WATER QUALITY AND PESTICIDES

2,4-D:

USE FOR CONIFER RELEASE AND WATER HYACINTH CONTROL

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PREFACE

This is one of a ten volume series of reports issued by the State Water Resources Control Board (SWRCB) on agricultural chemicals. Titles of volumes in this series: (1) Water Quality and Pesticides: A California Risk Assessment Program; (2) Toxaphene; (3) 1,2-Dichloropropane/1,3-Dichloropropene; (4) Rice Herbicides: Molinate and Thiobencarb; (5) Endosulfan; (6) Ethylene Dibromide; (7) Groundwater Contamination by Pesticides: A California Assessment; (8) Malathion; (9) 2,4-D; and (10) Glyphosate.

This report brings together under a single cover a number of staff reports prepared between 1981-84 that deal with water quality impacts from two separate uses of 2,4-D. The first use involves silviculture, while the second use involves direct application of 2,4-D to waterways to control water hyacinths. Both of these uses generated public concern due to claimed human health effects from the use of 2,4-D and 2,4,5-T as ingredients in Agent Orange.

State Board staff took the lead in assessing the water quality impacts of these uses and in bringing together all of the involved parties including regulatory agencies and interest groups opposed to and supportive of continued 2,4-D use. A 2,4-D study group was formed in 1982 with the objectives of developing California specific information on (1) aquatic toxicity and (2) the potential for 2,4-D to reach north coast waterways under quantifiably defined best management practice conditions. This report documents the accomplishment of these objectives. The second part of this report documents the State Board's contribution to an interagency Water Hyacinth Task Force.

The mention of a particular chemical or formulated product should not be interpreted as a recommendation for its use.

ACKNOWLEDGEMENTS

Scientific peer reviewers of all these documents are acknowledged, especially Drs. Charles Steffan and Gilman Veith, EPA Duluth, Minnesota. Dr. Al Rubin, EPA, Washington D.C., reviewed application of the EPA methodology in developing California water quality criteria for 2,4-D PGBE.

Department of Fish and Game staff conducted chemical and biological tests. The Department of Boating and Waterways incorporated SWRCB guidelines to protect beneficial uses of water, particularly for irrigated agriculture. Regional Board staff participated in field monitoring work, particularly Sue Warner in Region 1 and Bob Lewis in Region 5.

Charlene Sanders, Keith Turk, Glenda Howley, Cathy Reimel and Karen Larsen are acknowledged for typing, Hugh F. Smith for editorial assistance, and Sandy Karinen for assistance with report graphics.

The advice and technical assistance of the following 2,4-D Study Group members was especially appreciated:

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3. California State Water Resources Control Board. Toxic Substances Control Program. Staff Review of Issues Regarding the Change from 2,4-D Propylene Glycol Butyl Ether Ester (PGBEE) to 2,4-D Butoxy Ethyl Ester (BEE), February 16, 1982.

4. California Department of Fish and Game. Pesticide Investigations Unit. Toxicities of Butoxyethanol Ester and Propylene Glycol Butyl Ether Ester Formulations of 2,4-D to Juvenile Salmonids. (Interagency Agreement No. 1-119-420-1 (C-1557)). November 1983.

5. California State Water Resources Control Board. North Coast and Central Valley Regional Water Quality Control Boards. Staff Report. Monitoring of Silvicultural Use of 2,4-D in Northern California. January 1984.

B. Water Hyacinth Control

6. California State Water Resources Control Board. Toxic Substances Control Program. Water Quality Guidelines for Herbicides Used on Water Hyacinth in the Sacramento-San Joaquin Delta. October 1982.

