Data Analysis of Forestry Herbicide Residues in Plants of Interest to California Tribes

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1. Introduction

California Indian tribes continue the tradition of using various plant parts as food, medicine and basketry material. Many of them gather plant roots, shoots and leaves in the vicinity of national forests, which are managed and may be treated with various herbicides. Tribal people expressed concerns that herbicide residues in these plant materials may have negative effects on their health. To address this issue, the US Forestry Service funded DPR in late 1997, to monitor the offsite movement and dissipation of herbicide residues in plant materials after treatments [1,2,3]. After nearly three years of sampling and lab analysis, valuable monitoring data for commonly used herbicides has been collected for plant species and parts important to California Indian tribes.

In this report, we characterize the environmental fate of these herbicides, the levels of various herbicide residues in various plants species and parts, the classification of herbicide residues detected from plant samples, the rates of herbicides dissipation after treatments, the time needed for these chemicals to drop to certain thresholds, and the degree of off-site movement.

2. Methods and Materials

2.1 Field Sampling

After consulting with the local Indian tribes, four plants were selected for monitoring from many target plant species. Because different parts are used from different plants, samples were taken specifically from plant parts that are used by Indians. They were bracken fern roots, buckbrush shoots, golden fleece leaves and manzanita berries. Chemical residues from four herbicide/treatment combinations were monitored. They were Pronone® 10G (hexazinone), Velpar® L (hexazinone), Accord® (glyphosate) and Garlon® 4 (triclopyr). Granule Pronone® was applied by helicopters, while all other herbicides were applied with sprayers from ground. Four sampling sites (replications) were chosen for each plant/herbicide combination. These sampling sites were in the national forests of Eldorado, Lassen, Sierra and Stanislaus of California. Sixty-four sites were monitored over the period from 1997 to 2000[1,2]. The initial monitoring period was set to 36 weeks after treatment, but this period was extended until non-detectable residues were found in the sample (Table 1). In some cases, the monitoring period was as long as 130 weeks. The first sample was taken 1-3 days after the herbicide was applied. The sampling interval for the first 36 weeks was either 4 weeks or 8 weeks, and was longer thereafter. The sampling stopped if no herbicide was detected. Samples were taken from the same plants unless they died before the sampling was completed.

In order to determine how far the herbicides could move from treated areas, sampling was also conducted at certain distances from treated areas (0-15, 20-40, 50-70 and 80-100 ft) and at certain time intervals after application (0, 4, and 12 weeks) [1,2].

2.2 Time from treatment to non-detectable concentration level

The herbicide residues were expressed as concentration in the unit of parts per million (ppm). The lab analysis can only extract, detect and quantify herbicide residues above certain levels. The minimum concentration level the lab analysis can quantify is called the reporting limit. It changes with chemicals, plant species and protocols used for lab analysis. The reporting limits used for this study are listed in Table 1:

Table 1: Laboratory reporting limits of herbicides in various plant parts (ppm)

Herbicides	Bracken Fern Roots	Buckbrush Shoots	Golden Fleece Foliage	Manzanita Berries
Accord® (glyhposate)	0.1	0.1	0.1	0.1
Pronone® (hexazinone)	0.05	0.1	0.1	0.05
Velpar® (hexazinone)	0.05	0.1	0.1	0.05
Garlon®(triclopyr)	0.03	0.03	0.07	0.03

When a pesticide couldn't be detected in a sample, one-half of the reporting limit was used as the concentration value. The time from herbicide treatment to the first non-detectable concentration can be regarded as the lifetime of the herbicide for a particular plant media.

2.3 Mean and Standard Error of sampling concentration

The mean concentration is calculated as the arithmetic average of replicates:

$$\bar{Y} = \frac{\sum_{i=1}^{n} Y_i}{n} \tag{1}$$

where n is the number of replicates or sites for the same plant/herbicide combination, which varied from 1 to 4.

The sample standard deviation is defined as

$$s = \sqrt{\frac{\sum (Y_i - \bar{Y})^2}{n-1}} \tag{2}$$

The standard error of the mean (SEM) is then expressed as

$$\sigma_Y = \frac{s}{\sqrt{n}} \tag{3}$$

which measures the dispersion of sampling distribution, and is thus an index of variability of $\overline{Y}$ from sample to sample [4].

2.4 Half-life

The most commonly used equation for chemical decomposition is the exponential decay equation:

$$c = c_{\max} e^{-at} \tag{4}$$

where 'c' is the concentration at the time of t, c_{max} is the maximum concentration, and 'a' is the decay coefficient. c_{max} is usually detected immediately after the treatment. However, as samples were taken from various plant parts, the transportation and absorption of herbicides into plant tissues might take some time, especially when the herbicide was a granule form (Pronone®). Therefore, t was measured at the time when the maximum hexazinone concentration in the plant part was observed after Pronone® treatment. For other herbicides, t started from the time of treatment. The decay coefficient 'a' dictates the rate of concentration decline. A bigger 'a' value means faster dissipation and the less time it takes to reach a non-detectable concentration level.

The Marquardts Compromise method was employed to fit Equation (4). The process involved iterative calculation of parameter c_{max} and a. For a set of initial values of c_{max} and a, calculation was repeated until the sum of error squares using current parameter values and using the previous iteration was close enough. If the process does not converge after a large number of iterations, the first data pair is dropped and the process is repeated.

The half-life ($t_{1/2}$) was calculated by letting c = ½ c_{max} in equation (4) and solve for t:

$$t_{1/2} = \frac{\ln 2}{a} \tag{5}$$

For each sampling site, there was a time series representing the variation of concentrations over the sampling period. The site specific data set was used to fit the equation (4), and then the half-life was calculated using equation (5). It was common to get different parameter values and thus different half-lives if calculated separately from each of four sampling sites. In order to estimate the half-life for a particular herbicide in a plant part, the weighted average half-life from different sampling sites was calculated:

$$\bar{t}_{1/2} = \frac{\sum_{j=1}^{m} R_j t_{1/2}^{(j)}}{\sum_{j=1}^{m} R_j} \tag{6}$$

where $\bar{t}_{1/2}$ is the average half-life, $t_{1/2}^{(j)}$ is the half-life calculated from concentration data collected at site j, R_j is the coefficient of determination (r^2) when fitting equation (4), and m is the number of sites.

Two screening processes were performed when using model (6) to calculate the weighted average. First, some data fitting attempts for model (4) might not generate a significant regression, thus the half-life calculated using that set of coefficients does not have much credibility. It should be excluded from the weighted average calculation. Second, if a regression is significant, but the half-life is negative, it should not be included in model (6). The screening procedure is summarized as:

$$R_j = \begin{cases} r_j^2 & if\ r_j \geq r_{0.10} \\ 0 & if\ r_j < r_{0.10}\ or\ t_{1/2}^j < 0 \end{cases} \tag{7}$$

where r_j is the correlation coefficient and $r_{0.10}$ is the critical correlation value with a 90% significant level, which varies with sample size (Table 2).

