two reference chemicals used in Hawaii (the nematicide DBCP and the herbicide diuron) have distinct mean AFR values and variances (resulting from uncertainties in input parameters) and they do not overlap with each other. Compounds that have mean values greater than diuron have never appeared in Hawaii's ground water. Certain compounds including the insecticide chlordane and the broad spectrum pesticide methylbromide appear to be leachers in Hawaii according to Li et al. (1998). Chlordane has a high soil sorption value and long half-life. Methylbromide is highly volatile and it can be lost to the atmosphere very easily. Although these compounds have never appeared in water supply wells in Hawaii, their potential to leach to shallow ground water cannot be ruled out. There are only a few such discrepancies in the list of 40 compounds evaluated by Li et al. (1998) and they do not limit the applicability of the AFR approach. The HDOA conducted a study to evaluate the leaching behavior of a known leacher (bromacil) under reduced application rates. The results of this investigation showed that bromacil can be applied at 75% of the label application rate on pineapple grown using plastic mulch without much weed pressure.

In early 2000, HDOA completed a study of the leaching of five chemcials on three islands (five sites) and found that most of the applied mass of pesticides was still present in the top 80 cm after the 16 week study period. The aggregated oxisol at the Kunia site showed the most intensive leaching among the five sites. The revised attenuation factor screening approach used by the HDOA indicated that all five chemicals, with the exception of trifloxystrobin, had the potential to leach. Similarly, the groundwater ubiquity score ranked trifloxystrobin as a non-leacher. The field leaching data, however, suggested that trifloxystrobin was the most mobile compound among the pesticides tested.

3.0 Study Design

The study will be conducted at one experimental site on Oahu (Poamoho - UH experimental station), one on Maui (Kula - UH experimental station), and one on Kauai (location pending).The experimental sites will have different soil and hydrologic conditions to represent the diversity of agricultural areas in the state under production agriculture.

It is proposed to perform the leaching evaluation on bare soils. This will represent a worst- case scenario and avoid complications arising from sorption and biodegradation of pesticides in the rhizosphere. The herbicides will be applied together to one plot at each site. Similarly, the fungicides and insecticides will be applied together to another plot at the same sites. This will minimize interaction between compounds and possibly reduce toxicity effects for degradation when insecticides are applied to herbicide fields (e.g., the bacteria that biodegrade herbicides may be affected by the toxic effects of insecticides). Each site will have duplicate plots for herbicides and the insecticides/fungicide.

Irrigation water will be applied to the fields based upon potential evapotranspiration estimates for each site. Intensity of irrigation water application and that for rainfall will be measured.

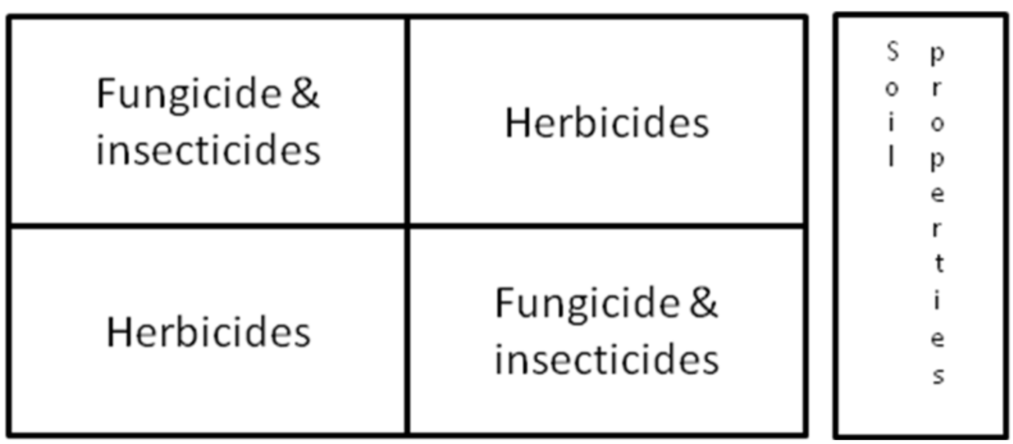
Antecedent (pre-application) concentrations of pesticides present in the soil profiles will be measured. Water content of the soils at the test sites will be measured before application and at intervals after application. Soil samples will be collected at intervals for the analysis of pesticides. Laboratory sorption and degradation experiments will be conducted to support the modeling work.

