PROGRESS REPORT: RESIDUES OF FORESTRY HERBICIDES IN PLANTS OF INTEREST TO NATIVE AMERICANS (PHASE II)

R. Segawa and A. Bradley
Environmental Hazards Assessment Program
Department of Pesticide Regulation

P. Lee, D. Tran, J. White, and J. Hsu
Center for Analytical Chemistry
California Department of Food and Agriculture

January 12, 1998

I. BACKGROUND

The use of native plant materials is a tradition among Native American tribes in California. Native Americans may be exposed to forestry herbicides through the use of plant materials. These unique exposure scenarios are not characterized in the risk assessment of these herbicides. The U.S. Forest Service uses three herbicides for site preparation and release operations in conifer tree plantations in California's national forests: glyphosate, hexazinone, and triclopyr. The U.S. Forest Service has requested the assistance of the Department of Pesticide Regulation (DPR) in assessing exposure of Native Americans to forestry herbicides. In order to estimate the potential exposure, the residue concentrations of forestry herbicides must be deterxnined.

The residues of forestry herbicides in plant materials are being conducted in two phases. DPR has completed phase one that involved the development of sampling and analytical methodology, and pilot sampling. This is a progress report of phase two with the following objectives: 1) determining the dissipation rate of herbicides in selected plants and 2) determining the off-site movement of herbicides in selected plants in areas adjacent to herbicide applications.

II. STUDY PLAN

At each national forest DPR consulted with the local California Indians and the U.S. Forest Service, and a plan for conducting phase two was developed and

described in detail in the enclosed protocol. Briefly, four application methods will be studied: Pronone® 10G (hexazinone) by air, Velpar® L (hexazinone) by ground, Accord@ (glyphosate) by ground, and Garlon® 4 (triclopyr) by ground. DPR will determine dissipation rates for each of these application methods in four plants/plant parts: bracken fern roots, buckbrush shoots, golden fleece foliage, and manzanita berries. Dissipation samples will be collected every four to eight weeks for 36 weeks following treatment. Off-site samples will be collected at four distances from 5 to 100 feet from the edge of the treated area. Analytical methods will be validated for each of 12 plant/herbicide combinations.

III. PROTOCOL REVISIONS

Some changes to the study protocol have been made due to some unforseen circumstances. The following changes in personnel are necessary. Adrian Bradley may not be available for next year's monitoring. In that event, Clarice Ando will be the field coordinator. Terry Jackson is also unavailable. Cindy Garretson will be the quality assurance officer for both the field and laboratory portions of the study.

The protocol specifies that the first set of samples be collected the day after herbicide application. This past year, we were unable to sample several locations the day after application because other applications occurred on the same day and we lack the resources to sample more than a few locations in a single day. The first set of samples for both dissipation and off-site locations will be collected one to three days after application. Since residues are detectable for several months, this will have no effect on the study's conclusions.

If the U.S. Forest Service follows the same timetable for herbicide applications this year (March - June) as last year, we will likely continue field sampling until March 1999, 36 weeks after the last application. This is longer than originally anticipated. We may also want to extend sampling if we detect residues in the samples collected on the last scheduled date. We have revised the study schedule to accomodate the extended sampling. The study will now be completed by December 3 1, 1999.

A copy of the revised study protocol is enclosed.

IV. STATUS OF METHOD VALIDATION

Validation has been completed for all 12 analytical methods. Each method was validated by analyzing a series of samples containing known amounts of herbicide (spiked samples). Recoveries for the 12 methods varied from 70 - 95% (Table 1). DPR compares the results of the method validation to quality control samples analyzed during the course of the study to ensure consistency of the laboratory analyses over time.

Storage stability has also been completed for each of the 12 methods (Table 2). Hexazinone in manzanita berries showed a significant decrease over the nine-week storage period. Additional stability analyses for hexazinone in manzanita berries showed a significant decrease in concentration after only one day of storage. Hexazinone in buckbrush also showed a slight decrease in concentration over the nine week storage period. DPR will evaluate the data and the results of field samples may be adjusted to account for losses during storage. DPR will make any data adjustments at the end of the study after all results have been reviewed.

V. STATUS OF DISSIPATION MONITORING

For each of the four application methods and four plants, DPR will monitor four sites (64 total sites). DPR has initiated dissipation monitoring for 28 of the 64 sites (Table 3). DPR will monitor the remaining sites during the second year of the study.

Results of the dissipation sampling and laboratory analyses from 148 samples completed as of December 3 1, 1997, are shown in Tables 4 - 7. Herbicide concentration in plant samples varies greatly, ranging from no detectable amount to 2 12 parts per million (ppm). There are insufficient data at this time to draw any conclusions about dissipation rates.

VI. STATUS OF OFF-SITE MONITORING

For each of the four application methods, DPR will monitor six sites (24 total sites). DPR has initiated off-site monitoring for eight of the 24 sites (Table 3). The remaining sites will be sampled during the second year of the study. DPR

selected three plant species for study this year: bracken fern, buckbrush, and deer brush. At each site, DPR is sampling the same plant species at all distances.

Results of the off-site sampling and laboratory analyses from 95 samples completed as of December 3 1, 1997, are shown in Table 8. Herbicides were detected in four (50 1- 120, E 12 1, Musick 07 1, R04 1) of the eight locations sampled and six of 95 samples. There is no apparent pattern to the detections. For two of the locations (E 12 1, R04 1), the concentrations did not decrease with distance from the treatment area. In addition, R041 was treated with Pronone® and residue was detected in plants the day after application. It is highly unlikely that hexazinone can be washed off Pronone® granules and absorbed by plants in one day. Therefore, it is unlikely that the detections in R04 1 and E 12 1 are due to drift. It is more likely that these detections are due to background residue or sample contamination. DPR has modified its procedures to decrease the possibility of sample contamination.

VII. OTHER MONITORING

Dissipation monitoring in redbud at a test application site was initiated, but terminated because all samples contained no detectable residue even 12 weeks after treatment. DPR and the U.S. Forest Service will attempt another test application next year.

Treatment units sampled this year as well as last year were surveyed for oaks producing acorns. Three treatment units contained oaks with acorns and DPR sampled all three, one treated this year with Accord@ (Jose 13 8), one treated this year with Pronone® (E 116), and one treated this year with Velpar® (E 12 1). Neither of the hexazinone samples contained a detectable amount of herbicide. The laboratory could not analyze for glyphosate due to worms and mold in the sample.

We did not find any treatment units containing mushrooms.