Table 2. 90% significant correlation levels for different sample size [5].

n	**df**	$\mathbf{r}_{0.10}$	$\mathbf{r}^2_{0.10}$
4	2	0.900	0.81
5	3	0.805	0.65
6	4	0.729	0.53
7	5	0.669	0.45
8	6	0.621	0.39
9	7	0.582	0.34
10	8	0.549	0.30

The half-life can not be determined if all of four sites fail to pass the screening criteria.

3. Results

3.1 The mean of herbicide residues

The dissipation of different herbicides or from different application method combinations have different characteristics (Fig. 1). In general, residues of glyphosate were significantly higher in all plant parts than other herbicides except in bracken fern roots. The residues remained above 100 ppm in the first 24 weeks except in bracken fern roots, and then declined quickly. At the time of 60 weeks after applications, the concentration reached the level of 1 ppm or lower in all plant parts. Residues of Velpar® were the next highest, the concentration after treatment was as high as 100 ppm in golden fleece leaves, but declined quickly in the first several weeks. It took about 28 weeks for Velpar® concentrations to reach the non-detectable level for the first time in most plants. Hexazinone is the common ingredient for both Pronone® and Velpar®, but Pronone® was applied as granules, therefore absorption by plants was much slower than liquid Velpar®. Therefore, the highest concentration of Pronone® was not observed immediately after application, instead, it was 10 weeks after treatment. Although the Pronone® concentration never exceeded 1 ppm, the low concentration remained in plants for a very long period. The concentration of Velpar® residue was much higher in leaves and shoots, but was roughly at the same low level as Pronone® in roots and berries. This suggests that Velpar® droplets were deposited on the surface of leaves and shoots, and caused the high concentrations in the first several weeks. Residues of triclopyr were modest, the concentration were below 10 ppm in most plants except in buckbrush shoots. It took about 40-50 weeks for the concentration to be lower than 1 ppm.

The herbicides had quite distinct concentrations in manzanita berries, ranging from less than 0.1 ppm to more than 100 ppm (Fig. 2). Whether or not the berries were already set on the plants at the time of treatments might explain the difference of herbicide concentrations in manzanita berries. Except glyphosate, all herbicides had small residues in manzanita berries. Velpar® and Pronone® were applied before the formation of manzanita berries, their concentrations in manzanita berries were very low throughout the sampling period. Manzanita berries may have been directly exposed to glyphosate and triclopyr at the time of application, thus the concentrations were much higher. Herbicide concentrations rarely exceeded 1 ppm in bracken fern roots, but remained stable during the monitoring period. The herbicides detected in bracken fern roots were through uptake and translocation, therefore, the concentrations were very low. The plant parts above the ground were detected to have higher herbicide residues if they were exposed to the sprays. This fact again suggests that the high level of herbicide residues was mainly due to direct deposition of herbicides on plant leaves and shoots during the application.

A conceptual model of herbicide environmental fate (Fig. 3) can explain the observed phenomena. Leaves and shoots were directly exposed to herbicide spray. Therefore, samples from leaves and shoots contained more herbicide residues than samples from roots and berries. Roots were not directly exposed to herbicides during applications. The degree of berries' exposure to herbicides was intermediate, depending on if the berries were set on the plants at the time of pesticide treatments. For those plant parts in the air, herbicide droplets directly deposited on the surface, thus high concentrations could be detected immediately after treatments. However, if the herbicide was applied as granules, leaves and shoots were not contacted, the residues were much lower. After

treatment, metabolic activities became the main pathway for herbicides to get into plant tissues, however, the uptake rate would be slow. Uptake and translocation were the major source of residues detected in roots and in berries as well, if they were not directly exposed to spray. Vigorously growing plant parts, such as leaves and shoots and in some cases fruits, were affected by both physical and physiological pathways. The concentration was much higher and exhibited a fast decline pattern with time.

3.2 The variation of herbicide residues at different sites

The average concentrations and the standard errors of various herbicides in different plants are shown in Fig. 4 - Fig. 7. The error bar was calculated based on samples from one sites to four sites. In some cases there were only two data points, which may result in large error bars. In the case of only one sample, a point is shown on the plot. In general, the standard errors are large, indicating that the variation from site to site was very significant. Site to site variation of herbicide residues is the smallest in bracken fern roots, and the concentration itself was also low in roots.

3.3 The half-life of herbicides in various plant parts

Because of the large variability in the results, and the difficulty of including site specific factors in this analysis, the mean concentrations averaged from the four sites were not used to fit the model (4). It's more appropriate to fit the model with concentration data from the same sampling site so that the effect of site specific factors can be excluded. Using a nonlinear regression technique, coefficients in equations (4) were estimated, and the half-life was calculated for each herbicide and plant species (Table 2).

Table 2. Regression coefficients of model (4) and half-life estimated using site specific data

Herbicide	Plant&Part	Site	c_{max}	a	$t_{1/2}$ (week)	r^2	n
Accord® (glyhposate)	Bracken Fern Roots	1	0.144	0.060	11.46	0.72	7
Accord® (glyhposate)	Bracken Fern Roots	2	1.269	0.044	15.86	0.34	6
Accord® (glyhposate)	Bracken Fern Roots	3	0.753	0.014	49.26	0.24	6
Accord® (glyhposate)	Bracken Fern Roots	4	0.929	0.069	10.10	0.15	7
Accord® (glyhposate)	Buckbrush Shoots	1	311.274	0.122	5.69	0.65	6
Accord® (glyhposate)	Buckbrush Shoots	2	740.236	0.078	8.84	0.87	6
Accord® (glyhposate)	Buckbrush Shoots	3	40.294	0.034	20.36	0.43	7
Accord® (glyhposate)	Buckbrush Shoots	4	235.839	0.044	15.80	0.60	6
Accord® (glyhposate)	Golden Fleece Foliage	1	7.626	0.026	27.09	0.07	6
Accord® (glyhposate)	Golden Fleece Foliage	2	5.940	0.115	6.03	0.83	7
Accord® (glyhposate)	Golden Fleece Foliage	3	1178.00	0.062	11.26	0.61	6
Accord® (glyhposate)	Golden Fleece Foliage	4	7.478	0.036	19.42	0.24	7
Accord® (glyhposate)	Manzanita Berries	1	54.263	-0.007	-92.95	0.11	5
Accord® (glyhposate)	Manzanita Berries	2	397.896	0.028	24.65	0.47	6
Accord® (glyhposate)	Manzanita Berries	3	65.953	0.046	15.19	0.47	5
Accord® (glyhposate)	Manzanita Berries	4	n/a	n/a	n/a	n/a	n/a
Pronone® (hexazinone)	Bracken Fern Roots	1	0.040	0.017	40.25	0.15	7
Pronone® (hexazinone)	Bracken Fern Roots	2	0.387	-0.003	-229.29	0.00	7
Pronone® (hexazinone)	Bracken Fern Roots	3	0.124	0.011	62.28	0.05	7
Pronone® (hexazinone)	Bracken Fern Roots	4	0.183	0.010	70.29	0.14	9