LIST OF ABBREVIATIONS

AGENCIES

Federal:

NAS	National Academy of Sciences
USEPA	United States Environmental Protection Agency
USFWS	United States Fish and Wildlife Service

California:

DFA	Department of Food and Agriculture
DFG	Department of Fish and Game
DHS	Department of Health Services
DWR	Department of Water Resources
CVRWQCB	Central Valley Regional Water Quality Control Board
NCRWQCB	North Coast Regional Water Quality Control Board
SWRCB	State Water Resources Control Board

UNITS

A	Acres
C	Degrees celsius
cc	Cubic centimeter (milliliter)
g	Gram
kg	Kilogram
km	Kilometer
l	Liter
lb	Pound
M	Molar
m	Meter
mg	Milligram (10^{-3} gram)
ng	Nanogram (10^{-9} gram)
pH	Measure of acidity (negative logarithm of hydrogen ion activity)
ppb	Part per billion (10^{-9} gram/gram or 10^{-6} gram/liter)
ppm	Part per million (10^{-6} gram/gram or 10^{-3} gram/liter
torr	Unit of atmospheric pressure equivalent to millimeters of mercury
ug	Microgram (10^{-6} gram)
yr	Year

MISCELLANEOUS

ADI	Acceptable daily intake
AI	Active ingredient
BEE	Butoxy ethyl ester of 2,4-D herbicide
BMP	Best management practice
EC50	Effective concentration of a toxicant that severely affects normal function of 50 percent of a test population within a specified time
FIFRA	Federal Insecticide, Fungicide and Rodenticide Act
FR	Federal Register
HCT	Hematocrit
HGB	Hemoglobin
IPM	Integrated pest management
LC50	Lethal concentration of a toxicant that kills 50 percent of a test population within a specified time
LD50	Lethal dose of a toxicant that kills 50 percent of a test population within a specified time
MATC	Maximum allowable toxicant concentration
MCL	Maximum contaminant level
NA	Not available
ND	Not detected
NOEL	No observed effect level
PIK	USDA payment in kind program
RBC	Red blood cell
TL50	Median tolerance limit: Concentration in which 50 percent of the animals exhibit a specific response at a certain time
UC	University of California
WBC	White blood cell

2,4-D: USE FOR CONIFER RELEASE AND WATER HYACINTH CONTROL

I. Introduction

Two controversial issues involving water quality impacts of the herbicide 2,4-D are discussed in this report. The first issue, 2,4-D use in northern California conifer release programs, spans the period 1978 through 1984. California regulatory agencies, the public, and the timber industry have, during this period, interacted to address the potentially conflicting goals of maximizing conifer forest growth while keeping surface waters relatively free of 2,4-D, the major herbicide used for this purpose. The chronology of events which follows indicates that both goals are compatible. The initial regulatory emphasis of the North Coast Regional Water Quality Control Board (NCRWQCB) regulating herbicide concentrations in water through numerical limits has evolved to the current approach of achieving carefully controlled application by following specific field management guidelines. "Best Management Practices" (BMP) is the term used to describe this approach.

The second issue, 2,4-D use for water hyacinth control, spans the period 1982 through 1984. 2,4-D has been the focus of recent attention and public concern in the Sacramento-San Joaquin Delta. The target pest was different here than in the north coast, requiring a different 2,4-D formulation. The problem involves excessive water hyacinth growth which impairs navigation in narrow channels. An evaluation by the California Department of Boating and Waterways (DBW) of alternative means to control this growth determined that the most cost-effective method which also protected water quality was chemical control through the use of 2,4-D dimethylamine salt (2,4-D DMA). This formulation is somewhat less toxic to aquatic organisms than the 2,4-D ester products used in the north coast forest programs. The California Department of Health Services concluded that the current EPA drinking water limit of 100 ppb for 2,4-D DMA appears adequate to protect public health. A more protective guideline of 20 ppb 2,4-D DMA was recommended by State Board staff and adopted by DBW. This guideline takes into account the use of Delta water for crop irrigation and the sensitivity of certain broadleaf plants such as grapes and tomatoes to 2,4-D DMA.

II. Conifer Release

The phenoxy herbicide 2,4-D (2,4-dichlorophenoxyacetic acid) is widely used to increase timber yields by inhibiting or destroying vegetation that competes with commercially valuable conifers such as redwood and pine.