4.0 Field Methods

We propose to use soil sampling as the primary method of monitoring along with close monitoring of water content at the time of sampling and at various sampling periods. Moisture content and the soil bulk density will be used for estimating masses and concentrations of the compounds in the pore water. The following scope of work is proposed:

4.1 Site preparation

- We propose to use two sub-plots for herbicides and two sub-plots for insecticides/fungicide at each site as was done in the earlier study completed in 2004. Duplicate sub-plots are needed to account for pesticide application variability and soil heterogeneity. In addition, at each sampling, two soil samples from each of the sub-plots will be collected from two points in the sub-plot to account for variability. A fifth sub-plot will be used to characterize soil parameters. No pesticides will be applied to this sub-plot. Sizes of individual sub-plots will be adequate to represent heterogeneity of soils. Multiple subsamples of soil will be taken from each sub-plot before and after application. Post-application soil samples will be collected near the original sampling points. The following plot design will be used for the herbicide and insecticide/fungicide application:



Sub-plots within the plots.

- The soil sampling points will preferably be in level areas (to reduce surface runoff) and away from boundaries.
- Since close monitoring is planned during the entire study and the study period is about 16 weeks after application, sampling depth is limited to 10 ft prior to pesticide application and post application sampling depths will be determined to capture the chemical front in the soil.

4.2 Collection of basic data

- For initial sampling, soil cores will be continuously taken to ten feet. Eight samples from depth intervals of 0-0.5, 0.5-1, 1-2, 2-3, 3-4, 4-5, 7-8, and 9-10 ft will be used for initial chemical and physical characterization of soil. Chemical parameters listed in Table 1 (in Appendix) will be used for analysis. Composite samples may be prepared for certain parameters to reduce cost.

4.3 Collection of soil cores for transport studies

- At each site bulk density samples will be taken at selected points and depths.

- The locations of each core and the depth interval will be properly noted. This will provide information on heterogeneities in soil properties in a given field.

4.4 Plot Preparation and Pesticide Application

- Plots will be a minimum of 20' ×20' in size and will be located on a contour to prevent surface runoff. Assistance from the Agricultural Experiment Stations in preparing the plots and in getting necessary equipment for plot preparation will be sought.
- The plots will be tilled and prepared in a manner similar to that used for vegetable or other field crop production.
- Uniformity of pesticide application will be tested in a different location prior to application. A carbon dioxide pressurized sprayer will be used to spray the pesticides. At each site two sub-plots will receive the two herbicides (Amicarbazone and Quinclorac) combined together at label application rates. The two other sub-plots will receive the one fungicide (Fludioxonil) and three insecticides (Flupyradifurone, Chlorantraniliprole , and Cyantraniliprole) also at the label rates. Some of the compounds have different label rates for different uses. We will apply them at the higher label rate at one of the sites (to be determined).
- Water content of the soil prior to application and the amount of water used for pesticide application will be noted. Straw mulch will be used to cover the plots after pesticide application following the procedure of a previous pesticide leaching study Gavenda et al. (1996).

4.5 Record of rainfall, evaporation and irrigation

- The dates, rates, and exact amount of irrigation water application will be recorded.
- We will install tipping bucket raingages at the test sites and they will be equipped with tip counters for recording the rate and amount of rainfall at the site.
- Pan evaporation data, if measured at the Experiment Station, will be used for this purpose. Otherwise, Class A evaporation pans will be set up and water evaporation will be measured either manually or by transducers depending upon the budget. For automatic measurement, a pressure transducer with a data logger will be used.

4.6 Measurement of soil-water content/suction

- For model validation, the water content and soil matric potential at various time intervals are needed. For this purpose, we propose to use time domain reflectometry (TDR) probes. We will obtain a new TDR system to measure soil moisture in the experimental plots. Additionally, tensiometers will be used for measuring soil matric potential.

4.7 Collection and analysis of post-application soil samples

- Soil samples from the sites will be collected at time intervals (discussed in section 4.10) to a depth of five feet continuously. If auger extensions are available and the soil can be readily sampled, a limited number of deeper samples may be taken. If the pesticide front is observed to move deeper than five feet towards the later stage of the experiment, alternate measures will be considered for obtaining deeper samples.
- Metal sleeves may be used to prevent surface soil from falling into the open holes.
- Soil samples will be analyzed using appropriate protocols at the Hawaii Department of Agriculture laboratory. The pesticide manufacturers will be contacted to provide standards of the new compounds and analytical methods.

- Sample handling, preservation, storage procedures will follow those similar to other HDOA studies. Proper chain-of-custody will be followed.
- On occasion, soil organic carbon and bulk density will be measured to examine temporal variability.