Pronone® (hexazinone)	Buckbrush Shoots	1	0.617	0.008	81.91	0.20	10
Pronone® (hexazinone)	Buckbrush Shoots	2	0.461	0.002	287.37	0.00	7
Pronone® (hexazinone)	Buckbrush Shoots	3	0.568	0.005	133.27	0.01	7
Pronone® (hexazinone)	Buckbrush Shoots	4	0.126	-0.019	-36.21	0.17	7
Pronone® (hexazinone)	Golden Fleece Foliage	1	0.063	-0.038	-18.13	0.30	7
Pronone® (hexazinone)	Golden Fleece Foliage	2	0.302	0.007	100.19	0.05	9
Pronone® (hexazinone)	Golden Fleece Foliage	3	0.422	0.012	59.82	0.02	7
Pronone® (hexazinone)	Golden Fleece Foliage	4	0.702	0.037	18.89	0.35	7
Pronone® (hexazinone)	Manzanita Berries	n/a	n/a	n/a	n/a	n/a	n/a
Pronone® (hexazinone)	Manzanita Berries	n/a	n/a	n/a	n/a	n/a	n/a
Pronone® (hexazinone)	Manzanita Berries	3	3.705	0.407	1.70	0.96	5
Pronone® (hexazinone)	Manzanita Berries	4	n/a	n/a	n/a	n/a	n/a
Velpar® (hexazinone)	Bracken Fern Roots	1	n/a	n/a	n/a	n/a	n/a
Velpar® (hexazinone)	Bracken Fern Roots	2	0.472	0.037	18.50	0.58	7
Velpar® (hexazinone)	Bracken Fern Roots	3	n/a	n/a	n/a	n/a	n/a
Velpar® (hexazinone)	Bracken Fern Roots	4	n/a	n/a	n/a	n/a	n/a
Velpar® (hexazinone)	Buckbrush Shoots	1	3.833	0.104	6.69	0.48	7
Velpar® (hexazinone)	Buckbrush Shoots	2	0.937	-0.011	-60.86	0.03	7
Velpar® (hexazinone)	Buckbrush Shoots	3	1.086	0.023	30.51	0.41	9
Velpar® (hexazinone)	Buckbrush Shoots	4	n/a	n/a	n/a	n/a	n/a
Velpar® (hexazinone)	Golden Fleece Foliage	1	31.730	11.400	0.06	1.00	7
Velpar® (hexazinone)	Golden Fleece Foliage	2	5.200	-0.008	-87.74	0.02	6
Velpar® (hexazinone)	Golden Fleece Foliage	3	291.000	0.571	1.21	1.00	8
Velpar® (hexazinone)	Golden Fleece Foliage	4	n/a	n/a	n/a	n/a	n/a
Velpar® (hexazinone)	Manzanita Berries	1	0.149	0.012	56.54	0.01	5
Velpar® (hexazinone)	Manzanita Berries	2	0.190	0.068	10.25	0.49	5
Velpar® (hexazinone)	Manzanita Berries	3	n/a	n/a	n/a	n/a	n/a
Velpar® (hexazinone)	Manzanita Berries	4	n/a	n/a	n/a	n/a	n/a
Garlon®(triclopyr)	Bracken Fern Roots	1	0.149	0.019	35.95	0.07	7
Garlon®(triclopyr)	Bracken Fern Roots	2	0.277	0.060	11.56	0.73	7
Garlon®(triclopyr)	Bracken Fern Roots	3	0.099	0.379	1.83	0.96	6
Garlon®(triclopyr)	Bracken Fern Roots	4	n/a	n/a	n/a	n/a	n/a
Garlon®(triclopyr)	Buckbrush Shoots	1	9.856	0.273	2.53	0.89	9
Garlon®(triclopyr)	Buckbrush Shoots	2	n/a	n/a	n/a	n/a	n/a
Garlon®(triclopyr)	Buckbrush Shoots	3	87.355	0.317	2.19	0.99	6
Garlon®(triclopyr)	Buckbrush Shoots	4	16.226	28.039	0.02	0.00	5
Garlon®(triclopyr)	Golden Fleece Foliage	1	4.176	0.466	1.49	0.83	7
Garlon®(triclopyr)	Golden Fleece Foliage	2	11.800	17.477	0.04	0.97	7
Garlon®(triclopyr)	Golden Fleece Foliage	3	2.020	0.047	14.63	0.83	8
Garlon®(triclopyr)	Golden Fleece Foliage	4	n/a	n/a	n/a	n/a	n/a
Garlon®(triclopyr)	Manzanita Berries	1	2.525	-0.007	-100.91	0.07	7
Garlon®(triclopyr)	Manzanita Berries	2	2.620	0.008	84.26	0.08	6
Garlon®(triclopyr)	Manzanita Berries	3	n/a	n/a	n/a	n/a	n/a
Garlon®(triclopyr)	Manzanita Berries	4	n/a	n/a	n/a	n/a	n/a

Note: 'n/a' means the data fitting process for equation (4) did not converge during the iteration, or not enough number of samples for meaningful regression.

For some sites, using the time series of concentration data did not generate significant regressions. In other cases, iterations for the nonlinear regression did not converge, so regression coefficients for model (4) could not be obtained. In general, low correlations were associated with low concentrations. For example, glyphosate and triclopyr had higher concentrations, and the correlation coefficients were generally higher. Pronone® concentration was the lowest, and the correlation was also poor. Pronone® concentration fluctuated around the reporting limits throughout

the sampling period. Therefore it was difficult to obtain an accurate concentration measurement. The data did not present a logical decline tendency with time, and the regressions were poor. On the other hand, the concentration of glyphosate was much higher, the variation was relatively small compared to the concentration itself. A decline pattern was clear, and the regression fit was much better.

The average half-life of herbicides in each plant species was calculated based on equation (6) and (7). Results are shown in Table 3. Only a few site-specific data sets contributed to the calculation of average half-life at the 90 % significant level. In some cases (Pronone®), no regression can be used. Because of limited number of field samples, the estimated average half-life may not be reliable, and serious uncertainty exists in these values.

Table 3. Average half-life $\bar{t}_{1/2}$ (weeks) of four herbicides in four plant species (p=0.10)

Herbicide	Bracken Fern Roots	Buckbrush Shoots	Golden Fleece Foliage	Manzanita Berries
Glyphosate	11.5 (1)	9.8 (3)	8.2 (2)	n/a
Pronone	n/a	n/a	n/a	1.7 (1)
Velpar	18.5 (1)	17.6 (2)	0.6 (2)	n/a
Triclopyr	6.1 (2)	2.4 (3)	5.1 (3)	n/a

Note: 'n/a' means no meaningful regression could be obtained; the numbers in parentheses are sample sizes used for the calculation of mean.

In general, Velpar® had the longest estimated half-life (18.5 weeks), followed by glyphosate (11.5 weeks) and triclopyr (6.1 weeks). The dissipation mechanism for herbicides on plant surfaces could be quite different from those absorbed in plant tissues. Herbicides on the surface of leaves and shoots could be dissipated by rain or sunlight, while herbicides inside plant tissues can only dissipate through metabolic processes. The former is a physical process, and the later is a physiological process which could be much slower than the rain wash events. This may explain the longer estimated half-life observed for herbicides in bracken fern roots.