Over 200,000 pounds per year of 2,4-D were applied by backpack spraying or by helicopter to 117,000 acres of national forests in 1979/80 (Norris, 1980). This herbicide can pose a threat to aquatic life and municipal water supplies, because it can be transported from the target area to streams by wind drift and water runoff.

Most 2,4-D aerial applications for conifer release in

season, numerous small streams form a dense network of waterways that merge into larger streams and rivers. The slower and smaller headwater creeks are ideal production sites for aquatic insects and invertebrates, which in turn provide food for fish downstream. If the materials are applied by air (Norris, 1971), off-target movement of herbicides into forest water bodies can occur. Northern California's forest lands pose unique challenges because their steep slopes, numerous drainage courses, water-saturated soils, and high rainfall can increase the potential for applied chemicals to enter the aquatic system. The degree of off-target movement into water can be controlled with the use of buffer strips, anti-drift agents, and favorable weather conditions.

Chronology of State and Regional Board Actions on 2,4-D Discharge Related to Forestry Use

December 1978:
The California Department of Health Services, responding to public and regulatory agency concerns about silviculture herbicide toxicity, banned discharge of dioxin-containing 2,4,5-T, the most commonly used phenoxy herbicide for conifer release. The forest industry subsequently increased the use of the propylene glycol butyl ether ester

(DFA), and county agricultural commissioners to develop best forestry management practices (BMPs) that would protect water quality.

Debate continued concerning the validity and efficacy of the proposed 10 ppb limit for 2,4-D. A public interest group, the Humboldt Herbicide Task Force, had requested a zero discharge limit on 2,4-D and cited as evidence Canada's restrictions on the sale of some 2,4-D formulations. The forest and chemical industries and the California Department of Food and Agriculture (DFA) challenged the 10 ppb limit as "unattainable".

<u>April 10, 1981</u>:
SWRCB denied an appeal from the Humboldt Herbicide Task Force requesting zero discharge of 2,4-D for the north coast region. The SWRCB based its action on the absence of new information upon which to derive a 2,4-D limit different from that adopted by the NCRWQCB.

<u>May 18, 1981</u>:
SWRCB staff report (Appendix 1) reviewed currently available 2,4-D toxicology and environmental fate information. The Regional Board's 10 ppb limit for 2,4-D esters was supported by the Department of Fish and Game and State Board staff with the recommendation that the receiving water limit be related to the duration of exposure.

<u>May 19, 1981</u>:
An SWRCB public hearing was held on the NCRWQCB Basin Plan Amendment which proposed limiting 2,4-D concentration in receiving waters to 10 ppb.

<u>July 1, 1981</u>:
SWRCB staff review of issues raised at the May 19, 1981 hearing (Appendix 2) recommended that 2,4-D receiving water limits be developed using November 1980 EPA methodology (Reference 1). The limits include two numbers, a time dependent 24-hour average and an instantaneous maximum value.

<u>July 16, 1981</u>:
SWRCB remanded the North Coast Regional Board Basin Plan Amendments with a recommendation that the Regional Board adopt a two-number limit of 40 ppb 2,4-D acid equivalent (instantaneous maximum value) and 2 ppb 2,4-D acid equivalent (24-hour average). The two-number limit was developed using the 1980 EPA criteria development methodology. It was applied to the PGBE ester, the most widely used 2,4-D compound in the north coast region at that time. According to EPA, California was the first state in the nation to develop water quality limits for a toxic organic compound using this new methodology.

September 3, 1981:
The NCRWQCB adopted the State Board-recommended limits of 40 ppb and 2 ppb for all esters of 2,4-D.

September 17, 1981:
SWRCB approved the 40 ppb and 2 ppb limits adopted by the Regional Board.

The State Board recognized the need to develop site-specific data on 2,4-D in North Coast waters using native species. Staff was directed to develop 2,4-D acute and chronic toxicity data on aquatic species of ecological and economic importance to this region. A 2,4-D study group comprising local, state, and federal agencies, timber industry and public interest group representatives, and chaired by the State Board's Toxics Special Project Manager, was formed to provide input into this study and review the results before presentation to the Board for approval.