4.9 Sorption and degradation behavior of pesticides

- Soil samples from the plots will be used to evaluate their maximum equilibrium sorption capacity in the laboratory.
- Batch-equilibrium method will be followed in which the soil samples will be shaken with pesticide solutions for twelve to eighteen hours. The samples will be centrifuged and the liquid samples will be pipetted into glass containers and sent to the HDOA laboratory for extraction and analysis. For consistency, it will be desirable to use the same laboratory and same methods for pesticide analysis. The remaining concentration in the liquid phase will be used to estimate sorption distribution coefficients for the samples. These values will be used with organic carbon values for estimating organic carbon partition coefficient of each chemical and it these will be compared to literature values.
- Desorption of pesticides from sorbed soils will be conducted in a similar manner. In this case, water at desired pH will be used to elute pesticides from the sorbed samples. The K_{oc} values of the pesticides will be obtained in this manner.
- Aerobic degradation of the pesticides will be conducted in the dark. Pesticides will be applied to soils and the moisture content of the soil will be maintained at 75% of field capacity during the experimental period. Soils will be kept in flasks and the tops will be covered with parafilm to reduce evaporation. Pinholes in the parafilm will allow air exchange between the flask and the atmosphere. Flasks will be taken out at weekly intervals and the samples will be analyzed for the parent compound and metabolites at the HDOA laboratory using GC/MS. This will continue for 7 to 10 weeks. This will provide half-life data for the compounds

4.10 Sample Collection Frequency

- Soil samples will be first collected prior to pesticide application.
- Soil samples will be taken near the same points to a depth of no more than five feet (hand augering) soon after application and subsequently at regular intervals (2, 4, 8, 12, and 16 weeks).
- After the conclusion of the experiment, deeper samples may be collected if the earlier samplings show the passage of pesticide front beyond the top five feet.

4.11 Plot maintenance

- The plots will be covered at all times to prevent weed growth.
- Plot boundaries will be properly maintained for preventing the entry or loss of runoff water.

5.0 Modeling Exercises

5.1 AFR simulations

- Input parameters for AFR (e.g., K_{oc} and $t_{1/2}$) will be generated.

- The K_{oc} and $t_{1/2}$ for existing and new compounds for various soil and hydrologic settings in Hawaii will help in model validation and estimating their relative leaching potential.
- Statewide mapping will be conducted for these models.

5.2 HYDRUS transport simulations

- This model is similar in physical concept to the Pesticide Root Zone Model (PRZM), but more accurate since it uses physically-based processes and the needed input parameters.
- HYDRUS uses rainfall intensity, evapotranspiration, irrigation data, soil physical parameters, and pesticide properties to estimate the profile concentration of a chemical.
- Center of mass and profile concentration from HYDRUS will be compared against field data. Degree of mismatch will be correlated with soil heterogeneity, macroporosity and other uncertainty in input data.

5.3 Sensitivity analysis

- The model should show the amount of leachate produced over the period of simulation, under episodic storm events, and under conditions when the timing between irrigation and rainfall in short.
- After the model is calibrated, sensitivity analyses should be performed to determine the parameters that have the most pronounced effect on leachate generation. Further, the window of time between weekly or monthly irrigation and typical storms should be adjusted to examine the quantity of leachate generated and the amount of leaching. This exercise should be conducted for various months of the rainy season involving storms of various intensities and durations.
- Simulation scenarios would account for changes in applied pesticide mass, organic carbon variations in soil surface, timing of planting, irrigation, and land management with respect to seasonal precipitation. The monitoring and modeling results would indicate relative leaching behavior of chosen compounds.

6.0 References

Gavenda, R.T., R.E. Green, and R.C. Schneider. 1996. Leaching of pesticides in selected Hawaii Oxisols and Andisols as influenced by soil profile characteristics. HITAHR Research Series 075, University of Hawaii, 35 p.

Li, Z.C., R.S. Yost, and R.E. Green. 1998. Incorporating uncertainty in a chemical leaching assessment, *Journal of Contam. Hydrol*., 29: 285-299.

Oshiro, W.C., C.J. Miles, and R.E. Green. 1993. *Physical-chemical properties of selected pesticides for environmental fate modeling*, Research Series 069, HITAHR, College of Tropical Agriculture and Human Resources, University of Hawaii.

Rao, P.S.C., A.G. Hornsby, and R.E. A.G., Jessup. 1985. Indices for ranking potential for pesticide contamination of groundwater, Soil Crop Sci. Soc, Fla. Proc. 44:1-8.

Appendix

Table 1. Chemical parameters for analysis by HDOA and Agricultural Diagnostic Laboratory for the study.

Test\Parameters	Pre-appl#	½-day	2 wks	4 wks	8 wks	12 wks	16 wks
Pesticides	8×5×2=80	2×5×2=20	4×5×2=40	6×5×2=60	6×5×2=60	7×5×2=70	8×5×2=80
Organic carbon	6×5×2=60	0		0			3×5×2=30
CEC	3×5×2=30	0		0			0
pH	5×5×2=50	0		0			0
NH^{4+} and NO_3^-	5×5×2=50	0		0			0
Phosphate	5×5×2=50	0		0			0
Ca++	5×5×2=50	0		0			0
Mg++	5×5×2=50	0		0			0
K+	5×5×2=50	0		0			0
Other residual pesticides*	5×5×2=50	0		0			0