3.4 The time from treatment to non-detectable level

Table 4 presents the number of weeks from the maximum concentration to the non-detect level in the sample. For some sites, the non-detectable level was not reached over the sampling period. In this case, no data was entered into the table. The earliest non-detectable level occurred at 4 weeks after the maximum concentration, and the last non-detect result occurred 130 weeks after maximum concentration. Herbicides lasted longest in buckbrush shoots where it took from 4 weeks to 130 weeks for the pesticides to decrease to the non-detectable levels. However, there was large variations in the number of weeks to reach the non-detectable concentration among different sites. In some cases there was no record for the non-detectable level, and sometimes only one observation was used to calculate the mean. For example, after 36 weeks, there were no manzanita berries left for sampling, so non-detectable levels for herbicides could not be determined.

Table 4. The time from the maximum concentration to non detectable level (weeks)

Pesticide	Plant	site 1	site 2	site 3	site 4	Average
Glyphosate	Bracken Fern Roots	8	n/a	n/a	4	6
Glyphosate	Buckbrush Shoots	n/a	n/a	n/a	n/a	n/a
Glyphosate	Golden Fleece Foliage	n/a	60	n/a	24	42
Glyphosate	Manzanita Berries	n/a	n/a	n/a	n/a	n/a
Pronone	Bracken Fern Roots	4	n/a	24	60	29
Pronone	Buckbrush Shoots	4	4	4	4	4
Pronone	Golden Fleece Foliage	12	16	20	12	15
Pronone	Manzanita Berries	8	8	8	8	8
Velpar	Bracken Fern Roots	4	n/a	n/a	n/a	4
Velpar	Buckbrush Shoots	n/a	n/a	n/a	130	130
Velpar	Golden Fleece Foliage	20		20	n/a	20
Velpar	Manzanita Berries	8	4	n/a	n/a	6
Triclopyr	Bracken Fern Roots	8	24	8	4	11
Triclopyr	Buckbrush Shoots	n/a	n/a	n/a	n/a	n/a
Triclopyr	Golden Fleece Foliage	n/a	n/a	n/a	56	56
Triclopyr	Manzanita Berries	n/a	n/a	n/a	n/a	n/a

Note: “n/a” means non-detectable level was not recorded.

3.5 Off-site movement

In all 240 off site samples (not including the background samples), only 19 samples (7.9%) showed detections (Table 5). About 1/3 of detected concentrations were close to the reporting limits. No herbicides were detected from bracken fern roots. Glyphosate, Pronone® and Velpar® were detected in buckbrush shoots and deerbrush shoots. Triclopyr, was repeatedly detected from two stands of deerbrush shoot, suggesting the positive concentration was not likely the result of sample contamination. Most offsite herbicides were detected during the week of treatment. However, the last positive detection was up to 12 weeks after treatment. If a positive result was detected in a later sample but not in a early sample, sample contamination might have played a role. Off target drift during the application and transport with runoff water after application might be the main mechanisms for the offsite movement.

Table 5. Detected off-site movement of herbicides

Pesticide	Plant Part	Forest	District	Stand	Distance (ft)	Weeks After Treatment	Concentration (ppm)
Glyphosate	Buckbrush shoots	Sierra	Pineridge	Musick 071	05 - 15	0	0.10
Glyphosate	Buckbrush shoots	Sierra	Pineridge	Musick 071	20 - 40	12	0.11
Glyphosate	Deerbrush shoots	Stanislaus	Mi-Wok	1171750	05 - 15	0	0.197
Glyphosate	Deerbrush shoots	Eldorado	Placerville	613-042	05 - 15	0	2.68
Glyphosate	Deerbrush shoots	Stanislaus	Mi-Wok	1171750	05 - 15	4	0.101
Glyphosate	Deerbrush shoots	Eldorado	Placerville	613-042	05 - 15	4	0.121
Glyphosate	Deerbrush shoots	Eldorado	Pacific	501-120	20 - 40	12	0.1 - 1
Velpar	Buckbrush shoots	Stanislaus	Mi-Wok	E121	80 - 100	0	0.124
Velpar	Buckbrush shoots	Sierra	Pineridge	336-149	50 - 70	12	0.673
Pronone	Buckbrush shoots	Stanislaus	Mi-Wok	E061	50 - 70	0	0.131
Pronone	Deerbrush shoots	Stanislaus	Mi-Wok	R041	50 - 70	0	0.1 - 1
Pronone	Deerbrush shoots	Stanislaus	Mi-Wok	R041	05 - 15	0	0.1 - 1
Triclopyr	Deerbrush shoots	Stanislaus	Mi-Wok	1171750	05 - 15	0	0.03 - 0.3
Triclopyr	Deerbrush shoots	Stanislaus	Mi-Wok	1171750	20 - 40	0	0.03 - 0.3
Triclopyr	Deerbrush shoots	Stanislaus	Mi-Wok	1171750	50 - 70	0	0.03 - 0.3
Triclopyr	Deerbrush shoots	Eldorado	Placerville	613-042	05 - 15	0	1.56
Triclopyr	Deerbrush shoots	Eldorado	Placerville	613-042	20 - 40	0	0.07
Triclopyr	Deerbrush shoots	Eldorado	Placerville	613-042	50 - 70	0	0.06
Triclopyr	Deerbrush shoots	Eldorado	Placerville	613-042	80 - 100	0	0.03

4. Discussion

There are two kinds of herbicide residues in plants: the surface residue and the tissue residue. The surface residues are those deposited on plant surfaces. The concentration from surface residues is high immediately after treatments. However, it drops rapidly with time. The tissue residues are those absorbed by plant tissues. Although the concentration of tissue residues is usually very low, it takes a long time to dissipate. The first type of concentration occurred mainly at plant surfaces that are directly exposed to droplets of herbicide spray, such as leaves and shoots, and sometimes the berries. The second type of contamination occurred in plant tissues both above and under the ground. Corresponding to these two contamination pathways, the herbicide residues on surface of plant leaves and shoots can dissipate by physical events, such as rainfall, volatility and sunlight, while herbicide residues inside plant tissues breakdown slowly. Therefore, herbicide residues decline faster in leaves and shoots, and slower in roots and berries. Off-site movements should not be a serious concern, as only a very low percentage of samples were detected to have herbicide residues at concentrations close to the reporting limits. Because spray droplets tend to introduce higher herbicide residues on plant surfaces, using a granular form will significantly reduce the risk of herbicide exposure to tribal people.

The data used for this analysis was from a large scale field survey that covered four areas and lasted more than three years. Variation among the repeated sampling was expected. Many factors, such as soil types, plant status, weather conditions, application methods, sampling techniques and lab analysis protocols, might have contributed to the variation. Therefore, uncertainties exist in above

quantitative analysis, such as the half-life time, the time needed to non-detectable levels, and the offsite movement. The values obtained from above analysis might not be representative, given the fact of limited number of samples for robust statistical analysis. However, the data presented a pattern that supports the conceptual model of herbicide dissipation and off-site movement. A better controlled experiment would be helpful to verify and refine the results obtained from this analysis.