During the planning stages of this study, the timber industry announced that for the fall 1981 season, the 2,4-D BEE (butoxyethanol ester) formulation would be used in place of 2,4-D PGBEE.

February 16, 1982:
SWRCB staff report highlighted issues related to the change to 2,4-D BEE from 2,4-D PGBEE (Appendix 3). The 2,4-D study group recommended modifying the aquatic toxicity study design to compare relative toxicities of both 2,4-D formulations. Due to budgetary constraints, the scope of the original study was reduced to the following components: (1) continual flow acute toxicity tests for two fish species; (2) continual flow chronic bioassay for one fish species; (3) water quality monitoring of 2,4-D in runoff in cooperation with the USFS at one site during spring and fall 1983. The acute tests were performed using 2,4-D PGBEE and 2,4-D BEE, while the chronic test was performed with 2,4-D BEE.

December 2, 1982:
The NCRWQCB amended the two-number (40 ppb and 2 ppb) limit in the Basin Plans to apply exclusively to 2,4-D PGBEE because these guidelines were developed using only 2,4-D PGBEE toxicity data. The Regional Board also issued Waste Discharge Requirements for aerial spraying of 2,4-D BEE limiting receiving water concentrations to 10 ppb 2,4-D. Regional Board staff had recommended a limit of 20 ppb; public interest group members recommended a zero limit; timber industry representatives recommended a protective two-number limit of 280 ppb and 37 ppb (instantaneous maximum and 24-hour average limit respectively).

March 17, 1983:
SWRCB approved the North Coast Regional Board Basin Plan Amendments restricting the 2,4-D two-number limit of 40 ppb and 2 ppb to 2,4-D PGBEE only.

June 14, 1983:
The North Coast Regional Board Staff Report recommended control of aerially applied 2,4-D and other pesticides applied to public lands through Best Management Practices (Reference 4). The bases for these BMPs are guidelines issued by the California Department of Food and Agriculture (DFA) and individual county agricultural commissioners.

July 28, 1983:
North Coast Regional Board adopted Best Management Practice guidelines as described in June 14, 1983 staff report.

March 17, 1983:
SWRCB approved the North Coast Regional Board Basin Plan Amendments restricting the 2,4-D two-number limit of 40 ppb and 2 ppb to 2,4-D PGBEE only.

June 14, 1983:
The North Coast Regional Board Staff Report recommended control of aerially applied 2,4-D and other pesticides applied to public lands through Best Management Practices (Reference 4). The bases for these BMPs are guidelines issued by the California Department of Food and Agriculture (DFA) and individual county agricultural commissioners.

July 28, 1983:
North Coast Regional Board adopted Best Management Practice guidelines as described in June 14, 1983 staff report.

September 1983:
North Coast Regional Board adopted Waste Discharge Requirements for aerial spraying of 2,4-D BEE to a timber harvesting company limiting receiving water concentrations of 2,4-D BEE to 10 ppb.

November 2, 1983:
Results of the 2,4-D Study Group-designated acute and chronic toxicity tests performed by the California Department of Fish and Game (Reference 5) were presented to the SWRCB (Reference 6).

The test results and conclusions were obtained under the following conditions: Continual-flow tests were conducted to determine acute toxic effects of two different 2,4-D esters (PGBEE and BEE) on two salmonid species, juvenile chinook salmon (Oncorhynchus tshawytscha) and steelhead rainbow trout (Salmo gairdneri). A continual-flow chronic toxicity test with early life stages of chinook salmon (eggs-to-fry) was conducted to determine effects of 2,4-D BEE on survival and growth.