* - from prior activities

#Please note that there are two sub-plots for each treatment. Samples from 0-0.5, 0.5-1, 1-2, 2-3, 3-4, 4-5, 7-8, 9-10 ft (eight samples) will be taken during pre-application round of sampling. CEC samples will be from 0-0.5, 1-2, and 4-5 ft depths. Other cations, anions, and pH will be from five depths (0-0.5, 0.5-1, 1-2, 2-3, and 7-8 ft depths). Soon after pesticide application (1/2 day after), samples will be taken from 0-0.25 and 0.25-0.5 ft depths. After two weeks, samples will be taken from 0-0.5, 0.5-1, 1-2, 2-3, and 3-4 ft (five samples). After four weeks, samples will be taken from the same depths as two-week samples and from 4-5 ft (total 6 samples). Samples collected during the 12th and 16th weeks will extend to the two next sampling depths (7-8 ft and 9-10 ft).

University of Hawaii Efforts

Samples for the measurement of bulk density, organic carbon and water content will be analyzed at the University of Hawaii. The number of samples for the analysis of each of these parameters will be adjusted for optimal distribution of sampling locations and budgeted manpower to conduct the work. In addition, sorption and aerobic degradation experiments will be conducted at the University of Hawaii and the prepared soil or water samples will be delivered to the HDOA laboratory for analysis. One research scientist will be working full-time on the project, and we hope to engage a research scholar (Ph.D. candidate or postdoc) in addition. A portion of the work (study design, review, data analysis, and modeling) will be conducted by Dr. Chittaranjan Ray from the University of Nebraska, acting as a consultant on the study. The PI will put appropriate amount of time for project completion. The following is a breakdown of efforts:

Task	***Time***
Preparation of equipment for lab/field	5 weeks
Preparation of plots	5 weeks
Pre-application field activities	5 weeks
Measurement of hydraulic conductivity (field) one site	1 week
Installation of water content and matric pressure sensors	2 weeks
Monitoring of soil water and pressure and sampling	5 weeks
Sorption and degradation experiments	10 weeks
Modeling effort	10 weeks
Total	***80 weeks***

Cost Estimates

HDOA laboratory
Analysis of pesticides in soil samples: ~410 (over 6-8 months)
Analysis of other residual of pesticides in pre-plant sampling: 50 one-time samples
Analysis of liquid samples (for sorption) during the first year: 200 minimum (5 compounds, 5 depths, 3-4 concentrations, and 2 plots)

Agricultural Diagnostic Laboratory
Sample analysis will cost $65 each for nitrate, ammonium, pH, CEC, and phosphate. From the three plots, three sets of soil samples from three depths (0-12, 12-24, and 24-36 inches) will be collected for a total of 27 samples. Additionally, particle soil particle size analysis will be carried out for three depths for one sample per plot (total nine samples at a cost of $30 per sample). Samples analysis will cost $10 for organic carbon per sample and $20 for major plant nutrients. This will be done for 27 samples (three plots, each having three sampling points and soils extracted from the same three depths).

University of Hawaii (24 month budget):
See the attached Excel file.

University of Hawaii contributions for the project
Computer software for simulation
Time from the PI

Budget for HDOA Project				
Item	Yr-1	Yr-2	Total	
LABOR SECTION				
PI (1 mo)	$0	$5,000	$5,000	
Staff scientist -1 ($3500/mo. Full time) Roll	$40,000	$41,600	$81,600	
Undergrad student $13.89/hour, 20 hours a week, 9 months. 2 years.	$10,000	$10,000	$20,000	
Fringe PI (2.32%)	$0	$116	$116	2.32%
Fringe RS (50.79%)	$0	$0	$0	50.79%
Fringe staff scientist(50.79%)	$20,316	$21,129	$41,445	50.79%
fringe Student help (.66%)	$66	$66	$132	0.66%
Total Labor	**$70,382**	**$77,911**	**$148,293**	
CONSULTANTS SECTION				
Research scholar -1 (12/mo) consultant Jankovec	$40,000	$41,600	$81,600	
Ray Consultant	$29,279	$32,819	$62,098	
Total Consultants	**$69,279**	**$74,419**	**$143,698**	
Labor + Consultants	**$139,661**	**$152,330**	**$291,991**	
Supplies				
Field work	$40,000	$0	$40,000	
Computer/software	$2,000	$500	$2,500	
Field travel	$15,349	$1,705	$17,054	
Conf travel	$0	$2,000	$2,000	
Labwork (Ag. Diagnostic lab)	$5,000	$2,000	$7,000	
Report	$500	$1,500	$2,000	
site plot rental and water	$4,000	$0	$4,000	
Subtotal	$206,510	$160,035	$366,545	
Indirect cost (10%)	$20,651	$16,004	$36,654	
Total	**$227,161**	**$176,039**	**$403,199**	