5. Summary

In general, residues of glyphosate were significantly higher in all plant parts than other herbicides except in bracken fern roots. Hexazinone from Pronone® had the minimum residue in all plant parts. The herbicides had the lowest residues in bracken fern roots of less than 1 ppm. Except glyphosate, all herbicides had low residues in manzanita berries. Buckbrush shoots and golden fleece foliage had higher herbicide residues(except glyphosate) than manzanita berries and bracken fern roots.

Acknowledgment

This report was reviewed by Kean Goh, the project supervisor, and by Terri Barry and Randy Segawa, the senior environmental research scientists in the Department of Pesticide Regulation. Clarice Ando, the project coordinator, provided the monitoring data for the analysis. They offered valuable comments and suggestions which greatly helped writing of this report.

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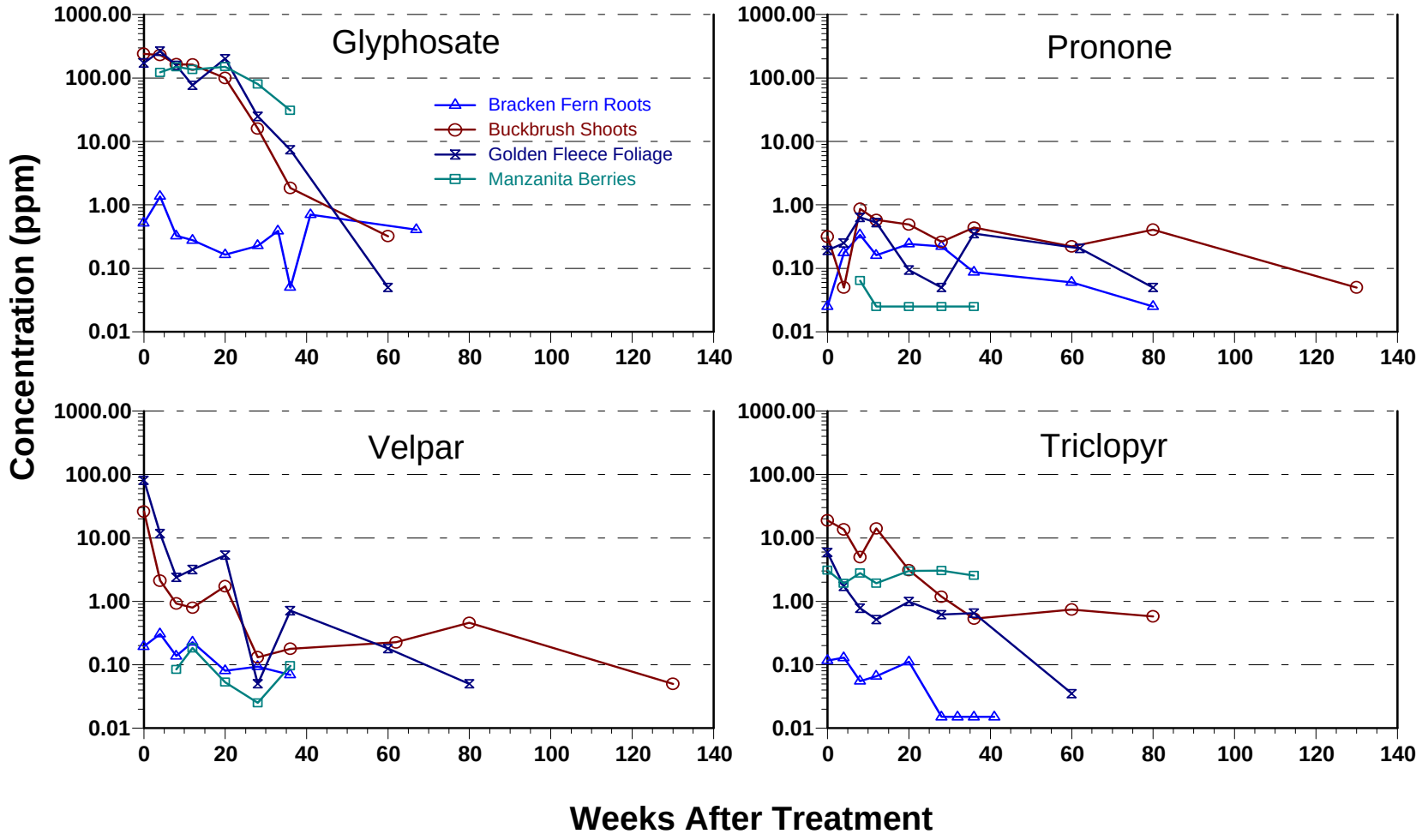

Figure 1 Herbicide dissipation in plant materials, sampled from Eldorado, Lassen, Sierra and Stanislaus in California, 1997-2000 (Grouped by herbicide)