The acute lethal concentration after 96 hours of exposure (LC50 tests) indicated that 2,4-D BEE was slightly less toxic (327 to 601 ug/l) than the PGBEE formulation (313 to 454 ug/l). Based on reduced survival and growth of chinook salmon larvae and fry in the laboratory test, the estimated maximum acceptable toxic concentration under continual-flow chronic conditions was determined to be 40 ppb (ug/l) 2,4-D BEE. The contractor noted in the study report that growth differences may have occurred at concentrations below 40 ppb if lab instruments had allowed measurements with a greater degree of precision.

State Board staff presented a paper to the fifth annual California Forest Vegetation Management Conference which summarized the 2,4-D aquatic toxicity study results as well as the regulatory roles and responsibilities of the State and Regional Boards (Reference 7).

January 1984:
Results of the 2,4-D Study Group-designated field monitoring studies were submitted to the SWRCB (Appendix 5). The studies demonstrated for the first time under California conditions that carefully planned and executed Best Management Practices could prevent 2,4-D from entering north coast streams in harmful concentrations. Even after a "worst case" storm event condition, no stream sample showed 2,4-D in excess of 2 ppb.

March 29, 1984:
North Coast Regional Board recommended control of aerially applied 2,4-D and other herbicides applied to private lands through Best Management Practices (Reference 9). The bases for these BMPs are guidelines issued by the California Department of Food and Agriculture and the U. S. Forest Service.

May 31, 1984:
North Coast Regional Board adopted Best Management Practice guidelines as described in March 29, 1984 staff report (Reference 9).

SUMMARY--Silviculture

The documentation by the 2,4-D study group verifies the ability of dischargers even during "worst case" storm events to maintain 2,4-D in north coast streams below harmful levels if "Best Management Practices" are followed. As a result of this

These practices are regulated by the Department of Food and Agriculture and the County Agricultural Commissioners. The North Coast Regional Board on May 31, 1984 adopted as a Basin Plan Amendment this BMP approach for 2,4-D application to privately owned timber lands. These amendments incorporate provision for waiving Waste Discharge Requirements when the approved BMPs are used to protect water quality. The controversy surrounding this issue has not completely disappeared. Groups representing public concern continue to oppose aerial application of 2,4-D and support numerical water quality limits. Careful monitoring for 2,4-D in subsequent use seasons will determine whether the reliance on BMPs to protect water quality is fully justified.

III. Water Hyacinth Control

In the last few years, the accelerated growth of floating water hyacinth plants has impaired navigation in some of the smaller channels of the Sacramento-San Joaquin Delta. In response, the California Legislature adopted SB 3144 which required a program for hyacinth control administered by the Department of Boating and Waterways (DBW). One control strategy considered the use of the herbicides 2,4-D [illegible] for sensitive agricultural and domestic plants and an additional margin of safety against possible unknown human health effects. The 1982 test spray data indicated that mitigation measures used by the water hyacinth control program (e.g., not spraying within 50 yards of a water intake) did maintain the 2,4-D DMA concentrations in intake waters below 20 ppb.

Diquat use for this purpose will probably be limited since it is more expensive and less effective than 2,4-D DMA. Diquat quickly and irreversibly binds to plant matter and clay particles. The EPA residue limit for diquat of 10 ppb in water appears adequate for protection of public health and irrigation. The 1982 test spray data indicate: (1) the diquat residue limit can probably be met in the hyacinth control program for water leaving the spray plot; (2) fish mortality did not occur below 10 ppb; and (3) some mortality of aquatic invertebrates may occur within the spray plot only.

SUMMARY--Water Hyacinth

The Department of Boating and Waterways in October 1984, announced the successful completion of the 1984 Water Hyacinth Eradication Program in San Joaquin, Sacramento, and Contra Costa counties. Formerly clogged waterways were opened for navigation [redacted]

maintain 2,4-D concentrations below the State Board recommended [redacted]

REFERENCES

2,4-D REPORTS RELATING TO: (A) CONIFER RELEASE; AND (B) WATER HYACINTH CONTROL

A. Conifer Release

1. California State Water Resources Control Board. Toxic Substances Control Program. Staff Review of North Coast Regional Board Basin Plan Amendment to Control Herbicide Discharge. May 18, 1981. (Appendix 1)

