Forest Herbicide Residues in Surface Water and Plants in the Tribal Territory of the Lower Klamath River Watershed of California

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MAY 2003

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By

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ACKNOWLEDGEMENTS

We would like to thank the members of the Yurok Environmental Monitoring Workgroup, (YEMWG) for their guidance: Lori Harder McKinnon (Yurok), John Melvin (Yurok), Ken Childs, Sr. (Yurok), Richard Myers (Yurok), Susan Burdick (Yurok), Jene McCovey (Yurok), Kevin McKernan (Yurok Tribal staff), Marty Geslak (Yurok Tribal staff), Ora Smith (Karuk), LaVerne Glaze (Karuk), Renee Stauffer (Karuk), Holly Hensher (Karuk), Ron Johnson (CSU Humboldt), Jennifer Kalt (CIBA), Wendy George (CIBA), Bessie Lee (former Yurok Tribal staff), and Chuck Striplen (former Hoopa Valley Tribal staff/Ohlone). We would also like to thank the California Department of Food and Agriculture Center for Analytical Chemistry Laboratory personnel, Cathy Cooper, Leanna Ortiz, Ryan Wichert, Irene Aguilar, Teresa Woreniecka, Jim Echelberry, Janice Temple and Aurora Vasquez for their hard work and the field sampling crew, Roger Sava, Johanna Walters, Nina Bacey, and the West Sacramento DPR crew, Carissa Gana and Jesse Ybarra, for sample handling and equipment assistance. We would like to thank Mark Pepple for reviewing this report. Special thanks to the Humboldt and Del Norte County Agricultural Commissioner's John Falkenstrom and Glenn Anderson, respectively, and especially their staff Jeff Dolf and Dave Cavyell. We would also like to thank the personnel at the Simpson Timber Company for their assistance, with special thanks to John Pricer for his invaluable help. Finally, we would like to thank Paul Gosselin, John Sanders, and Kathy Brunetti for their guidance and support.

This study was funded by the U.S. Environmental Protection Agency cooperative agreement E-999393-10-2. We acknowledge the assistance of Nancy Frost and the project manager Annie Yates.

DISCLAIMER

The mention of commercial products, their source, or use in connection with material reported herein is not to be construed as an actual or implied endorsement of such product.

ABSTRACT

This study addresses tribal concerns about the potential presence of herbicide residues in waterways and on plant materials in the Lower Klamath River Watershed as a result of applications of forestry herbicides in the vicinity. Five sites, where herbicides were applied by helicopter, were monitored for drift onto waterways during application: glyphosate was applied to one site and triclopyr or triclopyr/2,4-D mixture to four sites. Residues of 2,4-D and triclopyr were detected at one site only with the highest concentrations at 0.58 ppb and 1.06 ppb, respectively. Twelve sites were monitored for runoff from an application area during a rain event. No rain runoff was recorded from the four ground application sites for atrazine. Only three sites from aerial applications had runoff into the waterways below the application area. The highest concentrations detected in the samples were 0.24 ppb and 0.43 ppb for 2,4-D and triclopyr, respectively. All of the concentrations measured in the water samples were below the U.S. EPA's drinking water standards and any other federal or state recommended level for freshwater protection.

For impact on plants, four sites were monitored for off-site movement during application. Drift was detected at two application areas. The farthest distance that residues were detected on plants was 30 to 41 feet outside the application area, where plant samples averaged 0.14 ppb and 0.10 ppb for triclopyr and 2,4-D, respectively. For dissipation of herbicides after application, six sites in five treatment areas and four plant species namely, beargrass, huckleberry, yarrow, and manzanita berry, were monitored over time. Plants in four of the sites contained no detectable herbicide residues by approximately 150 days. The other two sites had measurable amounts of herbicide at approximately day 60, but contained no residues at the next sampling date of 370 days (53 weeks). Samples of new growth on plants collected more than a year after application contained no detectable amount of triclopyr or 2,4-D.

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INTRODUCTION

From time immemorial, the Yurok people occupied the Yurok ancestral territory (Figure 1). This territory encompasses the lower 52 miles of the Klamath River from a short distance above the confluence of the Trinity River to the Pacific Ocean, and a longer stretch of seacoast from Damnation Creek, Del Norte County, to the Little River in Humboldt County (Yurok Tribe, 1999). The Yurok Tribal Reservation boundary, partially designated in 1856 and reaffirmed in 1892, is located one mile each side of the lower Klamath River from Weitchpec to the mouth at Requa (Yurok Tribe, 1999). The reservation has a checkerboard pattern of Tribal, public, and privately owned property of which approximately 85 percent is privately owned. The majority of the private lands within the reservation are owned and managed by Simpson Timber Company.

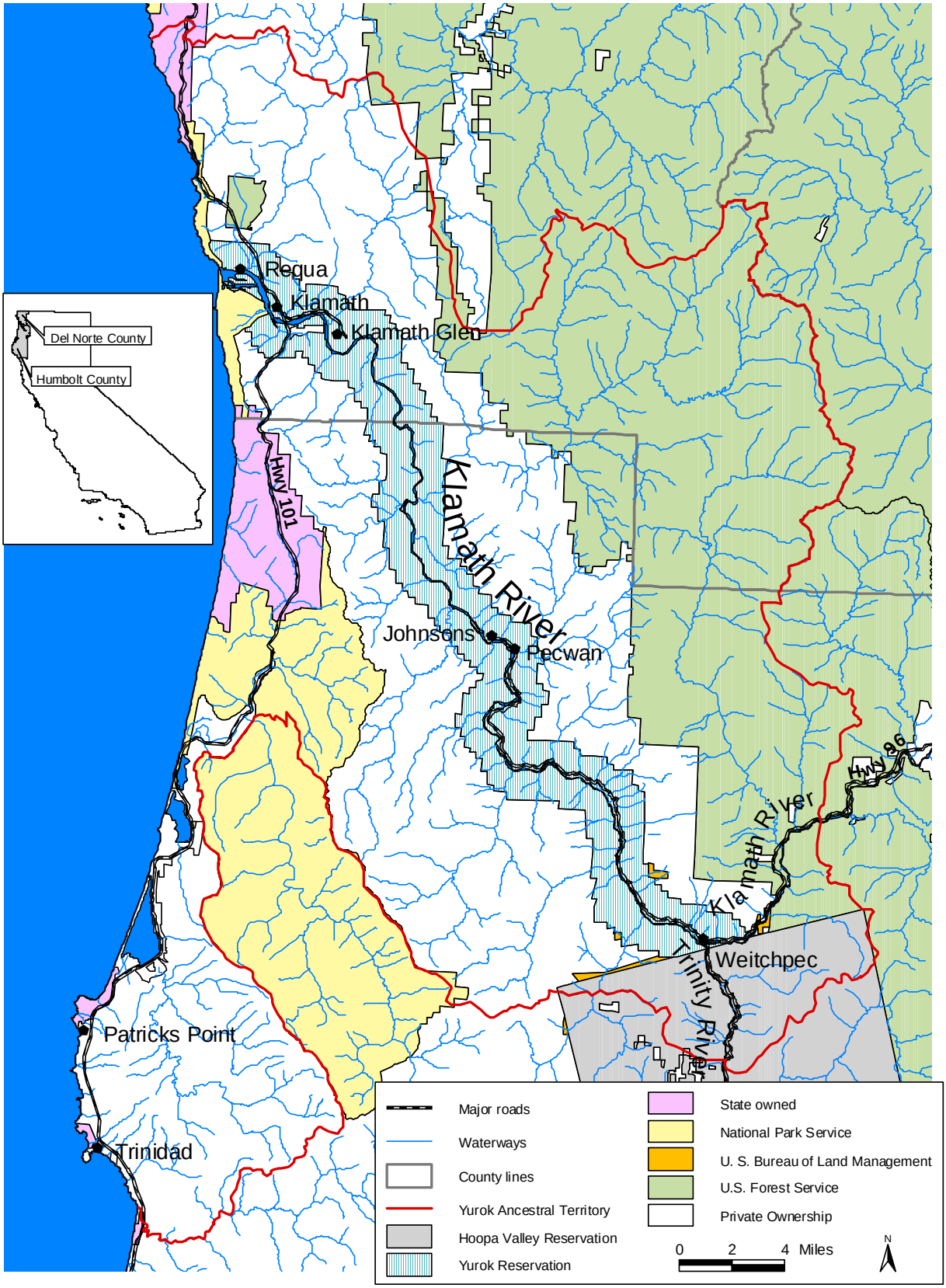
The timber industry uses "Best Management Practices", which may include the use of herbicides to control the growth of competitive vegetation prior to tree planting, during site preparation and for stand improvement. These herbicides are used on the private forest lands which lie within and adjacent to Yurok ancestral and reservation lands. California Indians have historically had a very intimate relationship with their environment, and a strong tradition of using native animals and plant materials for food, basketry, medicine, and other cultural activities. Plants are integral to many facets of Indian culture and are gathered and handled in the ways of tribal tradition. Food and material resources are gathered throughout the year, using sites and techniques that are passed down in the family. The tribal people hold plants in high reverence and are determined to protect their cultural resources and traditions.

Indian tribes gather a wide variety of plants in the following categories: berry or fruit plants, acorn or nut bearing plants, mushrooms, perennial grasses, ferns, riparian shrubs, and woody shrubs. These materials are collected in a variety of ways, depending on the plant species. Typically, each plant has a desirable part, whether it is roots, bark, foliage or stems, and only what is needed is taken. Basketweavers and other gatherers collect forest materials often with their bare hands, and some materials are placed in the mouth and chewed to prepare them for weaving. Since gathering sites may be near treated timber areas, tribes are concerned about

their potential exposure to forestry herbicides in gathering and use of these plant materials. Tribes are also concerned about pesticide residues in the animals they consume which feed on plants in the treated areas or fish which come from waters which may be contaminated by pesticide residues.

In addition to exposure to the herbicides on plant material and in animal tissue, tribes are also concerned with exposure to herbicides in waterways. Annual rainfall averages 20 to 100 inches per year (Barrett, 1995) and the surface water supply originates from a massive network of smaller watersheds linked by streams throughout the hydrologic basin (California Department of Forestry, 1979). The higher amounts of rainfall have more potential to move the herbicides off an application site into the watershed system. Studies conducted in other forested areas of California have shown that herbicide residues may be transported off-site in rain and/or snowmelt runoff water (Carlson and Fiore, 1993). Consequently, residents in the Klamath River basin, have expressed concern about the potential presence of herbicide residues in their drinking water.

Figure 1. The Yurok ancestral territory and study area.



For this reason, the tribal people of northwestern California have requested that the California Department of Pesticide Regulation (DPR) and the U.S. Environmental Protection Agency (U.S. EPA) Office of Pesticide Programs monitor surface waters and plants of interest for herbicide residues used in reforestation practices in that region. The herbicides used most often in the timber management industry include, atrazine, 2,4-dichlorophenoxyacetic acid (2,4-D), glyphosate, triclopyr, sulfometuron methyl, imazapyr, and hexazinone, all of which are compounds currently registered in California for forestry use. Hexazinone can damage redwood trees and is therefore not used in the Lower Klamath River basin.

This study was conducted in collaboration with U.S. EPA and the Yurok Tribe to address tribal concerns about the potential presence of herbicide residues in waterways and on plant material. In 1998, the Yurok Environmental Monitoring Workgroup (YEMWG) was formed to investigate Tribal concerns about pesticide use as it relates to community health. The YEMWG is composed of Tribal members and staff from the Yurok Tribe as well as members from the Karuk and Hupa Tribes. In addition, the workgroup included staff of DPR, the Del Norte and Humboldt County Agricultural Commissioners Office, the Simpson Timber Company, and members of the California Indian Basketweavers Association (CIBA). The Simpson Timber Company provided full assistance and access to the property for the monitoring study. The study plan was designed in consultation with the YEMWG. YEMWG meeting notes are located in Appendix A. This report summarizes data collected over a three-year period (1999-2002) in the Lower Klamath River Watershed Basin during the study.

Study Area

The study area boundary includes almost all of the areas encompassed in the ancestral territory of the Yurok Tribe and is located in Del Norte and Humboldt Counties (Figure 1). It is almost entirely privately owned property utilized for harvest of forestry products. The study area ranges from coastal redwood environment to fir and oak woodland. Much of the land is steeply inclined with small intermittent creeks and larger waterways flowing through it. The coastal climate is cool, moist and often foggy, with rainy winters in the lower elevations and

snow at the higher elevations. Inland the climate is much drier with low rainfall in the winter and hot, dry summers.

Pesticides Monitored

The pesticides monitored are chemicals applied to control non-commercial forest plants for the optimization of growth of the crop trees. Table 1 presents a general description of the herbicides monitored. Atrazine is a pre-emergent soil-applied herbicide used to control growth of new weedy plants following harvest, burning, and planting of seedling trees in a forested area. The application of the herbicide provides the new seedlings time to become established without competition from other plant species. Atrazine is a selective herbicide used to control broadleafs and grasses through absorption in the roots. Atrazine is usually applied directly to the soil using a hand-held backpack sprayer and needs some rainfall for incorporation into the soil. 2,4-dichlorophenoxyacetic acid (2,4-D), triclopyr, and glyphosate are post-emergent foliar-applied herbicides to control growth of established unwanted plants. 2,4-D and triclopyr are selective to broadleaf species, both herbaceous and woody. The application of the foliar applied herbicides is usually made to "release" the established conifer trees from competition from faster growing target broadleaf species. The applications can be made as an aerial application by helicopter, as a broadcast ground application with a backpack sprayer to target plants, or as a "hack and squirt" application made directly into a cut on the tree or bush. During this study, aerial applications were made with a helicopter at a height of 10 to 50 feet above the application area. The Bell helicopter was equipped with a 35' 6" back spray boom outfitted with 38 Tee jet D nozzles. In addition to these four herbicides, sulfometuron methyl (Oust®) herbicide was also applied in the area but the analytical laboratory used for this study did not have the methods available at the time. The herbicides are often applied as tank mixes for application to the same area. Table 2 presents the label information for the herbicide products applied during the study.

Table 1. Herbicides monitored during the study.

Pesticide	Use	Chemical Class
Atrazine	pre-emergent	triazine
2,4-D	post-emergent	phenoxy
Glyphosate	post-emergent	glycine phosphorus
Triclopyr	post-emergent	phenoxy

Table 2. The products used and label information.

Pesticide	Product Used	Formulation Type	Percentage of Active Ingredient	Label Application Rate per Acre
Atrazine	Aatrex 4L®	Not applicable	40.8 %	4 – 8 pints
2,4-D	Solve® 2,4-D, See ® 2,4-D	2-ethylhexyl ester	61.74 %	1.5 – 3 quarts
Glyphosate	Accord®	isopropylamine salt	41.5 %	2 – 10 quarts
Triclopyr	Garlon 4®	butoxyethyl ester	61.6 %	1 – 4 quarts

Physical and chemical properties for the herbicides monitored are located in Table 3. Atrazine is highly persistent in soil. Chemical hydrolysis and degradation by soil microorganisms account for most of the breakdown of atrazine. Although it has only moderate water solubility, it does not adsorb strongly to soil so has the potential to move off in water, whether surface or ground. Atrazine is not expected to adsorb strongly to sediment.

The 2,4-D 2-ethylhexyl ester formulations used during the study quickly degrades to the parent acid. 2,4-D has a moderate persistence in soil. Microbial degradation is considered to be the main route of breakdown in soil and water. The rate of breakdown increases with increased nutrients, sediment and dissolved organic carbon. Because 2,4-D has a high water solubility factor, it is susceptible to runoff.

Glyphosate is moderately persistent in soil. It is strongly adsorbed to most soils, and therefore has a low potential for runoff except when adsorbed to suspended matter which can be washed off into water. Glyphosate remains tightly bound to the suspended matter even in water. Microbes are responsible for most of the breakdown of the chemical.

The triclopyr formulation applied during this study was the butoxyethyl ester form which rapidly converts to the triclopyr acid by hydrolysis in both soil and water. Triclopyr acid is degraded by soil microorganisms and has a moderate persistence in soil. It is not strongly adsorbed to soil particles and has a potential to run off.

Table 3. Physical and chemical properties for the herbicides monitored.