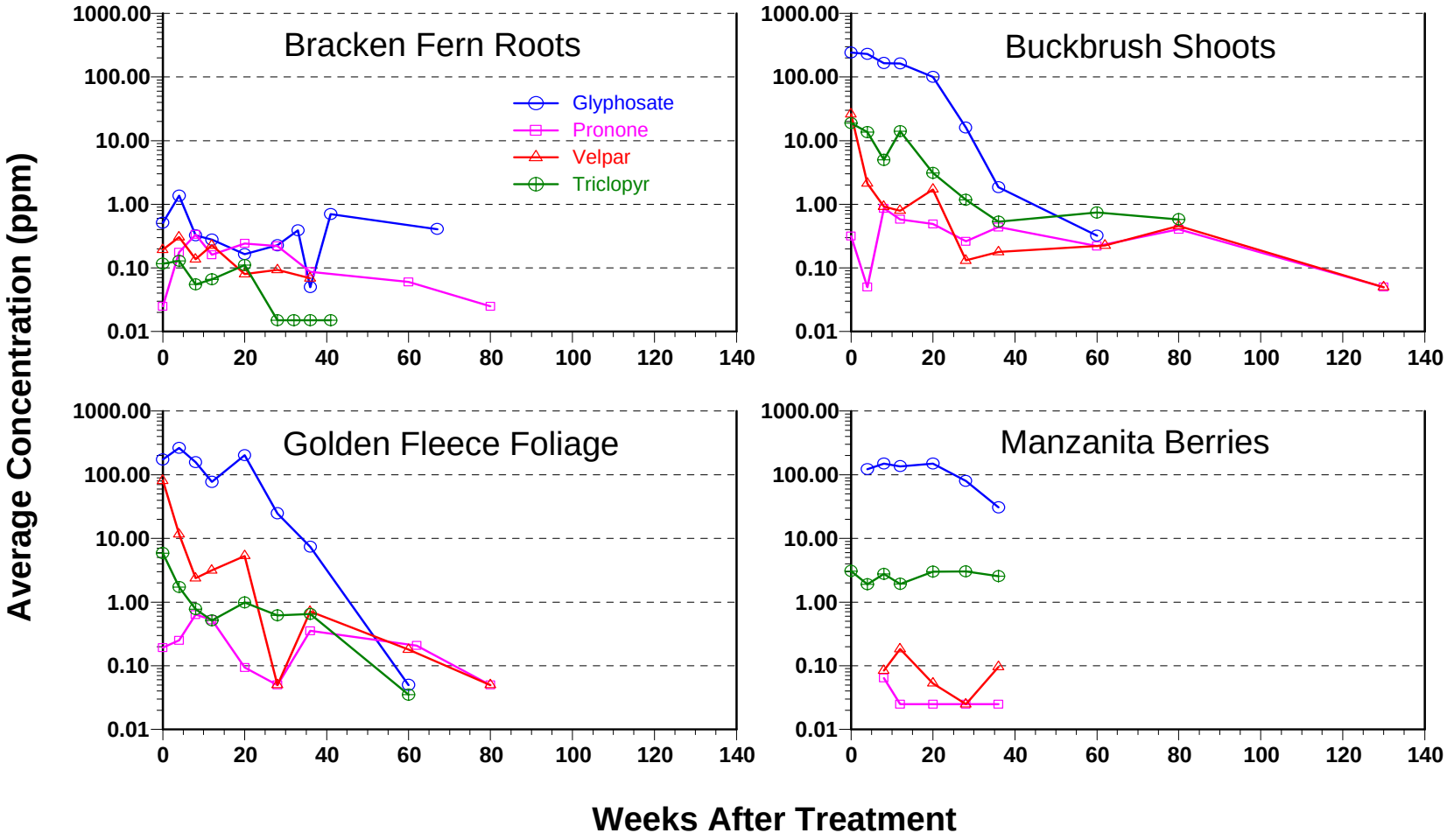

Figure 2 Herbicide dissipation in plant materials, sampled from Eldorado, Lassen, Sierra and Stanislaus in California, 1997-2000 (Grouped by plant material)