2. California State Water Resources Control Board. Toxic Substances Control Program. Staff Review of Issues Raised Regarding 2,4-D at the May 19, 1981 Public Hearing on North Coast Regional Board Basin Plan Amendment. July 1, 1981. (Appendix 2)

3. California State Water Resources Control Board. Toxic Substances Control Program. Staff Review of Issues Regarding the Change from 2,4-D Propylene Glycol Butyl Ether Ester (PGBEE) to 2,4-D Butoxy Ethyl Ester (BEE) February 16, 1982. (Appendix 3)

4. North Coast Regional Water Quality Control Board Public Report. (1) Proposed Action to Amend the Klamath River Basin and North Coastal Basin Policy and Action Plan for Control of Discharges of Herbicide Wastes from Silvicultural Applications. (2) To Consider Adoption of the United States Forest Service Proposed Best Management Practices to Control the Discharge to Waters of the State of 2,4-D and Other Pesticides Applied to Timberlands. June 14, 1983.

5. California Department of Fish and Game. Pesticide Investigations Unit. Toxicities of Butoxyethanol Ester and Propylene Glycol Butyl Ether Ester Formulations of 2,4-D to Juvenile Salmonids. (Interagency Agreement No. 1-119-420-1 (C-1557)). November 1983. (Appendix 4)

6. California State Water Resources Control Board. Workshop Session - Special Projects. November 2, 1983. Report on Special Study of the Herbicide 2,4-D.

7. California State Water Resources Control Board. Fifth Annual Forest Vegetation Management Conference. November 3, 1983. Panel Discussion: Implementing Pesticide Policy - The Regulatory Framework.

8. California State Water Resources Control Board. North Coast and Central Valley Regional Water Quality Control Boards. Staff Report. Monitoring of Silvicultural Use of 2,4-D in Northern California. January 1984. (Appendix 5).

9. North Coast Regional Water Quality Control Board Public Report. (1) Proposed Action to Amend the Klamath River Basin and North Coastal Basin Policy and Action Plan for Control of Discharges of Herbicide Waste from Silvicultural Applications. (2) Adoption of the Existing Regulatory Program of the Department of Food and Agriculture and the County Agricultural Commissioners as Practices which Combined with Existing Basin Plan Requirements Control the Discharge of 2,4-D and other Herbicides Applied to Timberlands and Comprise "Best Management Practices" for Protection of Water Quality. March 29, 1984.

B. Water Hyacinth Control

10. California State Water Resources Control Board. Toxic Substances Control Program. Water Quality Guidelines for Herbicides used on Water Hyacinth in the Sacramento-San Joaquin Delta. October 1982. (Appendix 6)

APPENDICES

APPENDIX I

CALIFORNIA STATE WATER RESOURCES CONTROL BOARD
TOXIC SUBSTANCES CONTROL PROGRAM

STAFF REVIEW
OF
NORTH COAST REGIONAL BOARD BASIN PLAN AMENDMENT TO CONTROL HERBICIDE DISCHARGE

MAY 18, 1981

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REVIEW OF NORTH COAST REGIONAL WATER QUALITY CONTROL BOARD RESOLUTION NO. 81-1 (BASIN PLAN AMENDMENT TO CONTROL HERBICIDE DISCHARGES)

Conducted Under Supervision of Dr. G. W. Bowes

SUMMARY

The proposed North Coast Regional Water Quality Control Board Basin Plan Amendment relating to discharge of three phenoxy herbicides (2,4,5-T; 2,4,5-TP; and 2,4-D) is reviewed. The prohibition against discharge of 2,4,5-T and 2,4,5-TP to water is supported acknowledging the present EPA ban and consent with this position from the California Department of Health Services (DOHS). With respect to the proposed ten parts per billion (10 ppb) limit on 2,4-D in water, the limit is supported taking into account the specific chemical form of 2,4-D most commonly used on north coast forest lands and its persistence. The California Department of Fish and Game has found the proposed limit to be reasonable in affording adequate protection to aquatic resources and one that industry has indicated it can meet. (Seven letters included as Appendix 1.) Current 2,4-D regulations and activities of the U. S. Environmental Protection Agency (EPA) are reviewed, as are those of Canada and Sweden.