Chemical	Molecular Weight (g/mole)	Water Solubility[a] (ppm)	Vapor Pressure[b] (mmHg)	Hydrolysis Half-life[c] (days)	Aerobic Soil Half-life[d] (days)	Soil Photolysis Half-life (days)
Atrazine	215.68	32.5	3.00×10^{-7}	>30	146	38
2,4-D	221.04	3.39×10^{4}	1.40×10^{-7}	39	66	393
Glyphosate	169.08	1.16×10^{4}	7.5×10^{-8}	>35	96	N/A
Triclopyr (butoxyethyl ester)	356.67	6.81	3.60×10^{-6}	0.5	N/A	N/A

data from Kollman and Segawa, 1995.
[a] 20 -25 °C, pH 7
[b] 20 - 25 °C
[c] 20 - 25 °C; pH 7 - 7.5 average over several soil types
[d] 25 °C
N/A = Not available.

Pesticide Use

The information given in this section was extracted from DPR's pesticide use report database (PUR). The PUR contains information on nearly all production agricultural pesticide use and all commercial use (agricultural and nonagricultural). The data collected for production agricultural uses include the pesticide product used, the date it was applied, the amount applied, and application location to a square-mile section. A complete description of the pesticide use report database is given in DPR, 1995.

Between 1997 and 2001, approximately 27,000 pounds of active ingredient of the four herbicides were used for forestry production in the Yurok ancestral territory, with an average of approximately 4,200 pounds of active ingredients (a.i.) per year (Table 4). The amount of herbicide use varies from year to year.

Table 4. Total pounds of chemical active ingredient and acres treated for 1997 – 2001 for forestry production in the Yurok ancestral territory.

	1997		1998		1999		2000		2001	
	Pounds a.i.	Acres Treated	Pounds a.i.	Acres Treated	Pounds a.i.	Acres Treated	Pounds a.i.	Acres Treated	Pounds a.i.	Acres Treated
2,4-D	276	130	233	128	424	300	2642	1870	1450	1002
Atrazine	48	117	279	79	522	136	989	210	283	78
Glyphosate	25	83	0	0	145	140	0	0	0	0
Imazapyr	0	0	0	0	2	10	686	1370	606	1342
Triclopyr	1185	311	1897	828	3073	1615	4731	2798	2856	1600
Grand Total	**1534**	**641**	**2409**	**1035**	**4166**	**2201**	**9048**	**6248**	**5195**	**4022**

Data from DPR (1997, 1998, 1999, 2000, 2001)

Sampling Site Selection

Sampling sites were determined by proximity to application areas, accessibility, safety of the sampling crew, and availability of sampling material (water or plant material). Sample sites were selected in collaboration with Simpson Timber company personnel prior to application.

Water Sampling Sites

During the YEMWG meetings, the Yurok Tribal representatives had selected several creeks that were of interest. These included the Blue Creek, Hunter Creek, Pecwan Creek, Redwood Creek, Roach Creek and Wilson Creek (Figure 2). It was agreed that these watersheds would be considered first for monitoring if applications were made in their watersheds. Others creeks and rivers were also selected for monitoring due to proximity to an application and presence of water.

Water sampling sites were located as close as possible to an application area. Water samples were collected during and immediately following application to monitor drift during aerial applications. In addition, water samples were collected during the first rainfall events following application to monitor movement of the herbicide off-site into waterways. Sampling sites for rainfall events were selected to catch runoff from as much of the total application area as possible, while still being as close as possible to the application areas. Sites were often

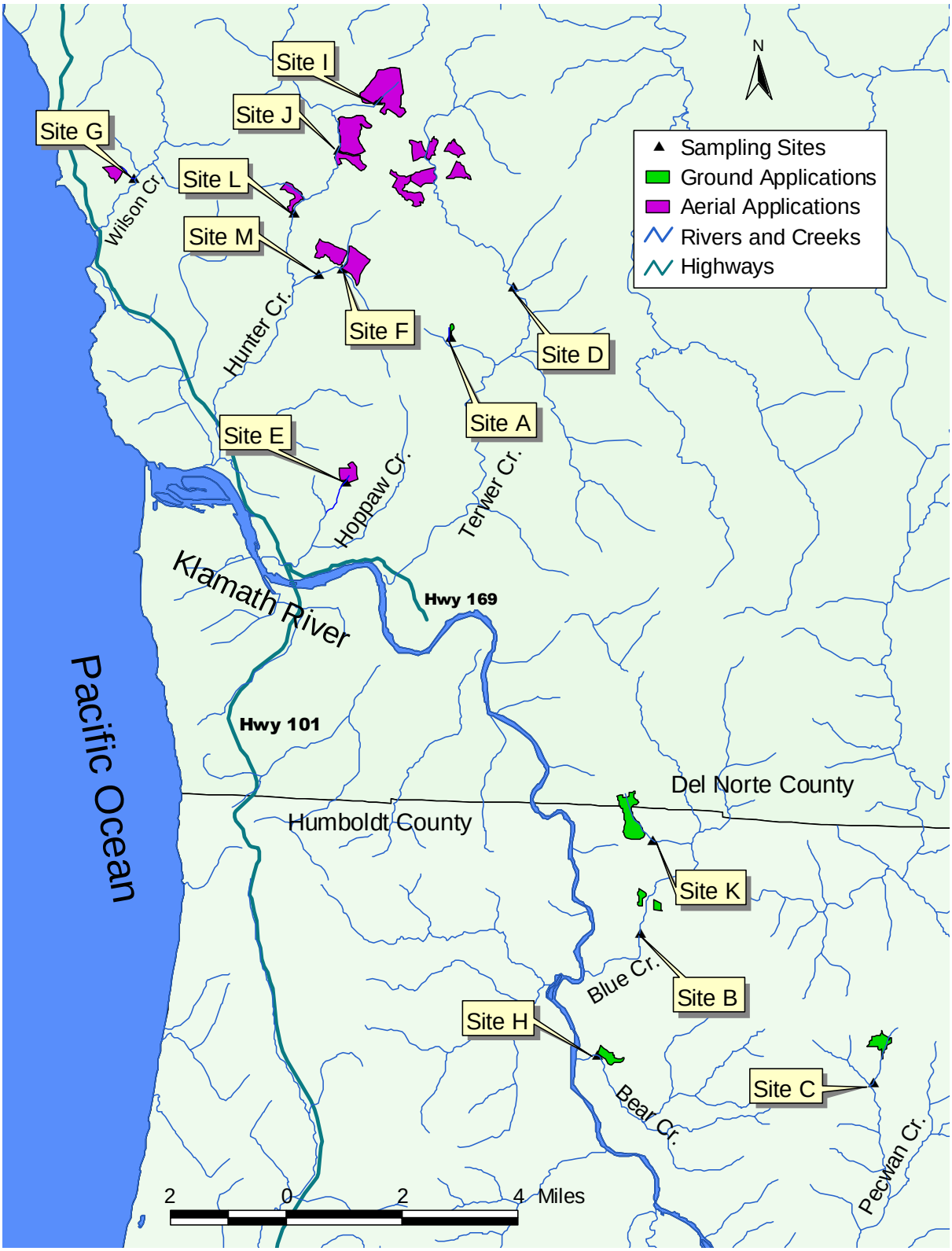
selected to correspond with North Coast Regional Water Quality Control Board (NCRWQCB) approved monitoring locations used by the Simpson Timber Company.

Plant Sampling Sites

Concern was expressed over the exposure to pesticides around areas treated with herbicides in the forest. The YEMWG decided to sample within application areas to determine how long it would take for herbicides to break down and in areas alongside applications to determine how far away from applications to gather plant material. Additional plant sampling was conducted in cooperation with Karuk Tribal members and Hoopa Valley Tribal staff at traditional gathering sites and in a site previously treated for a noxious weed.

Plant sampling sites were determined mainly by the availability of selected plant species and accessibility to the plants. The YEMWG selected eight plants to monitor based on the importance of use and the availability of existing analytical methods. Plant sample areas to test for off-site movement of the applied herbicides were generally located on the downwind side of the application, and were primarily chosen based on the availability of an adequate amount of selected plant material at various distances from the edge of the application area. The selection of dissipation sites was mainly determined by the availability of enough plant material to allow sample collection over multiple time periods.

Figure 2. Locations of water sampling sites.



MATERIAL AND METHODS

The sample collection design was based on the data quality objectives as well as on input from the YEMWG. This section describes the types of samples collected, sample collection methods, sampling materials used, sample handling and quality control methods.

Water Monitoring

All samples were collected in accordance with the Environmental Monitoring Study 172 protocol " Surface Water Monitoring for Forest Herbicides in the Yurok Aboriginal Territory" (Appendix B). All water samples were collected as a grab sample from the main flow of the creek using an ISCO® automatic sampler model 6700 or 2700 (SOP EQWA005.00, Appendix C). The sampler was triggered by a sensor that was set to activate when the water level in the waterway had risen approximately one inch or 0.5 inches of rain had collected in a rain collector beaker. At each sampling site and interval, one liter of water was collected for each herbicide to be analyzed. The ISCO® sampler contains sampler collection bottles which are secured within the base of the sampler. Following sample collection by the autosampler, the base was opened up and the samples were poured from the sampler collection bottles into a one-liter amber glass bottle through a stainless steel funnel. The funnel was triple rinsed with deionized water between each sample. The samples collected were analyzed only for the herbicide or herbicides applied to the site.

In addition to collection of water samples, water quality measurements were made at each sampling site. Water quality parameters measured *in situ* included temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO). Water pH was measured using a Sentron model 1001 pH meter. Water temperature and EC were measured using an Orion model 140 conductivity-salinity meter. DO was measured using a YSI® model 58 dissolved oxygen meter.

Sampling Procedure

Samples from the application tank were collected for each area monitored to determine the percentage of active ingredient being applied. Water samples were collected during applications and/or during the first rain runoff event following applications that produced a significant increase in water level at the sampling site.

Samples taken during and after an aerial application were collected in coordination with Simpson Timber Company personnel. Simpson Timber Company collects water samples during aerial applications in accordance with an agreement with the North Coast Regional Water Quality Control Board (NCRWQCB) who reviews the Monitoring and Reporting Program for the Simpson Timber Company. The NCRWQCB reviews monitoring sites for the applications and determines the time when the sample should be collected depending on distance from the application, slope of the waterway, and length of the waterway in the application area. The samples collected for this study were set to bracket the timing of the timber company's sample and then extend over a period of time to catch any residual drift settling after the end of the application period. Eight samples were collected for each sampling event, four were collected within the short time period of the timber company's sample, and four over the period of the remaining application time.

Runoff samples were collected during the first rainfall event following application, that produced a significant increase in water level at the sample sites. During the first sampling season in spring of 1999, four samples were collected to allow for backup samples in case of problems. It was then decided to collect all eight samples as primary samples so a longer time span could be monitored. When analyzing for atrazine with triclopyr, only four samples of each could be collected since each required a separate sample for analysis.

Sample Handling

All samples were stored on wet ice and maintained at approximately 4°C through storage and transportation to the laboratory for analysis according to procedures in DPR's SOP QAQC004.1 (Appendix D). Tank samples were stored on wet ice in a cooler separate from the other samples. Each shipment of samples was accompanied by a Hobo® Temp

temperature data logger which recorded sample temperatures from collection to delivery to the lab as described in DPR's SOP EQOT001.01 (Appendix C). Samples were shipped or delivered as soon as possible after final sample collection. Each sample was accompanied by chain of custody record which was signed by the field personnel and laboratory personnel handling the sample. All samples followed sample receipt log-in and verification procedures described in Appendix D.

Quality Control Methods

In addition to field samples collected during monitoring, rinse blanks were collected at various times to assure that the sampling equipment cleaning procedures used were effective. Deionized water is run through the entire sampling system as a rinse, then a final rinse of deionized water is run through and collected for analysis.

Laboratory continuing quality control followed EHAP SOP QAQC001.00 (Appendix D). The spikes were prepared by a chemist in another section of the analytical lab and submitted for analysis by the Quality Assurance/Lab Liaison. As part of CDPR's quality control program, data generated during method validation was used to assess all subsequent study results. The mean percent recovery and standard deviation values from the validation data were used to establish warning and control limits at ±2 times and ±3 times the standard deviation, respectively, for each pesticide analysis (Appendix D). Continuing quality control (QC) samples consisted of two water samples spiked with an analyte at a given concentration, extracted and analyzed with samples from each extraction set. In addition, a blank water sample was analyzed with each extraction set. Based on a recommendation made by the U.S. EPA's Quality Assurance Office, duplicate matrix spikes were required to assess laboratory precision (Taylor, 1998). During the course of the study, continuing QC samples were compared back to the warning and control limits. In addition, blind spikes were analyzed. A blind spike is a surface water sample that is spiked by one chemist and submitted to another chemist by DPR staff for extraction and analysis with the primary samples for analysis. Water used in matrix spikes and blind spikes were collected from the North Fork or Middle Fork of the American River in Auburn, CA.

As an additional quality assurance measure, field blank samples were prepared periodically after sample collection. Deionized water was poured into one-liter amber glass bottles (the same used for all other samples) for each analysis at the site and then transported and stored as a primary sample. These samples served to determine whether or not contamination occurred in the field.

Laboratory Methods for Analysis of Water Samples

All samples were analyzed by the California Department of Food and Agriculture Center for Analytical Chemistry. Atrazine, a triazine herbicide, was analyzed using high performance liquid chromatography (HPLC) with an ultraviolet (UV) detector, and gas chromatography (GC) with a nitrogen phosphorus detector (NPD). The phenoxy herbicides, 2,4-D and triclopyr, were analyzed by GC on a capillary column using a mass selective detector (MSD). Glyphosate was analyzed using (HPLC) with post-column derivatization and fluorescence detection. Detailed analytical methods are included in Appendix E. The method validation results for recovery from surface water spiked with a known amount of chemical are located in Table 5.

Minimum Detection Limit

The Minimum Detection Limit (MDL) for each herbicide is located in Table 5. The MDL is the minimum concentration of a substance that can be measured with the analytical method and equipment and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined for each analyte by analyzing a standard at a concentration with a signal to noise ratio of 2.5 to 5. The spiked matrix is analyzed at least seven times, and the method detection limit is determined by calculating the 99% confidence interval of the mean. This procedure is described in detail in U.S. EPA (1990).

Table 5. Recovery and detection limits for the herbicides monitored in surface water.

Herbicide	Method Recovery (%)	Method Detection Limit (ppb)
Atrazine	85.2	0.05
2,4-D	92.0	0.10
Glyphosate	72.2	2.00
	108.7	0.10

Plant Sampling

Plant sampling was conducted both inside and outside the aerial application treatment areas. All samples were collected in accordance with the protocol for Study 191: "Monitoring for Herbicide Residues in Plants of Interest to the Tribal People in Their Aboriginal Territory of Northwestern California" (Appendix B). The plant species and plant parts sampled were selected based on its use by Native Americans as well as the availability of the plant in an application area. For this study, the following plant materials were selected for sampling:

Achillea millefolium (yarrow: stems and leaves)
Arctostaphyllos spp. (manzanita: berries)
Berberis nevosa (Oregon grape: roots)
Vaccinium ovatum (huckleberry: berries)
Xerophyllum tenax (beargrass: stems and leaves)
Adiantum pedatum (northern maidenhair fern: stems; used in pilot study only)
Salix spp. (willow: shoot)
Lithocarpus densiflorus (Tanoak: acorn)

Samples were collected outside of application areas to monitor drift (offsite movement) from the aerial application and inside the application to determine the degradation of the herbicides over time (dissipation). Only applications of triclopyr and/or 2,4-D were monitored because methods have not been developed to analyze the other herbicides used in this study on the plants. Sample procedures were conducted following SOP FSOT001.01 (Appendix C). All samples were collected with disposable gloves and sterile clippers and placed in one-quart glass jars with foil covers under the lid. Gloves and clippers were changed for each sample. Samples were weighed and placed on dry ice.

Sampling Procedure

Off-site samples were collected at varying distances away from the application area. Sites were generally selected for abundance of plants for sampling, and were located on the downwind side of the application, preferably with a road bordering the application to delineate

the edge of the treatment area. A composite sample was collected from all plants in the sampling area the day before application to determine if any background level of herbicide was present prior to the application. A tank sample was collected for each application area monitored for offsite movement. Samples were collected the day of application after allowing time for any applied droplets to settle out of the air. For most areas, three replications were collected within each distance range.