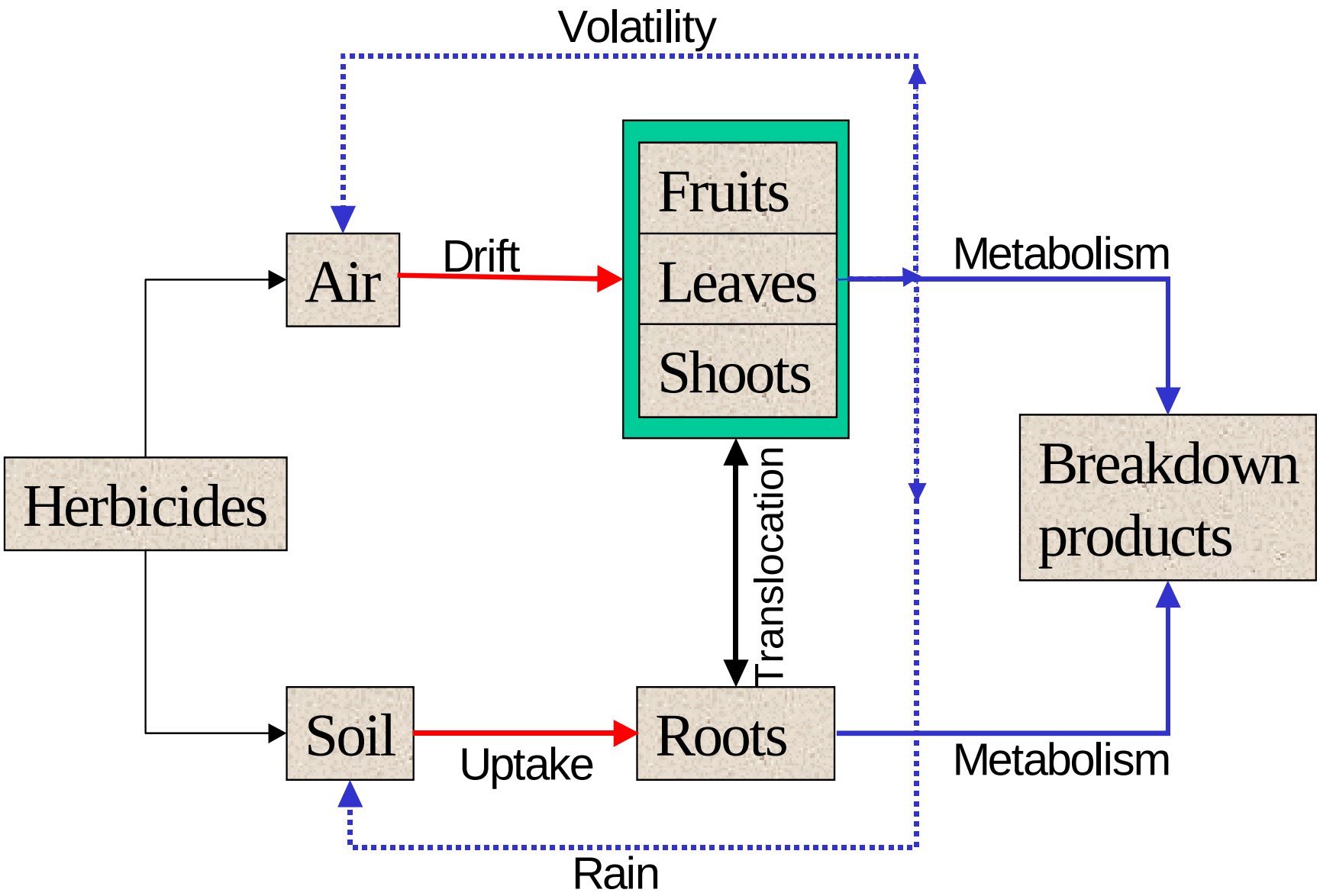

Figure 3 A conceptual model for the environmental fate of herbicides

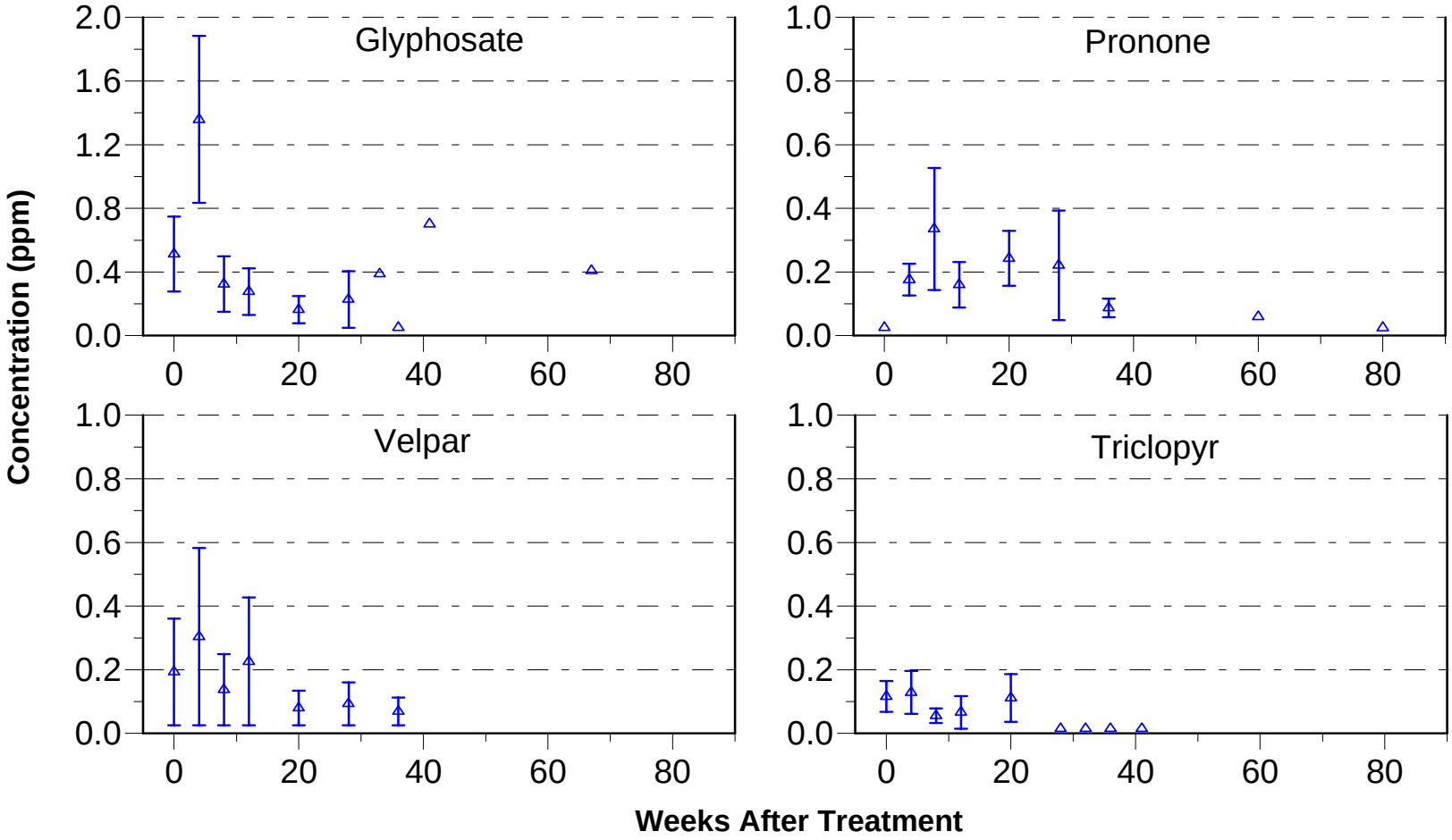

Figure 4 Herbicide Residuals in Bracken Fern Roots

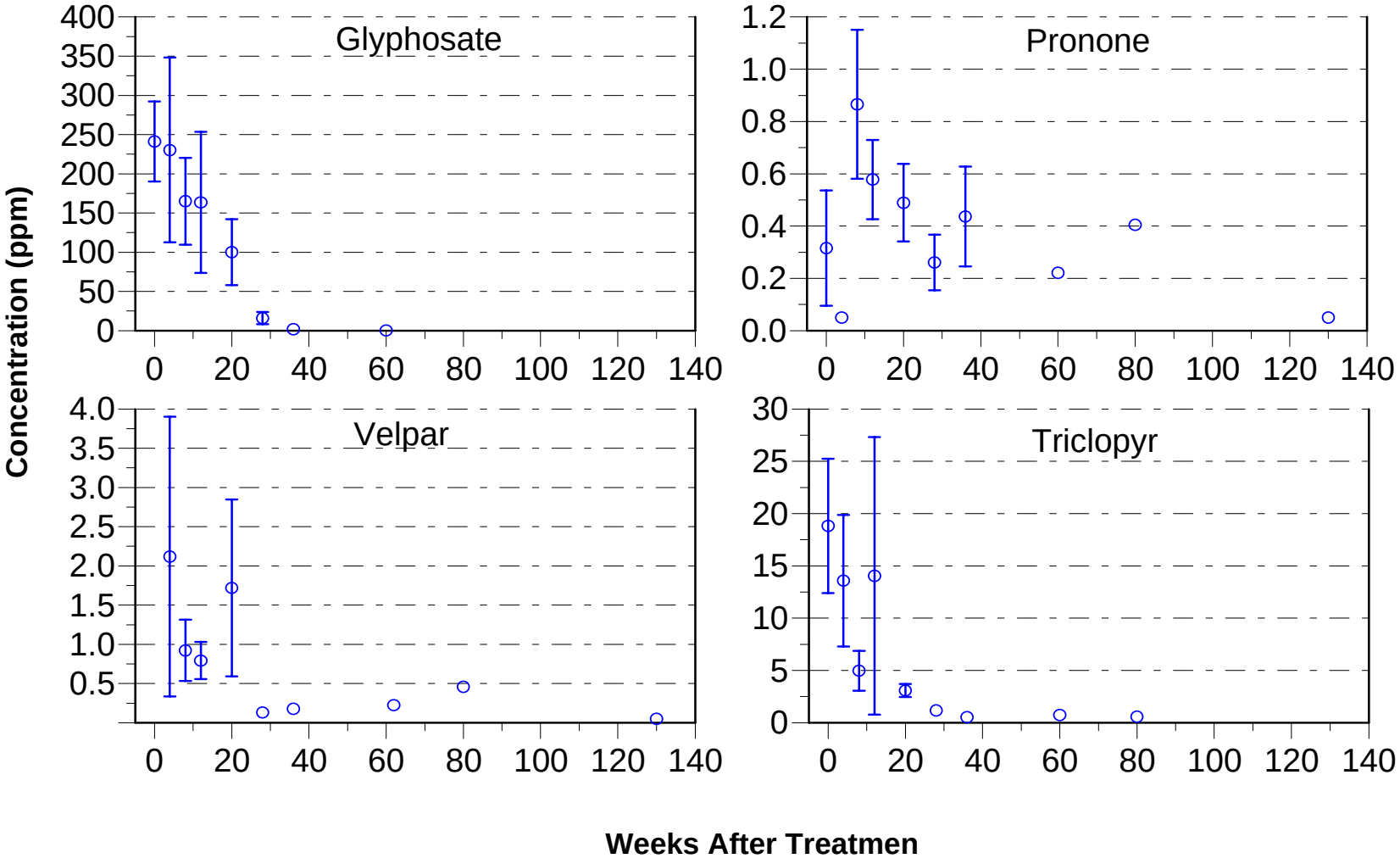