THE PROPOSED 2,4,5-T and 2,4,5-TP PROHIBITION

The North Coast Regional Board has recommended that "There shall be no discharge of 2,4,5-T or 2,4,5-TP to waters of the state". On January 22, 1981, this limit and the Basin Plan Amendment were described and adopted in Resolution No. 81-1. The resolution also states that DOHS recommends that no TCDD ("2,3,7,8" chlorinated dioxin isomer) be present (a) in water used for domestic consumption, and (b) in water inhabited by aquatic organisms that may be consumed by humans. Since TCDD is a contaminant in 2,4,5-T and 2,4,5-TP, the DOHS recommendation essentially means that the latter two compounds also should not be in these waters. The Regional Board limit on 2,4,5-T and 2,4,5-TP follows this rationale.

TCDD is highly toxic and has the most stringent proposed water quality criterion of all 129 EPA priority pollutants (March 15, 1979, Federal Register). Its potential impact on human health and aquatic life are controversial. The DOHS recommendations on TCDD and the Regional Board limits on 2,4,5-T and 2,4,5-TP are deemed reasonable on the basis of existing information as well as uncertainties concerning the toxicological implications of TCDD and potential human health impacts resulting from spraying operations.

EPA has held hearings on 2,4,5-T for more than a year and may reconsider its suspension of some 2,4,5-T uses. (Chemical and Engineering News, April 20, 1981, page 8).

THE PROPOSED 2,4-D DISCHARGE LIMIT

In Resolution No. 81-1, the North Coast Regional Board also recommended that concentrations of the herbicide 2,4-D not exceed 10 ppb in water for protection of aquatic life. The documentation supporting this recommendation is contained in the "yellow binder" submitted both to the Division of Technical Services and the Toxic Substances Control Program. Additional data is included in files located at the Regional Board and in tapes of hearing transcript totalling approximately 40 hours. These recommendations require careful consideration due to special features in the Region including (1) the presence of many streams; (2) high rainfall; (3) steep terrain; and (4) decreased soil water holding capacity due to removal of trees and other vegetation. Together these characteristics enhance potential for runoff during spray operations and periods of high rainfall.

1. ISSUES INVOLVED

The major technical issue is toxicological. The published information on 2,4-D is considerable. The best single comprehensive source of information on 2,4-D and other phenoxy herbicides was published by the National Research Council of Canada in 1978. The title of the publication is "Phenoxy Herbicides-Their Effects on Environmental Quality" (440 pages).

Various aspects of the 2,4-D toxicology issue are described in several parts as follows:

2. THE 2,4-D FAMILY

The herbicide 2,4-D is really a number of different, yet structurally similar compounds. They all have the basic structure as that shown at the top of Attachment 1 (2,4-D "acid"). They differ in the nature of the groups (amines, esters) that are attached to the acid structure shown at the top of the six-sided (benzene) ring. The significance of these modifications is that they result in markedly different toxicities of the various 2,4-D member compounds. The most common 2,4-D compound used in the North Coast Region is the propylene glycol butyl ether (PGBE) ester (see Attachment 1).

The reported 1980 use of various 2,4-D formulations in California is shown in Attachment 2 in three tables.

3. TOXICOLOGY IN AQUATIC SYSTEMS

Chapter Six from the Canadian document referred to above (included in Attachment 3), provides a good description of what we know about 2,4-D effects on all levels of aquatic food chains from the primary, photosynthetic producers (algae) to fish. It includes a description of laboratory data, as well as observations made in the field.

3.1 Primary Producers. Algal cells in culture "do not appear to be very sensitive to phenoxy herbicides". Sensitivities were recorded in the parts per million (ppm) range.