Dissipation samples were collected from three separate areas as replicates within an application sampling site. The replicate areas could be an individual plant or all plants within a designated area. A total of 70 – 100 grams of plant material was collected for each sample. Dissipation samples were taken one day before application (background), shortly after application, and at varying time intervals (in days) post-application. A tank sample was collected for each application area monitored for dissipation of the herbicides. Replicate samples were combined when the minimum quantity of plant material was no longer available for replicate samples.

Sample Handling

All plant samples were stored on dry ice in a Freez-safe® immediately after collection and during transport, and maintained at below -10°C according to procedures in DPR's SOP QAQC004.1 (Appendix D). Each shipment of samples was accompanied by a Hobo® Temp temperature data logger which recorded sample temperatures from collection to delivery to the lab as described in DPR's SOP EQOT001.01 (Appendix C). Samples were shipped or delivered as soon as possible after final sample collection. Each sample was accompanied by chain of custody record signed by the field personnel and laboratory personnel handling the sample. All samples followed sample receipt log-in and verification procedures described in Appendix E.

Tank samples were stored on wet ice in a cooler separate from the other samples. They were maintained at approximately 4°C through storage and transportation to the laboratory for analysis (SOP QAC004.01 Appendix D). Each shipment of samples was accompanied by a Hobo® Temp temperature data logger

Quality Control Methods

Samples from the application tank were collected for each area monitored to determine the percentage of active ingredient being applied. Laboratory continuing quality control followed EHAP SOP QAQC001.00 (Appendix D). The spikes were prepared by a chemist in another section of the analytical lab and submitted for analysis by the Quality Assurance/Lab Liaison. As previously noted above for the water samples, data generated during method validation was used to assess all subsequent study results for the plant samples. The mean percent recovery and standard deviation values from the validation data were used to establish warning and control limits at ±2 times and ±3 times the standard deviation, respectively, for each pesticide analysis (Appendix D). Continuing quality control (QC) samples consisted of two plant samples spiked with an analyte at a given concentration, extracted and analyzed with samples from each extraction set. In addition, a blank plant sample was analyzed with each extraction set. Based on a recommendation made by the U.S. EPA's Quality Assurance Office, duplicate matrix spikes were required to assess laboratory precision (Taylor, 1998). During the course of the study, continuing QC samples were compared back to the warning and control limits. Plants used in matrix spikes and blind spikes were collected from surrounding areas which had not been recently sprayed with herbicides.

Laboratory Methods for Analysis of Plant Samples

All samples were analyzed by the California Department of Food and Agriculture Laboratory for Analytical Chemistry. Phenoxy herbicides 2,4-D and triclopyr were analyzed by gas chromatography (GC) on a capillary column using an electron capture detector (ECD). Detailed analytical methods are included in Appendix E. The method validation results for recovery from plant material spiked with a known amount of chemical are located in Table 6.

Minimum Detection Limit

The method detection limit is determined for each analyte by analyzing a standard at a concentration with a signal to noise ratio of 2.5 to 5. The spiked matrix is analyzed at least seven times, and the method detection limit is determined by calculating the 99% confidence interval of the mean. This procedure is described in detail in U.S. EPA (1990). The method detection for each herbicide and plant material collected is given in Table 6.

Table 6. The part of the plant sampled and method validation results for each herbicide on each type of plant sampled.

Plant	Part of Plant Sampled	Recovery (%)		Method Detection Limit (ppm)	
		2,4-D	Triclopyr	2,4-D	Triclopyr
Beargrass	leaves	72.3	79.2	0.05	0.05
Huckleberry	berries	80.2	82.6	0.05	0.05
Maidenhair Fern	frond stems	76.2	86.4	0.05	0.05
Manzanita	berries	72.2	81.1	0.03	0.03
Oregon Grape	root	no validation	no validation	0.05[a]	0.05 [a]
Tanoak	acorn	81.2	81.2	0.05	0.05
Yarrow	leaves and stem	52.5	59.8	0.1	0.1

[a] Estimated method detection limit based on other plant validation

RESULTS AND CONCLUSIONS

Water Sampling

Sampling Site Locations

The surface water monitoring sites are listed in Table 7 and mapped in Figure 2. The sites are located in both Del Norte and Humboldt counties. The application sites were generally on very steep hillsides which sloped down into valleys with waterways running through them. Depending on the date of sampling, water may or may not have been running within the application areas.

Table 7. Water sampling site descriptions.

Site	Description	Coordinates	Elevation*	Distance from application site
A	Terwer Creek Tributary	41° 35' 1.5" N, 123° 58' 53.9" W	1250 ft	80 feet
B	Blue Creek	41° 26' 5.7" N, 123° 54' 38.8" W	86 ft	0.5 miles
C	Pecwan Creek Tributary	41° 23' 55.4" N, 123° 49' 58.2" W	2330 ft	0.5 miles
D	Terwer Creek	41° 35' 37.6" N, 123° 57' 42.9" W	560 ft	2.0 miles
E	Hoppaw Creek Tributary	41° 32' 40.4" N, 124° 00' 53.1" W	920 ft	in application boundary
F	Hunter Creek Tributary	41° 35' 52.5" N, 124° 01' 13.6" W	120 ft	1700 ft
G	Wilson Creek Tributary	41° 37' 2.8" N, 124° 05' 25.0" W	40 ft	1100 ft
H	Bear Creek	41° 24' 13.6" N, 123° 55' 25.2" W	80 ft	500 ft
I	West Fork Hunter Creek Tributary	41° 38' 20.1" N, 124° 00' 33.6" W	680 ft	200 ft
J	West Fork Hunter Creek	41° 37' 36.2" N, 124° 01' 18.5" W	240 ft	400 ft
K	Blue Creek Tributary	41° 27' 27.0" N, 123° 54' 22.9" W	1160 ft	1300 ft
L	West Fork Hunter Creek	41° 36' 39.7" N, 124° 02' 05.5" W	160 ft	200 ft
M	Hunter Creek	41° 35' 46.7" N, 124° 01' 35.6" W	160 ft	1600 ft

* Elevation data from TrimbleNavigation GeoExplorer I GPS or estimated on USGS 7.5 minute Quad maps

The types of applications monitored for drift into waterways during application and rain runoff following application are described in Table 8. The applications monitored included ground applications of atrazine (with or without triclopyr) and aerial applications of 2,4-D, triclopyr and glyphosate.

Table 8. Types of application and samples collected.

Site	Description	Application Type	Herbicide Monitored	Sample Type Collected
A	Terwer Creek Tributary	ground	atrazine	rain runoff
B	Blue Creek	ground	atrazine triclopyr	rain runoff
C	Pecwan Creek Tributary	ground	atrazine	rain runoff
D	Terwer Creek	aerial	triclopyr 2,4-D	rain runoff
E	Hoppaw Creek Tributary	aerial	triclopyr	application rain runoff
F	Hunter Creek Tributary	aerial	triclopyr	application rain runoff
G	Wilson Creek Tributary	aerial	glyphosate	application rain runoff
H	Bear Creek	ground	atrazine triclopyr	rain runoff
I	West Fork Hunter Creek Tributary	aerial	triclopyr 2,4-D	application
J	West fork Hunter Creek	aerial	triclopyr 2,4-D	application rain runoff
K	Blue Creek Tributary	ground	atrazine	rain runoff
L	West Fork Hunter Creek	aerial	triclopyr 2,4-D	rain runoff
M	Hunter Creek	aerial	triclopyr 2,4-D	rain runoff

Application Monitoring for Drift

Five applications were monitored for drift into waterways within or adjacent to an application area during two application seasons. Table 9 presents the details of the applications and a description of the slope of the application area and the slope down to the sampling sites.

Table 9. Description of applications and application areas monitored for drift.

Corresponding Sampling Site	Description	Application date	Application time	Acres treated	Total Pounds of Active Ingredient Used	Application slope (%)[a]	Intermediate slope (%)[b]	Distance from application site
E	Hoppaw Creek	9/16/99	10:00	40	60 lb triclopyr	47	none	in application boundary
F	Hunter Creek Tributary	9/14/99	11:00	105	158 lb triclopyr	52	7	1700 ft
G	Wilson Creek Tributary	9/20/99	13:50	13	13 lb glyphosate	27	26	1100 ft
I	West Fork Hunter Creek	4/23/00	08:21	245	245 lb triclopyr 230 lb 2,4-D	34	30	200 ft
J	West fork Hunter Creek	4/24/00	11:12	230	230 lb triclopyr 216 lb 2,4-D	44 to 60	20 to 53	400 ft

[a]change in elevation from top to bottom of application site (ft)/distance (ft) X 100
[b]change in elevation from bottom of application to sampling site (ft)/distance (ft) X 100

Three aerial applications were monitored during the fall application period of 1999 (Figure 3). Two of the application areas were treated with triclopyr and one site was treated with glyphosate. There were no detectable amounts of the herbicides monitored in any of the samples (Table 10).

Two aerial applications were monitored in the spring of 2000 (Figure 4). Both applications consisted of a tank mixture of 2,4-D and triclopyr. During the first application on April 23, 2000, concentrations of both 2,4-D and triclopyr were detected (Table 11). The sampler was started at the completion of the application around the buffer areas in the application site. The application ended at 10:55 and the last sample was collected almost 0.5 hours later at 11:26. The detections were made during the hourly sampling at the end of the application to the buffer areas (Figure 5). The highest concentrations were 0.584 ppb and 1.06 ppb for 2,4-D and triclopyr, respectively.

The tank samples results were within acceptable label rate range. Some tank samples were not collected on the actual application day due to a delay in the application.

Table 10. Results from application monitoring in fall of 1999.

Date	Time	Sample type	Site	Triclopyr	Glyphosate
9/16/99	09:30	tank	E	1.07%	---[a]
9/13/99	07:50	tank	F	1.45%	---
9/20/99	09:00	tank	G	----	0.46%
9/16/99	12:19	water	E	ND [b]	----
	12:22			ND	----
	12:25			ND	----
	12:28			ND	----
	12:38			ND	----
	12:44			ND	----
	12:51			ND	----
	12:58			ND	----
Application started at 12:18 and ended at 12:43					
9/14/99	11:14	water	F	ND	----
	11:19			ND	----
	11:24			ND	----
	11:29			ND	----
	11:52			ND	----
	12:07			ND	----
	12:22			ND	----
	12:35			ND	----
Application started at 11:13 and ended at approximately 12:00					
9/20/99	13:55		G	----	ND
	13:58			----	ND
	14:01			----	ND
	14:07			----	ND
	14:12			----	ND
	14:18			----	ND
Application started at 13:53 and ended at approximately 14:15					

[a] Not applied, so was not analyzed for.

Figure 3. Applications monitored for drift during the fall of 1999.

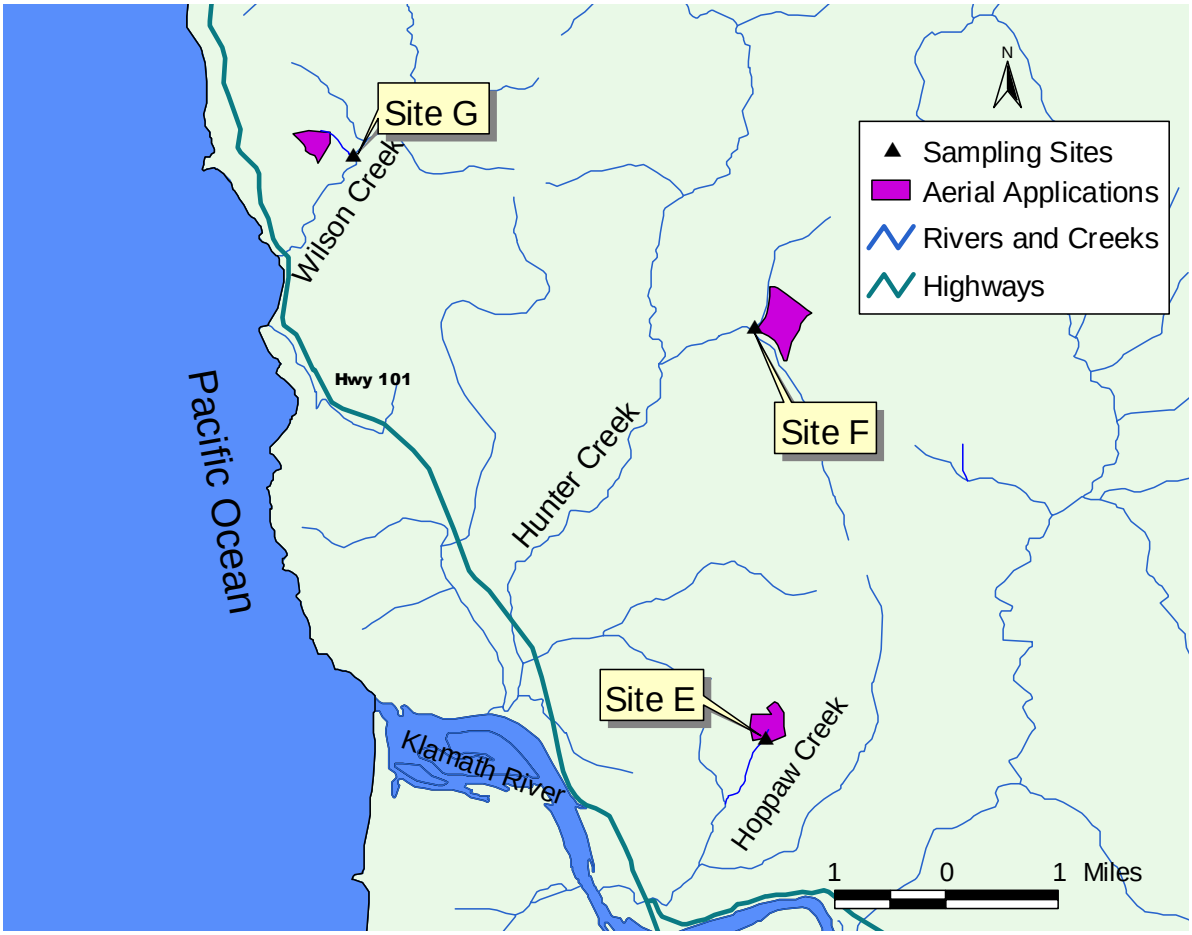


Table 11. Results from application monitoring in spring of 2000.

Date	Time	Sample type	Site	2,4-D	Triclopyr
4/22/00	09:15	Tank	I	1.06%	1.08%
4/24/00	11:45	Tank	J	1.46%	1.47%
04/23/00	08:26	Water	I	ND [b]	ND
	08:28		I	ND	ND
	08:30		I	ND	ND
	08:32		I	ND	ND
	08:34		I	ND	ND
	09:26		I	0.163 ppb	0.223 ppb
	10:26		I	0.491 ppb	1.06 ppb
	11:26		I	0.584 ppb	1.02 ppb
Application started at 08:21 and ended at 10:55					
04/24/00	11:27	Water	J	ND	ND
	11:29		J	ND	ND
	11:31		J	ND	ND
	11:33		J	ND	ND
	11:35		J	ND	ND
	12:27		J	ND	ND
	13:27		J	ND	ND
	14:27		J	ND	ND
Application started at 11:12 and ended at 11:46					

[a]ND-none detected at the reporting limit for that chemical.
Minimum reporting limit: triclopyr and 2,4-D = 0.1 ppb

Figure 4. Application sites monitored for drift during the spring of 2000.