Figure 5 Herbicide Residual in Buckbrush Shoots

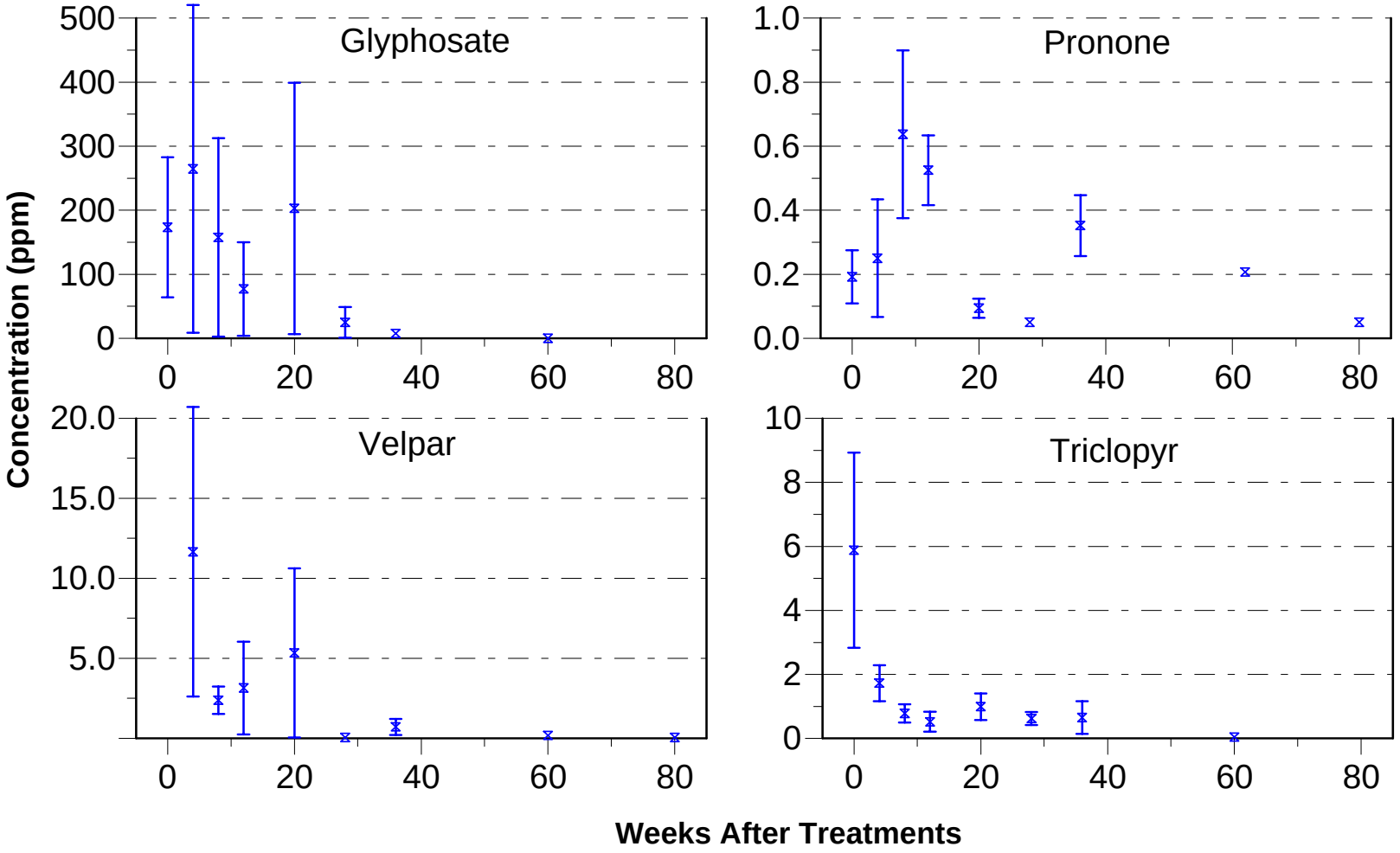

Figure 6 Herbicide Residuals in Golden Fleece Foliage

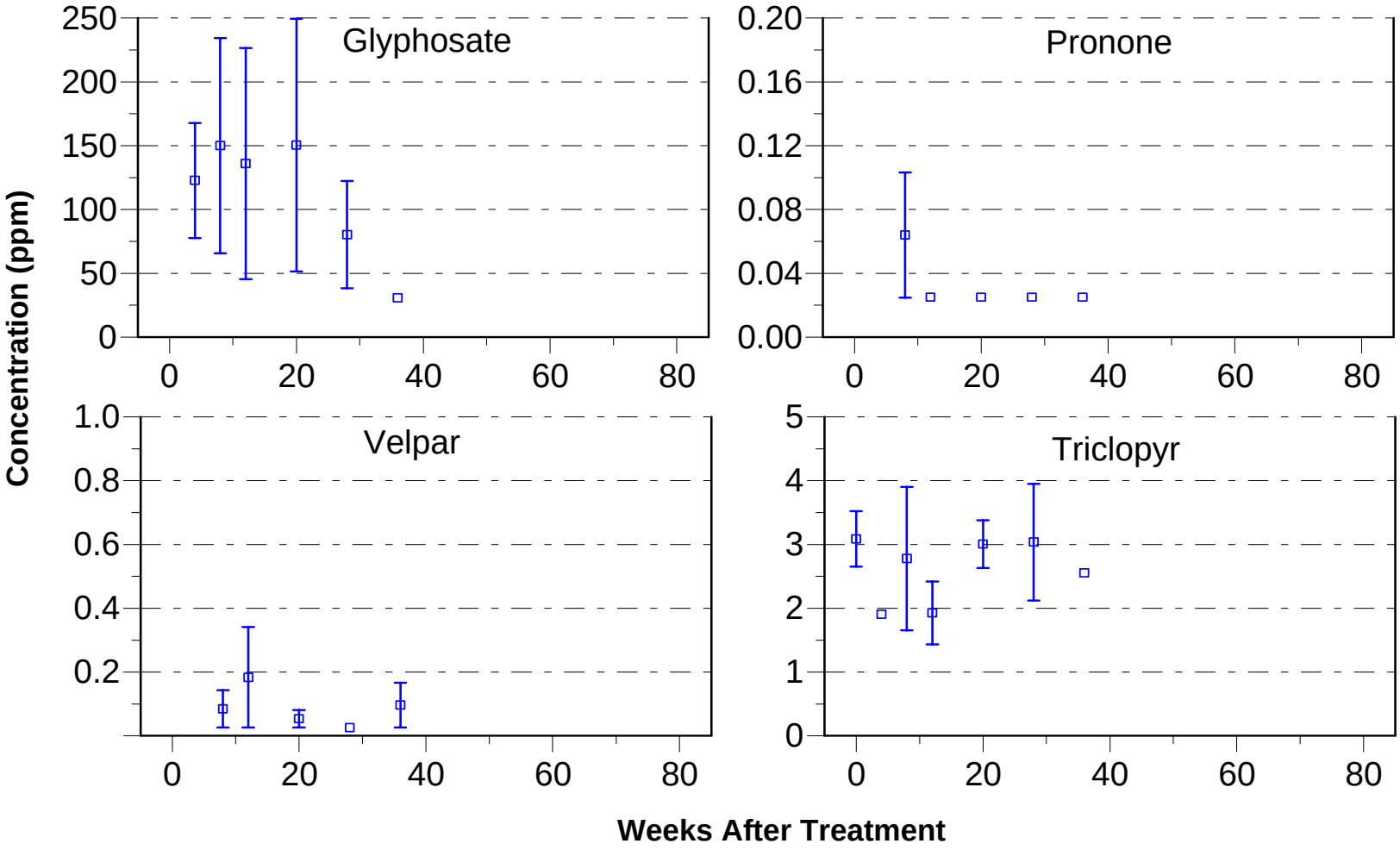

Figure 7 Herbicide Residuals in Manzanita Berries