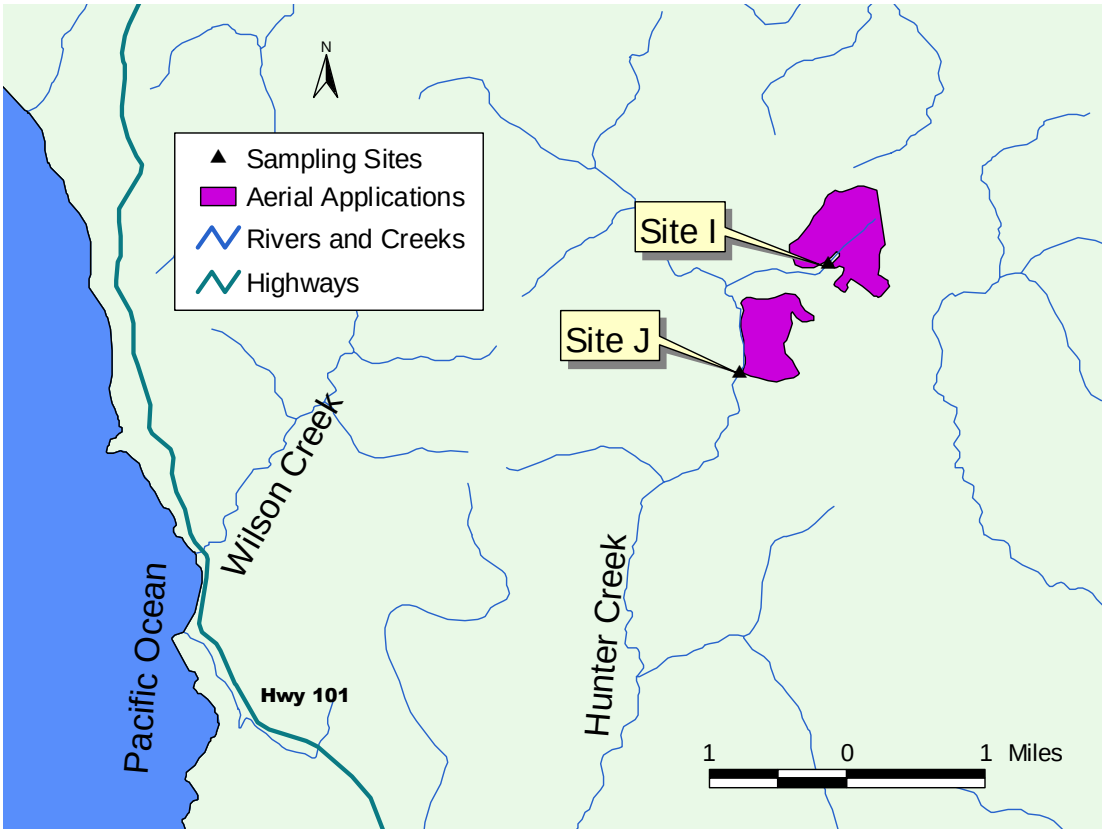
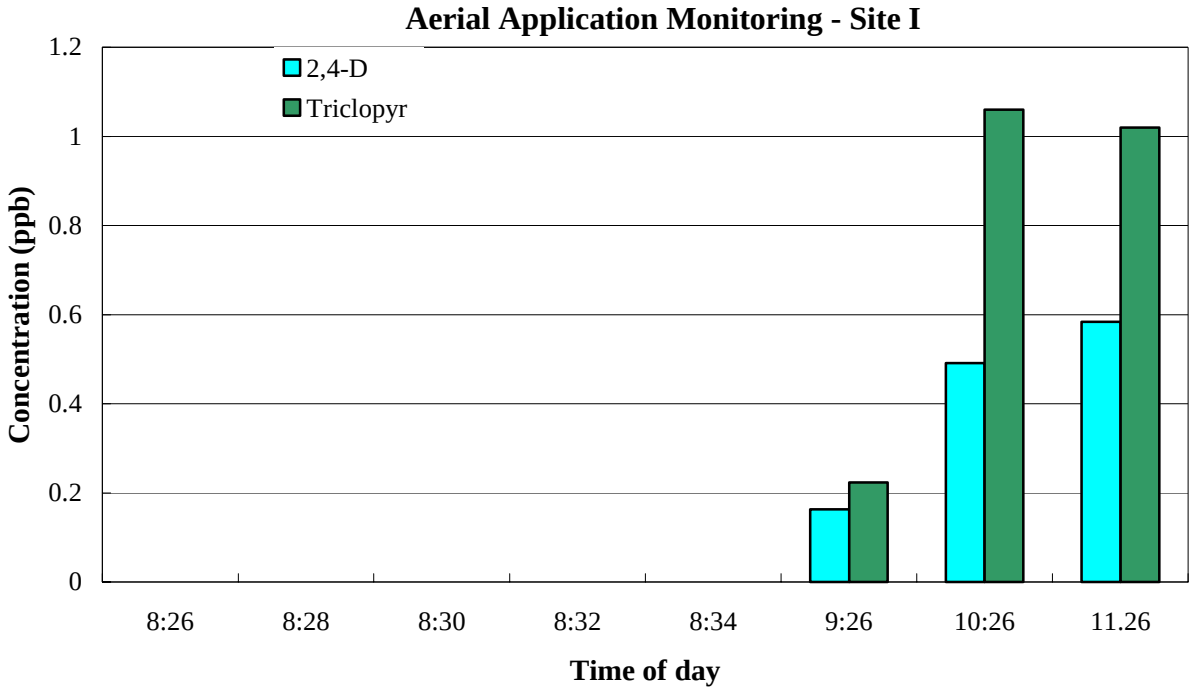


Figure 5. Concentrations detected in the monitored tributary during an aerial application on April 23, 2000.



Rainfall Event Monitoring

Twelve application areas (sites A – M) were monitored for off-site movement of the applied herbicides in runoff during the first rainfall event following the application. Table 12 presents the details of the applications and a description of the slope of the application area and the slope down to the sampling site. The sites were located as close as possible to the application area.

Table 12. Description of applications and sites monitored for runoff during a rainfall event.

Corresponding Sampling Site	Description	Application date	Acres treated	Total Pounds of Active Ingredient Used	Application slope (%)[a]	Intermediate slope (%)[b]	Distance from application site
A	Terwer Creek Tributary	4/20/99	9	32 lb atrazine	40	31	82 ft
B	Blue Creek	4/21/99	36	130 lb atrazine 20 lb triclopyr	33	3	0.5 miles
C	Pecwan Creek Tributary	4/26/99	25	91 lb atrazine	27	3	0.5 miles
D	Terwer Creek	5/5/99	360	360 lb triclopyr 338 lb 2,4-D	34	8	2 miles
E	Hoppaw Creek Tributary	9/16/99	40	60 lb triclopyr	47	none	in application boundary
F	Hunter Creek Tributary	9/14/99	105	158 lb triclopyr	52	7	1700 ft
G	Wilson Creek Tributary	9/20/99	13	13 lb glyphosate	27	26	1100 ft
H	Bear Creek	3/23/00	36	143 lb atrazine 22 lb triclopyr	30	30	500 ft
I	West Fork Hunter Creek Tributary	4/23/00	245	245 lb triclopyr 230 lb 2,4-D	34	30	200 ft
J	West Fork Hunter Creek	4/24/00	230	230 lb triclopyr 216 lb 2,4-D	44 to 60	20 to 53	400 ft
K	Blue Creek Tributary	4/24/00	80	260 lb atrazine	56	9	1300 ft
L	West Fork Hunter Creek	4/24/00	20	20 lb triclopyr 19 lb 2,4-D	44 to 60	20 to 53	200 ft
M	Hunter Creek	4/24/00	100	100 lb triclopyr 94 lb 2,4-D	30	10	1600 ft

During the spring of 1999, sites A through D were monitored for herbicide runoff during the first rainfall event following application (Figure 6). The first site (A) located on a Terwer Creek tributary was sampled on May 1, 1999, eleven days after a ground application of atrazine was made to nine acres in the watershed area upstream from the sampling site. The water level in the tributary had risen to trigger the sensor to turn on the sampler, but a later check of the data from a water-level gauging station at Terwer Creek operated by DWR and USGS indicated that only 0.08 inches had fallen at the time sampling started (Table 13). After additional rainfall during the night, sampling at two other monitoring sites downstream from ground applications (sites B and C) resulted in no measurable concentrations of atrazine or triclopyr in any of the samples. A fourth site was monitored following an aerial application of triclopyr and 2,4-D on May 5, 1999. Unfortunately, only two samples survived an automobile accident which destroyed the other samples. Neither of the two samples contained any measurable amount of triclopyr or 2,4-D.

Figure 6. Applications and sites monitored for runoff during a rainfall event in the spring of 1999.

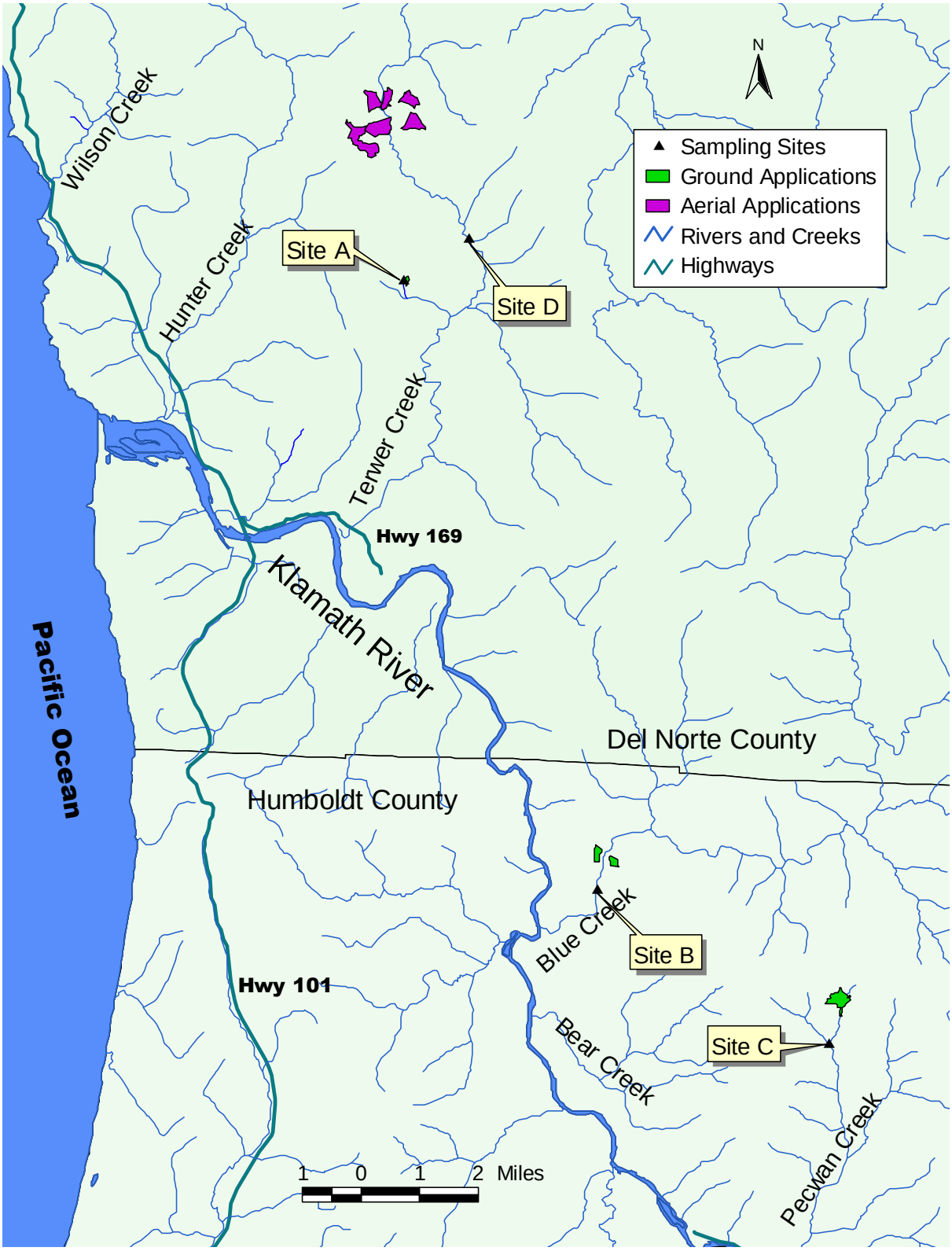


Table 13. Results from rainfall event sampling in the spring of 1999.

Application Date	Sample Date	Time of Sample	Sample type	Site	Atrazine	Triclopyr	2,4-D	Total Precipitation at Start of Sampling[c]
4/20/99	4/20/99	8:50	Tank	A	2.37%	--	--	
4/21/99	4/21/99	10:31	Tank	B	2.28%	0.26%	--	
4/26/99	4/26/99	10:45	Tank	C	2.93%	--	--	
5/5/99	5/4/99	15:45	Tank	D	--[a]	1.27%	1.13%	
4/20/99	5/1/99	19:13	Water	A	ND[b]	--	--	0.08 inches
		19:36			ND	--	--	
		20:36			ND	--	--	
		21:36			ND	--	--	
4/21/99	5/2/99	11:22	Water	B	ND	ND	--	1.12 inches
		12:22			ND	ND	--	
		13:22			ND	ND	--	
		14:22			ND	ND	--	
4/26/99	5/2/99	10:02		C	ND	--	--	1.32 inches
		11:02			ND	--	--	
		12:02			ND	--	--	
		13:02			ND	--	--	
5/5/99	5/14/99	9:16	Water	D		ND	ND	0.64 inches
		12:10				ND	ND	

[a]Herbicide not used and hence not analyzed

[b]ND-none detected at the reporting limit for that chemical.
Minimum reporting limit: atrazine = 0.05 ppb, triclopyr and 2,4-D = 0.1 ppb

[c]Total precipitation from application date to sampling date, gauged at Terwer Creek station operated by DWR and USGS. Location = 41.5120°N, 123.999° W

Sites E through G were monitored during the fall of 1999 for runoff during the first rainfall event at the same sites monitored during application (Figure 3). All three sites were sampled on October 27, 1999 (Table 14). There were no measurable concentrations detected in samples collected below a 52-acre application of triclopyr (site F) or a 27-acre application of glyphosate (site G). Site E was located within the application boundary of a 40-acre application of triclopyr treated 41 days earlier. All of the samples collected during a 7-hour time-span

contained measurable amounts of triclopyr. The concentrations peaked at 0.430 ppb (Figure 7).

The tank samples results were within acceptable label rate range. Some tank samples were not collected on the actual application day due to a delay in the application.

Table 14. Results from rainfall event sampling in the fall of 1999.

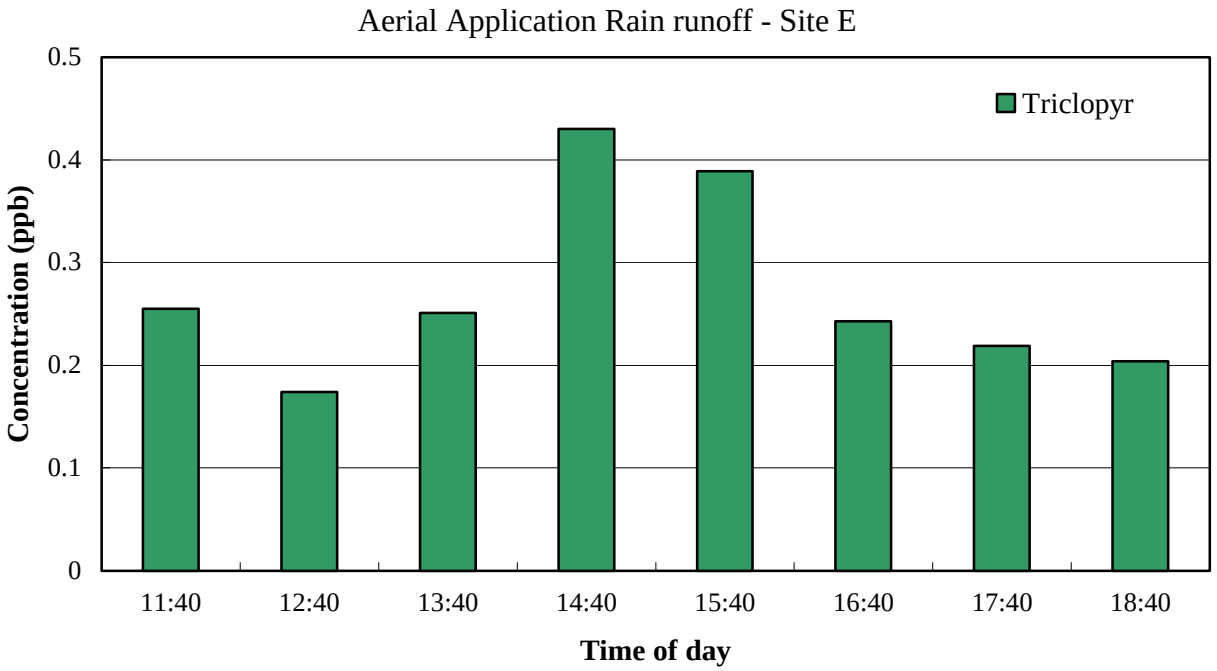
Application Date	Sample Date	Time of Sample	Sample Type	Site	Concentration		Total Precipitation at Start of Sampling[c]
					Triclopyr	Glyphosate	
9/16/99	9/16/99	09:30	Tank	E	1.07%	---[a]	
9/14/99	9/13/99	07:50	Tank	F	1.45%	---	
9/20/99	9/20/99	09:00	Tank	G	----	0.46%	
9/16/99	10/27/99	11:40	Water	E	0.255 ppb	--	0.65 inches
		12:40			0.174 ppb	--	
		13:40			0.251 ppb	--	
		14:40			0.430 ppb	--	
		15:40			0.389 ppb	--	
		16:40			0.243 ppb	--	
		17:40			0.219 ppb	--	
		18:40			0.204 ppb	--	
9/14/99	10/27/99	10:06	Water	F	ND[b]	--	0.50 inches
		11:06			ND	--	
		12:06			ND	--	
		13:06			ND	--	
		14:06			ND	--	
		15:06			ND	--	
		16:06			ND	--	
		17:06			ND	--	
9/20/99	10/27/99	09:19	Water	G	--	ND	0.37 inches
		10:19			--	ND	
		11:19			--	ND	
		12:19			--	ND	
		13:19			--	ND	
		14:19			--	ND	
		15:19			--	ND	
		16:19			--	ND	

[a]Herbicide not used and hence not analyzed

[b]ND-none detected at the reporting limit for that chemical.
Minimum reporting limit: triclopyr and glyphosat = 0.2 ppb

[c]Precipitation in rain gauges located at the sites from 10/26/99 at 18:00 to start of sampling. (additional precipitation measured at Terwer Creek station operated by DWR and USGS from 10/5/99 to 10/26/99 at 11:00 = 1.0 in. Location = 41.5120°N, 123.999° W.)

Figure 7. Concentrations detected during rainfall event at site E.



Sites H through M were monitored for runoff during the spring of 2000 (Figure 8). None of the samples collected below the ground application sites (sites H and K) contained measurable amounts of atrazine (Table 15). The sampling occurred 24 days after application for site H and one day after application at site K. A sampler was set up on the West Fork of Hunter Creek (site J) to monitor drift during a 230-acre application of triclopyr and 2,4-D on April 24, 2000. The sampler was left in place due to impending rain. The sampler was triggered for sample collection during the following day. The water level in the creek did not appear to increase so it was decided that the first sample would be kept and the other seven would be poured out to allow for more samples to be collected after more rain had fallen. The sampler was moved further down the West Fork of Hunter Creek (site L) to a location which would capture runoff from additional applications. The sample collected on April 25th did contain a measurable amount of both triclopyr and 2,4-D (Table 15). In addition, the samples collected two days later at the relocated sample site also contained measurable amounts of both herbicides. The concentrations peaked at 0.241 ppb and 0.388 ppb for 2,4-D and triclopyr, respectively. There

were no detectable amounts of either herbicide detected in the samples collected in Hunter Creek at site M.

The tank samples results were within acceptable label rate range except for the atrazine tank mix at site H. The 4.47 % atrazine concentration was above the 4% label rate maximum concentration. This may have been due to incomplete mixing of the tank mixture or settling of the chemical.

Figure 8. Applications and sites monitored for runoff during a rainfall event in the spring of 2000.

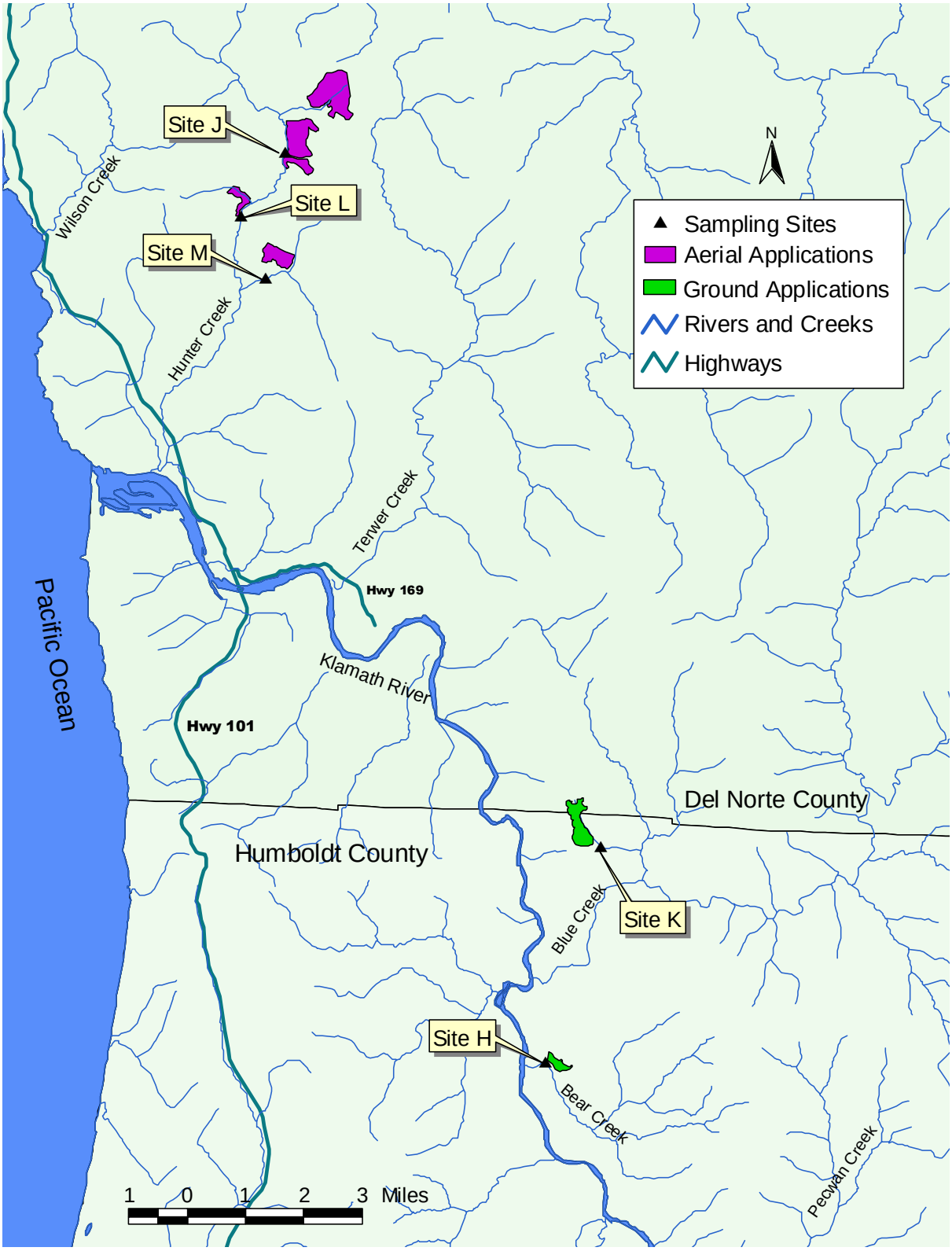


Table 15. Results from rainfall event sampling in the spring of 2000.

Application Date	Sample Date	Time	Sample Type	Site	Concentration			Precipitation at Start of Sampling[c]
					2,4-D	Triclopyr	Atrazine	
					[a]			
4/22/00	4/22/00	09:15	Tank	I	1.06%	1.08%	--	
4/24/00	4/24/00	11:45	Tank	J,M	1.46%	1.47%	--	
4/24/00	4/24/00	12:30	Tank	K	--	--	2.50%	
3/23/00	4/16/00	12:40	Water	H	--[a]		ND[b]	1.22 inches
		13:40			--		ND	
		14:40			--		ND	
		15:40			--		ND	
		16:40			--		ND	
		17:40			--		ND	
		18:40			--		ND	
		19:40			--		ND	
4/24/00	04/25/00	10:14	Water	J	0.103 ppb	0.122 ppb	--	0.55 inches
4/24/00	04/25/00	07:28	Water	K	--	--	ND	0.46 inches
		08:28			--	--	ND	
		09:28			--	--	ND	
		10:28			--	--	ND	
		11:28			--	--	ND	
		12:28			--	--	ND	
		13:28			--	--	ND	
		14:28			--	--	ND	
4/24/00	4/27/00	12:36	Water	M	ND	ND	--	0.63 inches
		13:36			ND	ND	--	
		14:36			ND	ND	--	
		15:36			ND	ND	--	
		16:36			ND	ND	--	
		17:36			ND	ND	--	
		18:36			ND	ND	--	
		19:36			ND	ND	--	
4/24/00	4/27/00	13:22	Water	L	ND	ND	--	0.72 inches
		14:22			0.146 ppb	0.195 ppb	--	
		15:22			0.241 ppb	0.362 ppb	--	
		16:22			0.218 ppb	0.388 ppb	--	
		17:22			0.232 ppb	0.383 ppb	--	
		18:22			0.190 ppb	0.319 ppb	--	
		19:22			0.163 ppb	0.293 ppb	--	
		20:22			0.152 ppb	0.285 ppb	--	

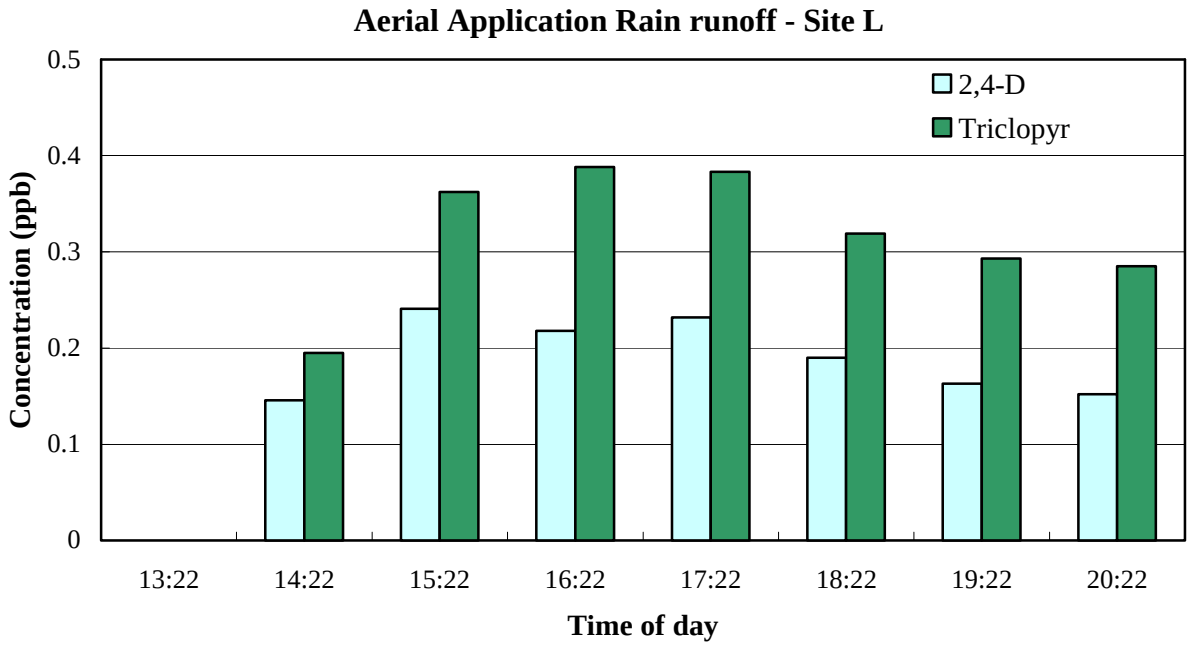
[a]herbicide not used and hence not analyzed.

[b]ND-none detected at the reporting limit for that chemical.

Minimum reporting limit: atrazine = 0.05 ppb, triclopyr and 2,4-D = 0.1 ppb

[c]Precipitation in rain gauges located at the sites.

Figure 9. Concentrations detected during a rainfall event at site L.



Water Quality Measurements

All water quality parameter measurements are located in Table 16. The NCRWQCB (CRWQCB, 1994) lists the following water quality guidelines as acceptable for the Lower Klamath River hydrologic area (HA): DO above 8.0 mg/L, pH between 6.5 and 8.5, and EC below 200 µS/cm 90% of the time (90% Upper Limit) and below 125 µS/cm 50% of the time (50% Upper Limit). The water quality guidelines do not provide an acceptable range for temperature, but the Lower Klamath River HA is designated as cold interstate water. All water quality measurements taken fall within the NCRWQCB's acceptable guidelines.

Table 16. Water quality measurements for each sampling event.

Site	Location	Date	Temperature (^{0} C)	pH	Dissolved Oxygen (mg/L)	Electroconductivity (µS/cm)
A	Terwer Creek Tributary	5/2/99	9.3	7.5	10.88	NA
B	Blue Creek	5/2/99	8.8	7.7	11.06	NA
C	Pecwan Creek Tributary	5/2/99	7.3	6.9	10.99	NA
D	Terwer Creek	5/14/99	9.5	7.6	11.23	58.7
E	Hoppaw Creek Tributary	9/16/99	11.7	NA	9.15	49.4
F	Hunter Creek Tributary	9/14/99	12.5	7.2	9.30	77.0
G	Wilson Creek Tributary	9/20/99	12.2	5.9	9.77	96.0
E	Hoppaw Creek Tributary	10/28/99	11.0	7.5	10.12	60.0
F	Hunter Creek Tributary	10/28/99	11.4	7.5	10.32	81.0
G	Wilson Creek Tributary	10/28/99	11.0	7.0	10.84	109.0
H	West Fork Hunter Creek Tributary	4/16	10.3	7.2	11.02	46.4
I	West Fork Hunter Creek	4/23	8.5	7.2	11.18	61.8
J	Blue Creek Tributary	4/24	10.7	6.9	9.69	62.0
K	West Fork Hunter Creek	4/25	9.4	7.0	10.85	42.5
L	Hunter Creek	4/28	9.4	7.0	11.0	58.9
M	West Fork Hunter Creek Tributary	4/28	9.5	7.2	10.93	55.8

NA Not available; unable to take reading due to equipment failure

Quality Control

Average recoveries ranged from 93.0 percent to 109.0 percent for all of the herbicides analyzed (Table 17). The data presented in this report have not been adjusted for laboratory quality control results. The raw data for the quality control sample results is located in Appendix G. All of the samples analyzed for atrazine, 2,4-D and triclopyr were within the control limits. More than half of the quality control samples analyzed for glyphosate were above the upper the

control limits. Which may indicate concentrations reported may be an over estimate of concentration. There were no measurable concentrations of glyphosate detected in any of the water samples collected.

Table 17. Average laboratory quality control recovery results in water.

Analyte	Maximum Recovery (%)	Minimum Recovery (%)	Average Recovery (%)
Atrazine	83.5	103.0	93.0
2,4-D	97.0	106.5	102.6
Glyphosate	88.8	101.0	94.2
Triclopyr	94.0	126.5	109.0

Summary and Conclusions for Water Sampling

During the study, 13 applications were monitored for application drift and/or runoff during the first rain event following application. Except for one ground application tank sample of atrazine, all tank samples concentration results were within an acceptable label rate range. Some tank samples were not collected on the actual application day due to a delay in the application. A total of five application sites were monitored for drift onto waterways during application and 12 water sampling sites were monitored for movement of a herbicide off of application areas in rain runoff. The application areas ranged from 9 acres to 360 acres. A total of 109 water samples were collected (Table 18) of which 19 were positive detections. None of the samples from the four sites monitored for rainfall runoff from ground applications of atrazine had measurable concentrations of the herbicide. One site was monitored for glyphosate during both the aerial application and a rain event with no residues detected in the water samples. Of the other four aerial applications of triclopyr or triclopyr and 2,4-D, one application sampling site detected in positive concentrations during application. The sampling site was located 200 ft downstream on a tributary flowing from the application area. Since the last sample collected had the highest concentration of 2,4-D, it cannot be determined if the peak concentrations were captured. The highest concentrations detected at the site were 0.58 ppb and 1.06 ppb for 2,4-D and triclopyr, respectively.

Three of the 12 sites monitored during a rain event detected measurable amounts of the herbicides in the water. The highest concentrations detected in the samples were 0.24 ppb and 0.43 ppb for 2,4-D and triclopyr, respectively. The sampling at two of the sites appeared to capture the peak concentrations. Unfortunately, at the third site only one sample was analyzed to allow additional samples to be collected since it was decided there may not have been enough rainfall to produce runoff. The additional samples were collected from one of the sites with positive detections.

The U.S. Environmental Protection Agency sets drinking water standards for many contaminants (U.S. EPA, 2000a). The standard is presented as a maximum contaminant level (MCL), which is the highest level of a contaminant that is allowed in drinking water supplied by public water systems. MCLs are enforceable standards. The levels are set as close as possible to the maximum contaminant level goal (MCLG) for a contaminant. The MCLG is the level of a contaminant in drinking water below which there is no known or expected risk to health. The MCLG and MCL for the herbicides monitored are listed in Table 19. No MCLG or MCL has been established for triclopyr. The concentrations of 2,4-D detected were all below the MCL's for drinking water. There were no detections of atrazine or glyphosate in samples collected during the study.

The only federal or state criteria listed for freshwater aquatic life protection for any of the herbicides is a U.S. EPA recommended criteria for atrazine. The recommended draft criteria are a continuous concentration (4-day average) limit of 12 ppb and a maximum concentration (one-hour average) of 350 ppb no more than once every three years on the average (U.S. EPA, 2001). There were no detections of atrazine during this study.

The Water Quality Control Plan for the North Coast Region states that "No individual pesticide or combination of pesticides shall be present in concentrations that adversely affect beneficial uses." (CRWQCB, 1994). The only herbicide still in use mentioned in the plan is 2,4-D. The plan states that there shall be no discharge "..to exceed an instantaneous value of 40 ppb or acid equivalent or a 24-hour average of 2 ppb acid equivalent." The highest concentration of 2,4-D measured during this study was 1.06 ppb for an instantaneous value.

There are no freshwater criteria for triclopyr or glyphosate. For triclopyr, the parent compound is considered to be practically non-toxic to fish and to the waterflea, an aquatic invertebrate. The ester form is more toxic but is rapidly converted to the parent acid. In 1994, California Fish and Game estimated a chronic threshold of 0.03 ppm (30 ppb) by using the lowest LC_{50} value (lethal concentration of the product to 50% of the test animals) of 0.3 ppm for chum salmon and divided by a safety factor of ten (Menconi and Siepmann, 1994). The highest concentration of triclopyr detected was 0.58 ppb. Glyphosate is considered to be nontoxic to fish and may be slightly toxic to aquatic invertebrates. There was no measurable amount of glyphosate detected during this study.

Table 18. A summary of all water samples collected during study

Sample Date	Watershed	Site	Application Type	Sample Type	Number of Samples	Number of Positives	Maximum Concentration Measured (ppb)			
							2,4-D	Triclopyr	Glyphosate	Atrazine
5/1/99	Terwer Creek Trib.	A	ground	storm runoff	4	0	--[a]	--	--	ND[b]
5/2/99	Blue Creek	B	ground	storm runoff	4	0	--	ND	--	ND
5/2/99	Pecwan Creek Trib.	C	ground	storm runoff	4	0	--	--	--	ND
5/14/99	Terwer Creek	D	aerial	storm runoff	2	0	ND	ND	--	--
9/16/99	Hoppaw Creek Trib.	E	aerial	application	8	0	--	ND	--	--
9/14/99	Hunter Creek Trib.	F	aerial	application	8	0	--	ND	--	--
9/20/99	Wilson Creek Trib.	G	aerial	application	6	0	--	--	ND	--
10/27/99	Hoppaw Creek Trib.	E	aerial	storm runoff	8	8	--	0.43	--	--
10/27/99	Hunter Creek Trib.	F	aerial	storm runoff	8	0	--	ND	--	--
10/27/99	Wilson Creek Trib.	G	aerial	storm runoff	8	0	--	--	ND	--
4/16/00	Bear Creek	H	ground	storm runoff	8	0	--	--	--	ND
4/23/00	West Fork Hunter Ck. Trib.	I	aerial	application	8	3	0.58	1.06	--	--
4/24/00	West Fork Hunter Ck.	J	aerial	application	8	0	ND	ND	--	--
4/25/00	West Fork Hunter Ck.	J	aerial	storm runoff	1	1	0.1	0.12	--	--
4/25/00	Blue Creek Trib.	K	ground	storm runoff	8	0	--	--	--	ND
4/27/00	Hunter Creek	M	aerial	storm runoff	8	0	ND	ND	--	--
4/27/00	West Fork Hunter Ck.	L	aerial	storm runoff	8	7	0.24	0.39	--	--
				Total	**109**	**19**				

[a]herbicide not used and was not analyzed.

Minimum detection limit: triclopyr and 2,4-D = 0.1 ppb, glyphosate = 2.0 ppb, and atrazine = 0.05 ppb.

[b]ND-none detected at the reporting limit for that chemical.

Table 19. The U.S. Environmental Protection Agency's drinking water standards.

Herbicide	Max. Contaminant Level Goal	Max. Contaminant Level
Atrazine	3 ppb	3 ppb
2,4-D	70 ppb	70 ppb
Glyphosate	70 ppb	70 ppb
Triclopyr	has not been set	has not been set

Plant Sampling

Pilot Study

A pilot study was conducted in September 1999 to monitor triclopyr concentrations on selected plants outside of the treatment areas as well as in the buffer areas (unsprayed areas) next to waterways. Maidenhair fern and huckleberry were sampled using composite samples from accessible areas within the buffer areas or near the application areas. Table 20 presents the results of the sampling.

Table 20. Plant sampling pilot study results.

Sample Date	Days After Application	Plant Type	Location Area	Sampling Location	Triclopyr (ppm)
9/15/99	1	Maidenhair Fern	Hunter Creek	300 ft from application	ND
9/18/99	4	Maidenhair Fern		Inside buffer area	ND
9/16/99	0	Huckleberry	Hoppaw Creek	1000 ft from application	ND
9/18/99	2	Maidenhair Fern		Inside buffer area	ND
9/18/99	2	Huckleberry		Inside buffer area	ND
9/18/99	2	Huckleberry		Inside application area	1.5

ND = no detectable amount.

Minimum reporting limit: 0.05 ppm for both maidenhair fern and huckleberry

Sampling Site Locations

The monitoring sites and application areas are mapped in Figure 10. The sites are located in both Del Norte and Humboldt counties. Four sites were monitored for off-site movement of the herbicides during aerial applications and six sites were monitored over time to monitor the length of time the herbicides are present on the plants. The descriptions of the applications are located in Table 21. Table 22 contains the descriptions of the sampling sites and sample types.

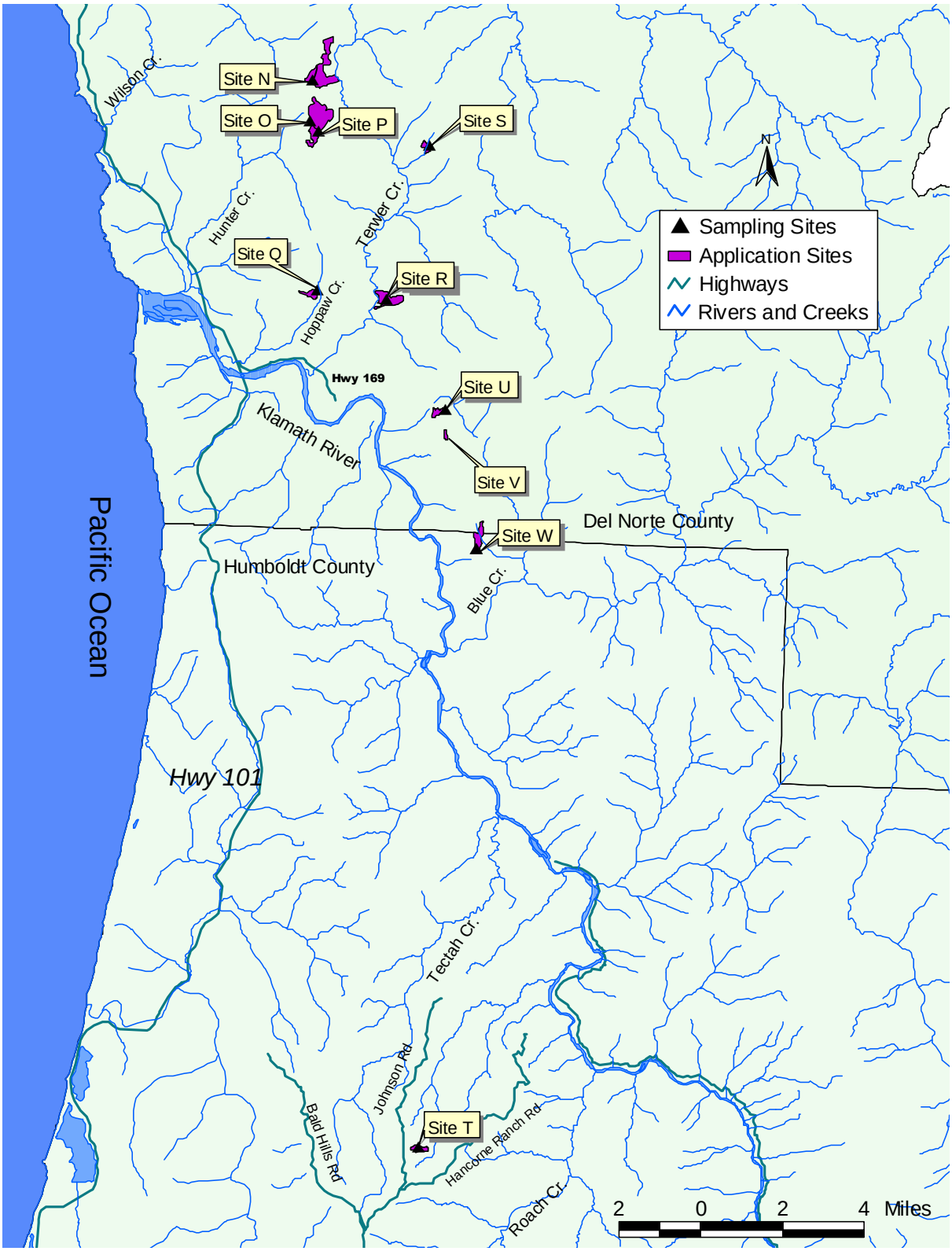
Table 21. Description of the herbicide applications.

Site	Description	Application Date	Acres Treated	Total Pounds of Active Ingredient Used	
				Triclopyr	2,4-D
N	Hunter Creek area	4/26/00	25	25	24
O	Hunter Creek area	4/26/00	66	66	62
P	Hunter Creek area	4/26/00	225	225	212
Q	Hoppaw Creek area	9/9/00	35	35	33
R	Terwer Creek area	9/10/00	116	116	109
S	Terwer Creek area	9/11/00	25	25	24
T	Bald Hills – Johnson Rd. area	9/13/00	45	45	42
U	West Fork Blue Creek	4/23/01	25	25	24
V	West Fork Blue Creek	4/23/01	25	25	24
W	West Fork Blue Creek	4/23/01	40	40	38

Table 22. Sampling site description.

Site	Description	Coordinates	Elevation	Sampling Type	Plant Sampled
N	Hunter Creek area	41^0 37' 23.3" N 124^0 00' 12.9" W	1,900 ft	Dissipation	Beargrass
O	Hunter Creek area	41^0 36' 22.1" N 123^0 59' 58.1" W	1,950 ft	Dissipation	Beargrass
P	Hunter Creek area	41^0 36' 26.1" N 123$^{0\,6}$59' 49.0" W	1,680 ft	Off-site	Beargrass
Q	Hoppaw Creek	41^0 32' 58.0" N 123^0 59' 47.3" W	700 ft	Off-site	Yarrow
R	Terwer Creek	41^0 32' 45.5" N 123^0 58' 52.6" W	650 ft	Dissipation	Yarrow, Huckleberry
S	Terwer Creek area	41^0 36' 09.0" N 123^0 57' 47.0" W	2,150 ft	Off-site	Beargrass, Huckleberry
T	Bald Hills – Johnson Rd. area	41^0 14' 48.2" N 123^0 56' 48.1" W	2,200 ft	Dissipation	Manzanita
U	West Fork Blue Creek	41^0 30' 32.7" N 123^0 56' 02.3" W	2,200 ft	Dissipation	Oregon grape
V	West Fork Blue Creek	41^0 30' 05.2" N 123^0 56' 57.0" W	2,450 ft	Off-site	Beargrass
W	West Fork Blue Creek	41^0 27' 35.5" N 123^0 55' 59.1" W	2,100 ft	Dissipation	Beargrass

Figure 10. The applications and monitoring sites for plant sample collection.



Monitoring Off-site Movement of Herbicide From an Application

Four sites were selected during the study to monitor the off-site movement of the applied herbicides due to drift from aerial applications. Only aerial applications were monitored. A background sample was collected at each site from numerous plants within the area to determine if any background level of the herbicides were present prior to sampling. All applications monitored were combined tank mixes of triclopyr and 2,4-D. Tank samples were collected prior to sampling for all applications monitored (Table 23). All tank samples were within expected concentrations of a label rate application. The results for the plant samples are calculated as an average of the replicate samples collected. When the herbicides were not detected in a replicate sample, one-half the reporting limit was used as the value for the average calculation. The raw data for all plant samples are located in Appendix F.

Table 23. Tank sample results for off-site application areas.

Date of Application	Site	Percent Active Ingredient (%)	
		Triclopyr	2,4-D
4/26/2000	P	1.01	1.02
9/9/2000	Q	1.12	1.00
9/11/2000	S	1.26	1.09
4/23/2001	V	1.10	1.04

In April of 2000, one application area was selected for sampling in the Hunter Creek watershed area (Figure 11). The site (site P) was located downwind from an application bordered by a dirt road. The edge of the road was considered to be the edge of the application area. The application of triclopyr and 2,4-D was made on April 26th at approximately 5:00 PM. Beargrass samples were collected at two distances; 121 and 210 feet from the edge of the application area 30 minutes after application. The samples contained no detectable amount of triclopyr or 2,4-D (Table 24).

Two application areas were selected for sampling the off-site movement of aerial herbicide applications (sites Q and S) during the fall 2000 aerial application period. The first application monitored was bordered on the downwind side of the application by a dirt road (Figure 11). The application was made on September 9th at approximately 10:30 AM. Yarrow was collected at two distance ranges (Table 24) one hour after completion of the application. Several yarrow plants were collected for each sample. At least three replicate samples were collected at each distance range. Both triclopyr and 2,4-D were detected at the closest (20 – 25 feet) distance only. The sampling area for the second application area (site S) was also located downwind of an application across from a wide dirt road (Figure 11). Huckleberry berries and beargrass were collected from three distances approximately 1 hour following application. Three replicate samples were collected for each plant at each distance range. One or two plants in close proximity were sampled for each sample. The closest plants sampled were 185 feet away from the edge of the application. No measurable amount of triclopyr or 2,4-D was detected.

During the spring of 2001, beargrass was sampled on the downwind side of a dirt road bordering an application (Site U). Since earlier results indicated that the distances selected for sampling in previous applications were too far from the application site, samples were collected from the edge of the application site and out to approximately 100 feet (Table 24). The road bordering the application was on a ridge of the mountain slope (Figure 11). The sampling area was down the slope from the road at the edge of the application site. Sampling commenced 2.5 hours after application. Samples were collected from one or two plant within close proximity. The furthest sample from the edge of the application site with a positive detection was at 41 feet (Table 24 and Appendix F).

Figure 11. Application and plant sampling sites for off-site movement during application.

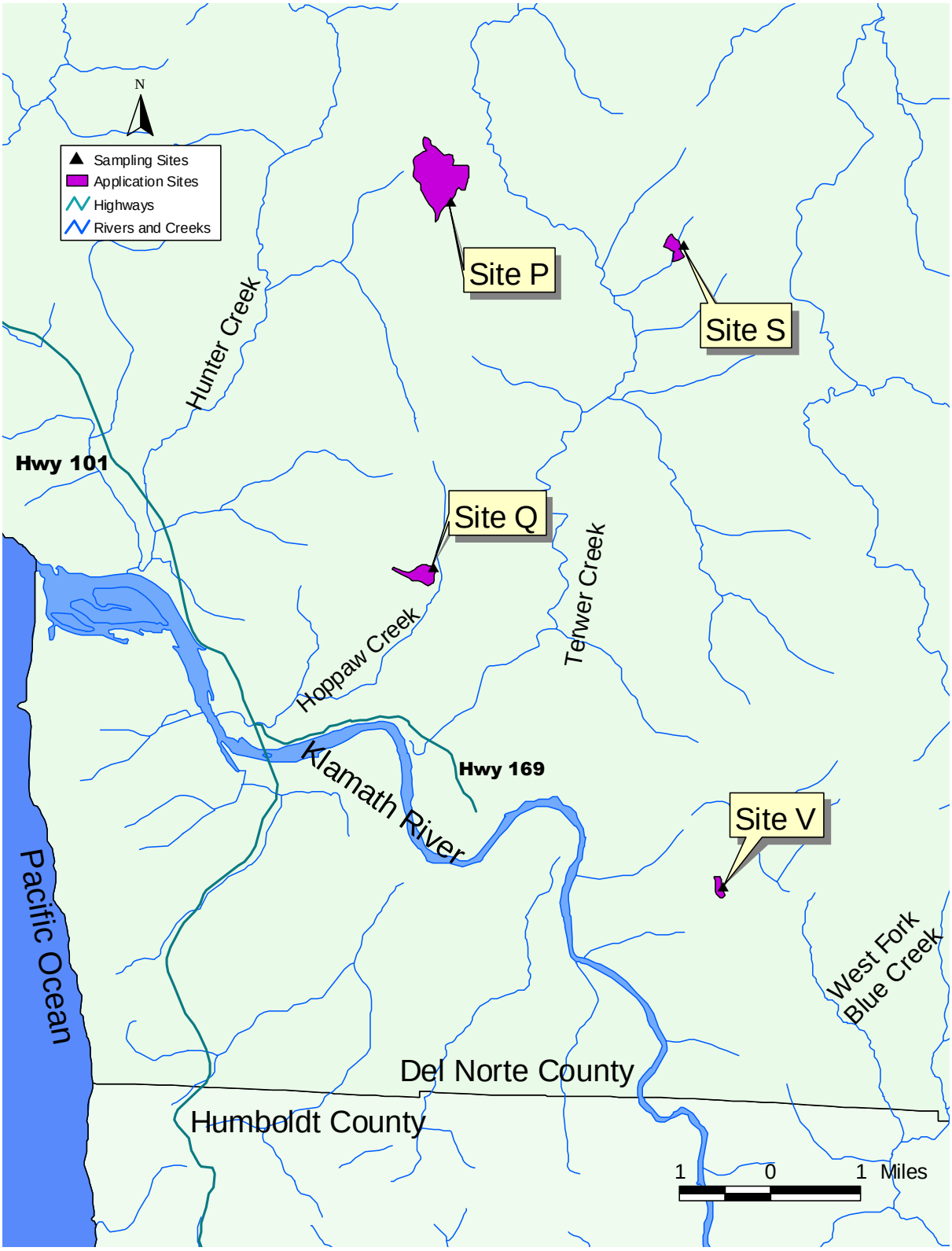


Table 24. Results of plant sampling for off-site movement of herbicides during aerial application.

Site	Sampling Date	Plant Type	Distance (feet)	No. of samples	Average Concentration (ppm)	
					Triclopyr	2,4-D
P	4/26/2000	Beargrass	121	1	ND[a]	ND[a]
		Beargrass	210	1	ND	ND
Q	9/11/2000	Beargrass	185 - 215	3	ND	ND
			220 - 240	3	ND	ND
			250 - 285	3	ND	ND
	9/11/2000	Huckleberry	185 - 210	3	ND[a]	ND[a]
			220 - 235	3	ND	ND
			245 - 260	3	ND	ND
S	9/11/2000	Yarrow	20 - 23	3	0.11	0.10
			100 - 150	4	ND[b]	ND[b]
V	4/23/2001	Beargrass	0	3	0.56	0.41
			30 - 41	3	0.14	0.10
			50 - 90	3	ND	ND

[a]No detectable amount. Minimum reporting limit: 0.05 ppm
[b]No detectable amount. Minimum reporting limit: 0.10 ppm

Monitoring Dissipation of Herbicide From an Application

Six sites were selected during the study to monitor the dissipation of the applied herbicides over time. Because methods were only available for 2,4-D and triclopyr, it was decided to monitor only aerial applications. All applications monitored were tank mixes of triclopyr and 2,4-D. A composite background sample was collected at each site from numerous plants within the area to determine if any background levels of the herbicides were present prior to sampling. Tank samples were collected prior to sampling for all applications monitored except for sampling site T in the Bald Hills Road (Table 25). All samples were within expected concentrations of a label rate application. Table 26 presents average of the replicate samples collected. The raw data for all plant samples are located in Appendix F.

Table 25. Results for application tank samples for dissipation monitoring sampling areas.

Date of Application	Site	Percent Active Ingredient (%)	
		Triclopyr	2,4-D
4/26/2000	N	1.14	1.08
4/26/2000	O	1.01	1.02
9/10/2000	R	1.12	1.00
9/13/2000	T	NA	NA
4/23/2001	U	1.10	1.04
4/23/2001	W	1.23	1.21

NA = not available

In the spring of 2000, sites N and O were selected for dissipation monitoring. Site N, in the Hunter Creek watershed (Figure 12), was treated on April 26th at approximately 14:00 and samples were collected starting one hour following completion of the application. A background sample collected the day before application indicated that background residues of both herbicides were present in the area before the application. Beargrass was sampled from day 0 (application day) to 146 days after application. Because of the limited number of plants available, only two replicates were collected at this site each sampling day. Triclopyr was detected through day 91 after application. No residues were detected 146 and 511 days from application. 2,4-D was detected through 43 days after application; no 2,4-D was detected 91, 146 and 511 days after application (Table 26 and Figure 13). The second area monitored (Site O) was also treated on April 26th, at approximately 17:30, and samples were collected starting 30 minutes later. Only one sample was collected at this site each sample date due to lack of plants. No residues were detected 43, 91 and 511 days from application.

Sites R and T were selected during the fall of 2000 to monitor for dissipation of triclopyr and 2,4-D over time. Site R was treated on September 10th, 2000 at approximately 8:30. Day 0 samples of huckleberry berries and yarrow plants were collected starting five hours following application. Samples were collected along the side of a dirt road that ran through the application area. Plants were sampled within 120-foot to 145-foot long spans for each replicate. Three replicates were collected for each plant species. Starting with the third sampling date (day 9), the entire stretch of huckleberry plants was composited as one sample due to the diminishing number of berries available. The herbicides were detected on both the

huckleberry and yarrow plants through 65 days after application (Table 26 and Figure 13). One hundred fifty days after application, there were no huckleberry berries and only enough yarrow for collection of one sample. The yarrow had no detectable amount of the herbicides. In September 2001, 372 days after application, new growth yarrow plants were sampled and no detectable amounts of the herbicides were measured.

The second site monitored during the fall of 2000 (site T) was located in the Bald Hills Road-Johnson Road area of Humboldt County (Figure 12). Manzanita berries were collected along a dirt road that ran through an application area. Three replicate samples were collected for each sampling date. Each replicate sample was made up from one or two plants next to each other. Table 26 and Figure 13 presents the data. Site could not be sampled 152 days after application due to snow. A final sample was collected the following fall (370 days after application) to see if there were any herbicide residues in the remaining manzanita berries. No measurable concentrations of triclopyr or 2,4-D were detected in the final samples.

The last application monitored took place on April 23, 2001 in the West Fork Blue Creek area. Two sites (U and W) were monitored. Site U was located within an application area of approximately 25 acres. Three replicate samples of Oregon grape were collected on days 0, 1, 8, and 37 after application (Table 26 and Figure 13). The plants within the area did not appear to show signs of herbicide damage and upon receipt of the results for samples taken through day 37 (all non-detect), it was determined that our site was outside of the application area and sampling was stopped. Replicate samples of beargrass were collected from three "monitoring" areas within the application area. All plants within each monitoring area were sampled. Samples were collected on days 0, 1, 8, 37, 87 and 150 days after application. The results are shown in Table 26. Concentrations of both herbicides were detected through day 87 (Appendix F). The final samples were collected 150 days after application. The final samples did not contain any measurable amount of either triclopyr or 2,4-D.

Figure 12. Herbicide dissipation sampling sites.

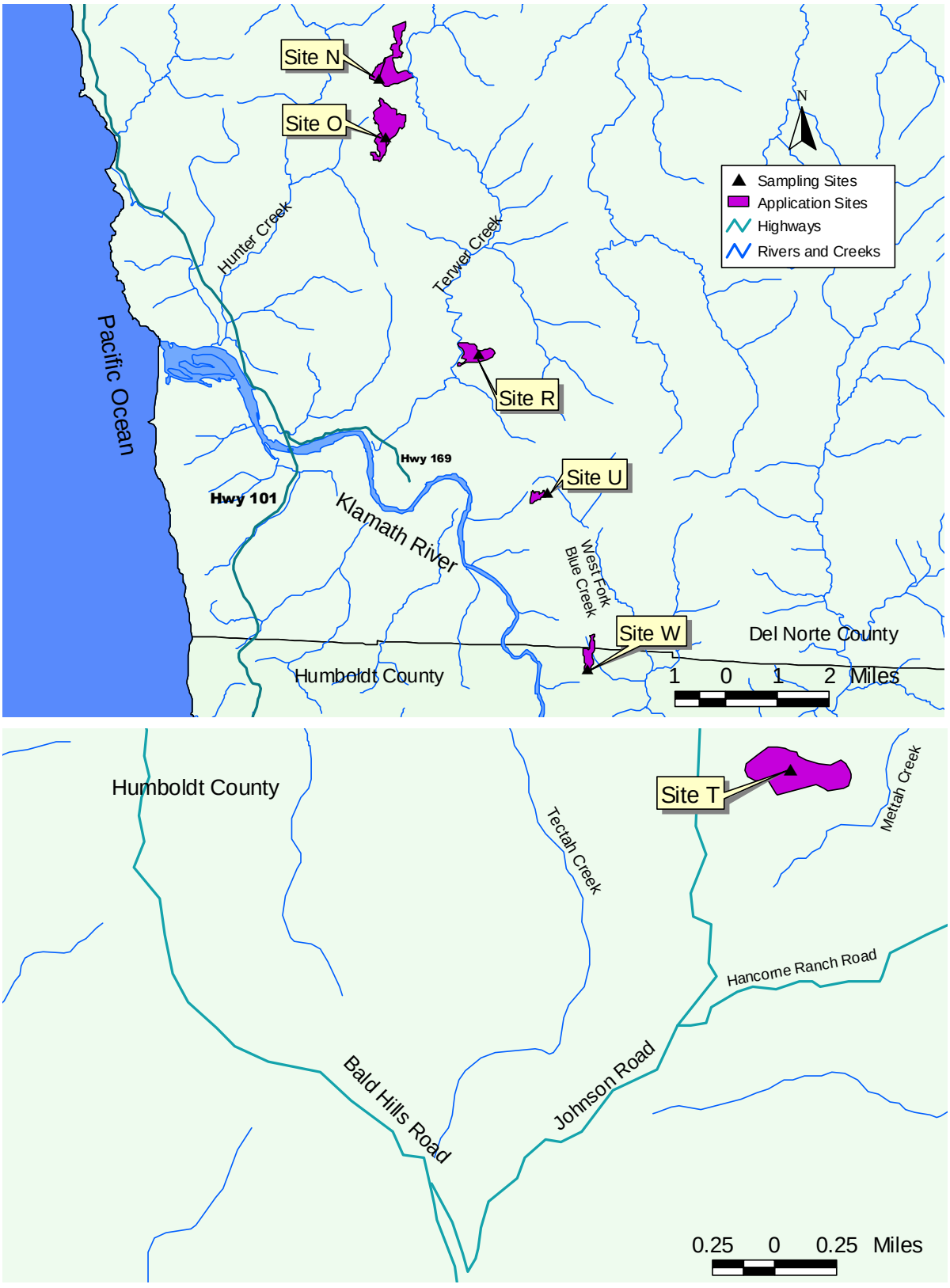


Table 26. Results of plant sampling for dissipation of herbicides on plants over time.

Site	Plant Type	Days From Application	Number of Samples	Average Concentration (ppm)	
				Triclopyr	2,4-D
		0	2	0.92	0.61
		1	2	0.19	0.15
		14	2	ND	ND
		43	2	0.04	0.07
		91	2	0.05	ND
		146	2	ND	ND
		511	3	ND	ND
O	Beargrass	-1	1	ND	ND
		0	1	0.46	0.41
		1	1	0.19	0.14
		14	1	0.13	0.07
		43	1	ND	ND
		91	1	ND	ND
		511	3	ND	ND
R	Huckleberry	0	3	0.40	0.12
		1	3	0.55	0.27
		9	1	0.63[a]	0.41[a]
		16	1	0.63[a]	0.41 [a]
		32	1	0.46[a]	0.33 [a]
		65	1	0.31[a]	0.22 [a]
		372	2	ND[a]	ND [a]
	Yarrow	0	3	6.61	3.62
		1	3	5.97	6.56
		9	3	5.87	5.24
		16	3	4.72	3.90
		32	3	1.35	0.62
		65	3	0.19	0.07
		157	1	ND	ND
		372	3	ND	ND
T	Manzanita	0	3	0.05	0.12
		1	3	0.79	0.31
		7	3	0.28	0.23
		13	3	0.32	0.27
		29	3	0.19	0.14
		62	3	0.22	0.15
		370	2	ND	ND
U	Oregon grape	0	3	ND	ND
		1	3	ND	ND
		8	3	ND	ND
		37	3	ND	ND

Table 27. Results of plant sampling for dissipation of herbicides on plants over time (cont.).

Site	Plant Type	Days From Application	Number of Samples	Average Concentration (ppm)	
				Triclopyr	2,4-D
W	Beargrass	0	3	1.48	0.73
		1	3	2.34	0.99
		8	3	1.11	0.75
		37	3	0.23	0.21
		87	3	0.04	0.03
		150	3	ND	ND

[a]Composite sample on this date.

Figure 13. Dissipation of triclopyr and 2,4-D over time on monitored plants.

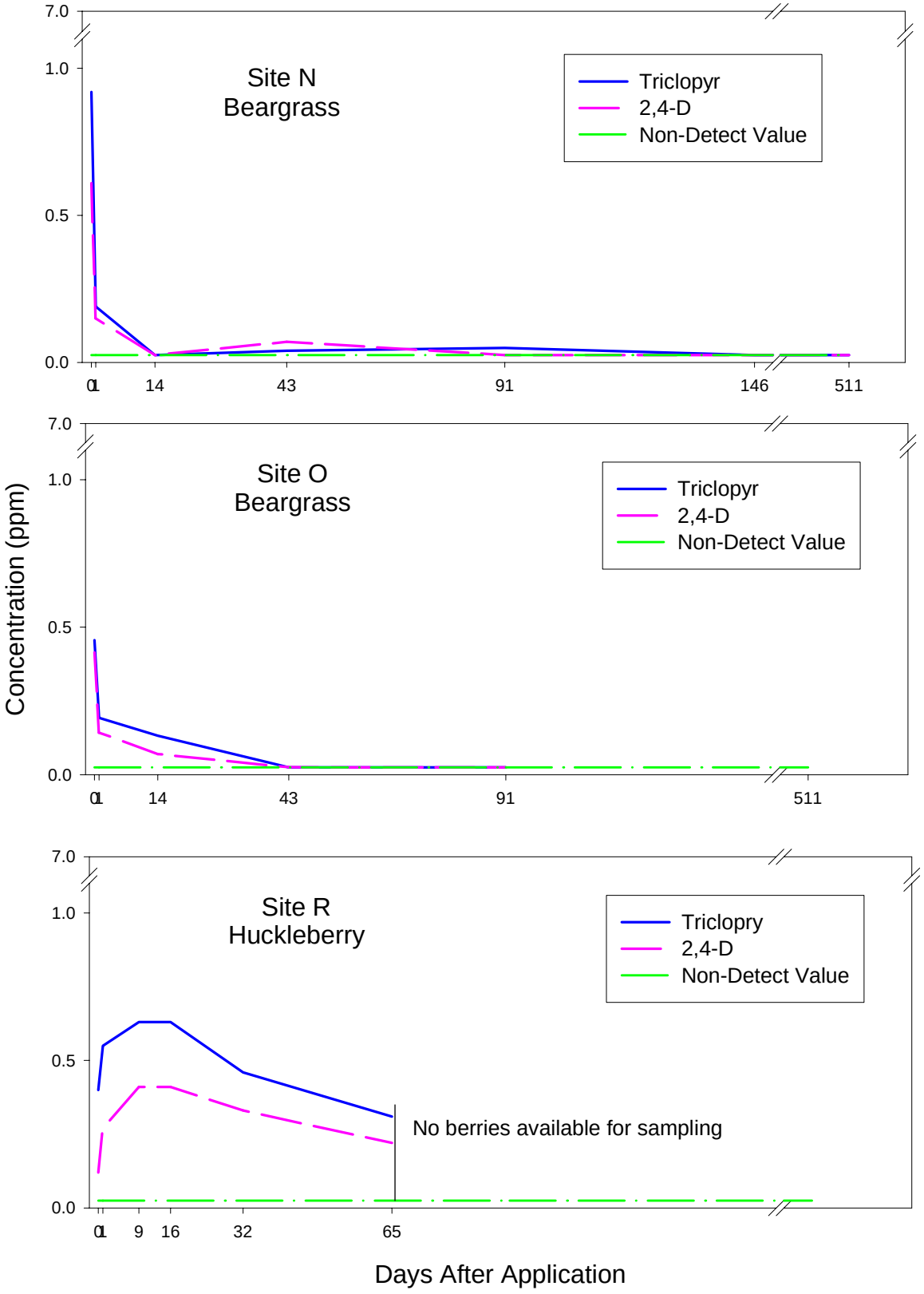
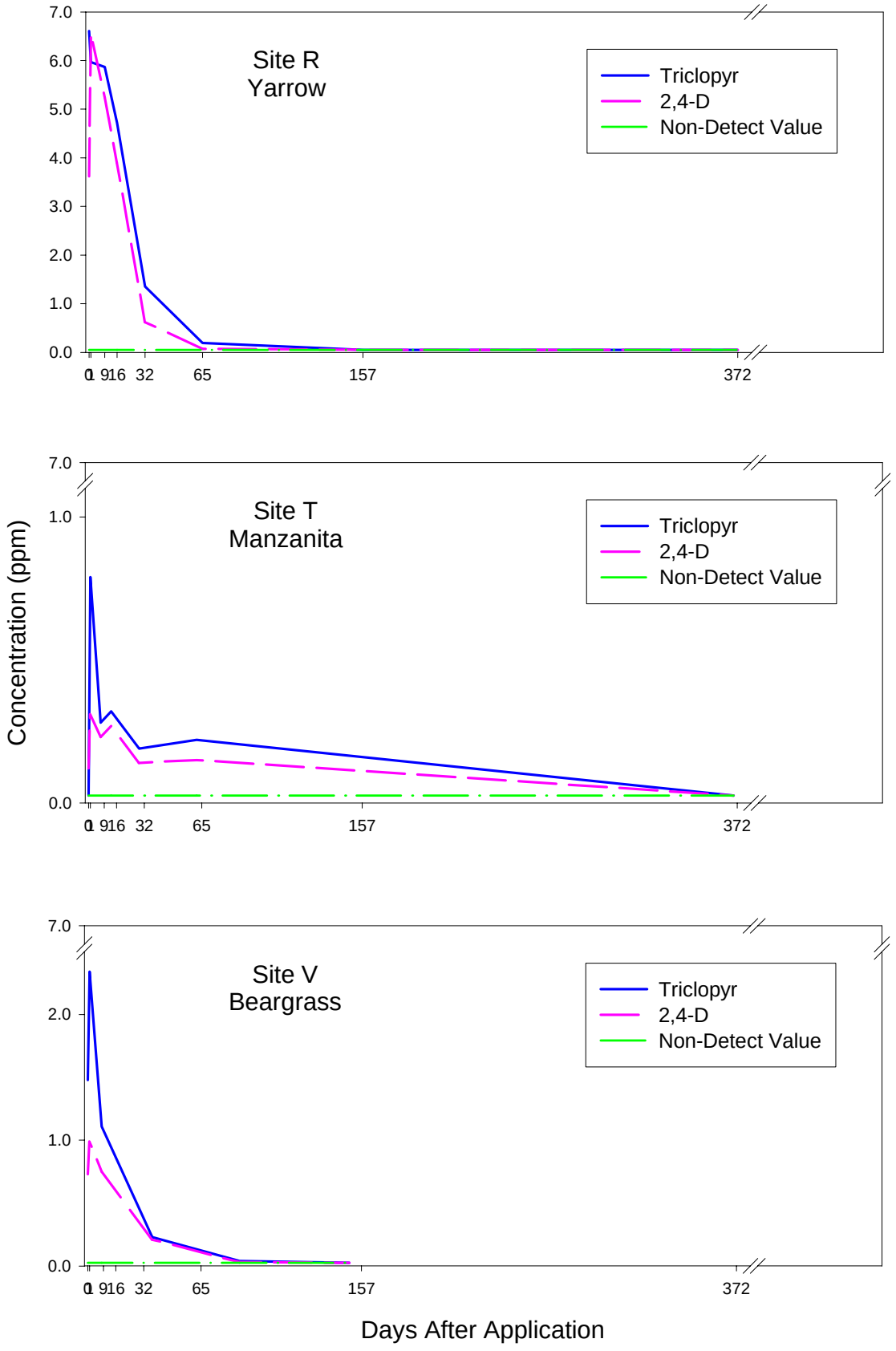


Figure 13. Dissipation of triclopyr and 2,4-D over time on monitored plants (continued).



Quality Control

The ongoing quality control results are presented in Appendix G. Average recoveries ranged from 68.2 percent to 96.8 percent for all of the herbicides analyzed (Table 27). As part of the quality control methods, control limits are determined for each chemical and plant combination (see quality control methods in Material and Methods section). If the spike samples extracted with each set of samples are above or below the control limits, the samples in the set are also considered out of the control limits (Appendix G.). If the one spike recovery is out of control and the other is not, the average between the two spikes is compared to the control limits. The number of spike recoveries, and therefore sample results, out of control limits indicates some difficulty with the analyte or plant material. Samples below the lower control limits may indicate an under estimation of concentrations, whereas samples above the upper control limits may be an over estimation of reported concentrations. Of the 151 plant samples collected, 6 percent of the samples were below the lower control limit and 19 percent were above the upper control limit for 2,4-D. Yarrow made up 25 of the samples that were above the upper control limits. For triclopyr, 7 percent of the samples were below the lower control limits and 15 percent were above the upper control limits. Again, yarrow made up most of the samples (21) that were above the upper control limits. The data presented in this report have not been adjusted for laboratory quality control results.

Table 28. Average laboratory quality control recovery results for plant samples**.**

Plant Type	Average Recovery (%)	
	2,4-D	Triclopyr
Beargrass	68.2	77.1
Huckleberry	91.7	93.4
Manzanita	88.8	96.8
Oregon grape	74.0	80.2
Yarrow	83.2	88.7

Additional Plant Sampling

In September 1998, staff from the Hoopa Valley Tribe took DPR personnel to two traditional gathering areas to collect plant material for 2,4-D and triclopyr analysis. Samples of both beargrass and woodwardia fern were collected. The following day, plant samples were collected with members of the Karuk Tribe at three traditional gathering sites. Grey willow shoots, Tanoak acorns, and Huckleberry berries were collected and sent in for analysis. There were no detectable residues of 2,4-D or triclopyr on any of the plant material.

In the summer of 1998, several small areas of the Klamath National Forest were sprayed with 2,4-D and picloram to eradicate the noxious weed spotted knapweed. The areas sprayed are within the traditional gathering areas of Karuk tribal members. On November 16, 2000, samples of deerbrush and Oregon grape roots were collected and analyzed for 2,4-D residues. Both samples had no detectable amount of 2,4-D.

Additional Water Sampling

Additional sampling was conducted in the spring of 2002 by staff of the Yurok Tribe Environmental Program. None of the samples collected contained measurable amounts of atrazine. In addition, Tanoak acorn and huckleberry samples were collected in the fall of 2002. A description of the sampling is located in Appendix I.

Fish Tissue Sampling

Fish samples were collected following the first rainfall after aerial applications of 2,4-D at two sites in the spring of 2001 (Table 28, Figure 14). M^{c}Garvey Creek and the West Fork of Blue Creek were selected since they were already being used by the Fisheries Department of the Yurok tribe. Sculpin (*Cottus gulosus*) were collected in a trap at M^{c}Garvey Creek and steelhead trout (*Oncorhynchus mykiss*) were collected with electrofishing equipment at the West Fork of Blue Creek. These species were selected because the sculpin are resident fish that remain in the local waters for their lifetime and

the steelhead for the first two to three years of their life. Three replicate samples were collected for each sampling period at each site, with a minimum of 30 grams of whole fish per sample. Water samples were collected at the same time for analysis. Water and fish samples were collected on April 13, 2001, for background, on May 1, 2001, approximately 48 hours after the first rain runoff event (0.50 inch) post-application, and again on May 8, 2001, approximately one week after the first rain runoff event post-application. All fish samples were collected in accordance with the California Department of Fish and Games Quality Assurance Manual (Appendix H). All fish samples were frozen soon after collection and maintained below -10°C through storage and transportation to the laboratory for analysis (SOP QAC004.01; Appendix D). Each shipment of samples was accompanied by a Hobo® Temp temperature data logger. All laboratory quality control data is located in Appendix H. None of the fish tissue samples contained any measurable amount of triclopyr, 3,5,6-trichloro-2-pyridinol (a breakdown product of triclopyr), 2-4-D or 2,4-dichlorophenol (a breakdown product of 2,4-D)(Table 29). None of the water samples collected with the fish samples contained any measurable amount of triclopyr or 2,4-D (Table 30).

Table 29. Description of fish tissue sampling sites.

Site	Location	Fish Species
McGarvey Creek	41° 29' 54.4" N 124° 00' 02.6" W	Sculpin
West Fork Blue Creek	41° 28' 09.0" N 123° 54' 49.1" W	Steelhead trout

Table 30. Fish tissue sample results.

Site	Date	Concentration (ppb)			
		Triclopyr	3,5,6-trichloro-2-pyridinol	2,4-D	2,4-dichlorophenol
McGarvey Creek	4/13/01	ND[1]	ND[2]	ND[3]	ND[4]
	5/01/01	ND	ND	ND	ND
	5/08/01	ND	ND	ND	ND
West Fork Blue Creek	4/13/01	ND	ND	ND	ND
	5/01/01	ND	ND	ND	ND
	5/08/01	ND	ND	ND	ND

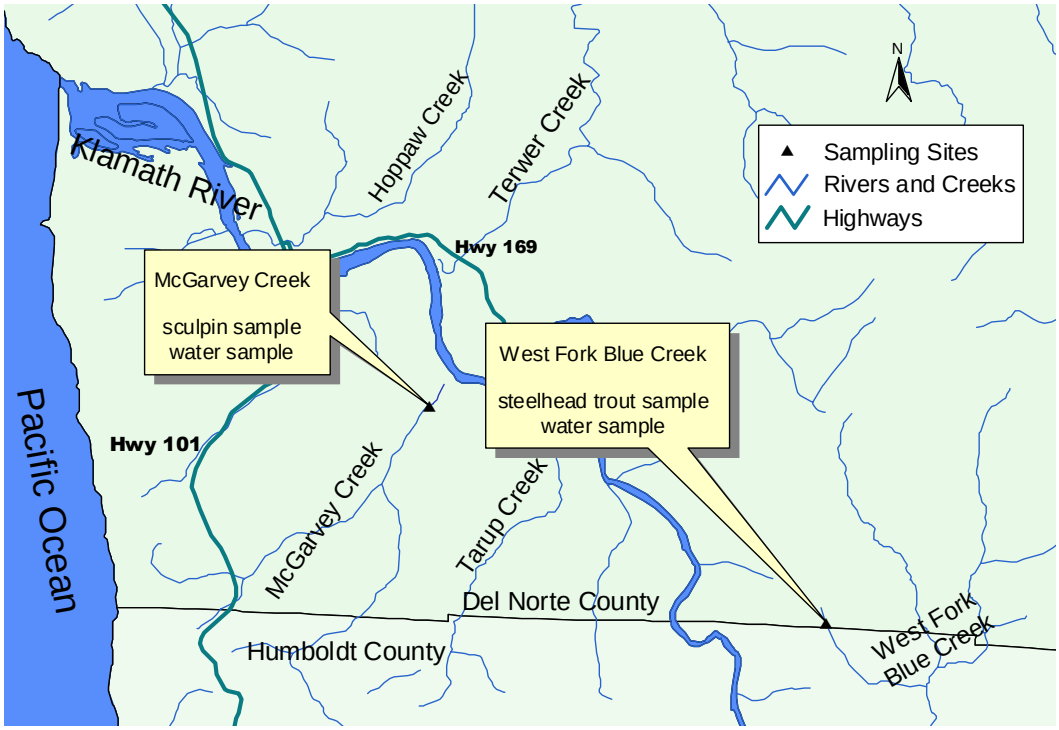
ND = no detectable residues. Minimum report limit: [1] 1 ppb, [2] 5 ppb, [3] 2 ppb, [5] 5 ppb

Table 31. Results for water samples collected with fish samples.

Site	Date	Concentration (ppb)	
		Triclopyr	2,4-D
McGarvey Creek	4/13/01	ND[1]	ND[1]
	5/01/01	ND	ND
	5/08/01	ND	ND
West Fork Blue Creek	4/13/01	ND	ND
	5/01/01	ND	ND
	5/08/01	ND	ND

ND = no detectable residues. Minimum report limit: 0.10 ppb.

Figure 14. Location of fish tissue sampling sites.



Summary and Conclusions for Plant Sampling and Additional Sampling

Four sites were monitored for off-site movement during application due to drift. The data indicates that some drift does occur outside of the treatment area. The farthest distance away from the treatment area with a detection of herbicide was at 41 feet. The highest concentrations measured away from the edge of the application were 0.14 and 0.10 ppm

for triclopyr and 2,4-D, respectively. A previous study conducted by the DPR on U.S. Forest Service properties found herbicide residues out to 100 feet away from the treatment area (Segawa et al., 2001).

Four plant species were monitored in six application areas (of which one site proved to be outside of the treatment area) to determine the dissipation time for herbicides after application. The highest levels were detected on the yarrow plants. At half of the sites, the concentrations were higher on the day after application compared to the application day. This may indicate that the plants are translocating the herbicides through the plant. All plants sampled showed signs of acute damage due to the treatment after approximately a month. No residues were detected at four of the sites by approximately day 150. The other site still had measurable amounts of herbicide at approximately day 60, but no residues were detected at the next sampling date of 370 days (53 weeks). In Segawa et al. (2001) glyphosate and triclopyr were detected up to 67 to 80 weeks after treatment, respectively. The plants were sampled a final time in the fall of 2001. At sites N and O the beargrass was producing new shoots and growth. The yarrow had new growth and the huckleberry had a new production of berries. The manzanita bushes at site T and beargrass at site W were in a state of decay so only old berries and growth was available for sampling. All final samples were below a measurable concentration.

As a comparison of what concentrations are allowed on food products, Table 31 lists some food tolerances which have been determined for the herbicides monitored in this study on various food products. Food products cannot exceed the established tolerances (Table 31). There are only a few tolerances established for atrazine and triclopyr. As noted earlier, the highest concentrations detected in the off-site plant samples were 0.14 and 0.10 ppm for triclopyr and 2,4-D, respectively, both below sample food tolerances.

The additional plant and fish tissue sampling resulted in no detections of the herbicides applied.

Table 32. Tolerances established for residues on or in raw food commodities[a].

Atrazine		2,4-D		Glyphosate		Triclopyr	
Item	Conc. (ppm)	Item	Conc. (ppm)	Item	Conc. (ppm)	Item	Conc. (ppm)
corn	0.25	apple	5	asparagus	0.5	fish	3.0
guava	0.05	apricot	5	avocado	0.2	shellfish	3.5
		citrus	5	banana	0.2		
		potato	0.2	berries	0.2		
		quince	5	guava	0.2		
		fish	1	nut (tree)	1.0		

[a]U.S. EPA Federal Code of Regulations (U.S. EPA 2000b)

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