3.2 Invertebrates. The zooplankton, which feed on the microscopic plants, give the first indication that 2,4-D has different toxicities depending on the particular structure. The 2,4-D "esters" can be much more toxic than the 2,4-D "salts". The most sensitive species apparently is the common animal plankton, *Daphnia*. It is "immobilized" (H. O. Sanders, personal communication) by 100 ppb of 2,4-D PGBEE (48 hour TL_{50}). A concluding remark on the invertebrates is as follows: "The literature on invertebrates was limited; unfortunately, no data were available on sublethal effects such as reproductive behavior."

3.3 Fish. Acute toxicity data indicates again that "The ester formulations are most toxic..." A comparison of the acute toxicity of 2,4-D to bluegills shows that the acid and amine salt formulations can be 1000 times less toxic than the esters. The differences are concentrations greater than 800 ppm compared to about 0.8 ppm, respectively.

3.4 Secondary effects may result from entry of phenoxy herbicides into water. This impact can reverberate through the food chain by decreasing aquatic vegetation which provides shelter for animals, or by killing a species that is food for another species. This type of cause-and-effect relationship would be difficult to determine for 2,4-D. A discussion of the bioconcentration of 2,4-D in aquatic ecosystems is included also in Attachment 3.

4. THE 10 PPB LIMIT - CAN WE LIVE WITH IT?

The literature described above shows that aquatic organisms are sensitive to certain 2,4-D formulations down to levels as low as 100 ppb. Most of that information is derived from short-term acute tests. Field exposure of sensitive organisms or sensitive life stages are generally longer than the duration of these acute tests. Therefore, concentrations lower than 100 ppb of 2,4-D could be having adverse long-term effects. The gap between 10 and 100 ppb begins to narrow when sub-acute and chronic effects are considered.

A paper published in the same year as the Canadian review brings this gap into focus. It comes from two scientists working at the U. S. Fish and Wildlife Service Laboratory in Jackson, Wyoming (Woodward, D. F., and F. L. Mayer, Jr., 1978; Toxicity of three herbicides - butyl, isooctyl, and propylene glycol butyl ether esters of 2,4-D - to cutthroat trout and lake trout. U. S. Fish and Wildlife Service, Technical Paper No. 97, pp 1-6). Two significant findings from this research were that (1) newly hatched fish were much more sensitive to 2,4-D esters than adults; and (2) the "no-effect" 2,4-D concentrations (based on survival and development) ranged from 24 to 52 ppb for butyl ester and PGBEE. The authors concluded that "these concentrations could be considered the maximum acceptable continuous concentrations for these species" (cutthroat trout and lake trout). These chronic tests were run under dynamic conditions with 2,4-D concentrations maintained at specified levels through 60 days after egg hatching.

An important observation in these experiments - not recorded in the paper - is that although the chronic toxicity test lasted 60 days, "alevin" mortality began in only 5 to 9 days after exposure to 2,4-D. ("Alevin" is the life stage between egg hatching and the fry stage; the fry stage begins when the fish have absorbed the yolk and begin feeding.) Tables 2 and 3 in the report describe alevin % survival after complete yolk absorption. The yolk absorption period can last from approximately 21 days for cutthroat trout up to 35 - 45 days for lake trout based on the test temperature and particular fish stock employed in the experiments. The cumulative mortality measurements which were made through the full 60-day tests, show that alevin mortality began at the following times: A. Cutthroat trout: 5 days at 44 ppb 2,4-D butyl ester (BE); 9 days at 60 ppb PGBEE; B. Lake trout: 4 days at 60 ppb BE; 6 days at 100 ppb PGBEE. (R. Knowlton, U. S. Fish and Wildlife Service, Jackson WY, personal communication.) The 2,4-D concentrations described are those for which statistically significant alevin mortality began to occur (i.e., one concentration level above the "no effect" levels).

A third significant finding resulted from simulating a field application exposure (which could be related to a single spraying of 2,4-D). In this experiment, 50 cutthroat trout were taken immediately after hatching and exposed to 2,4-D under static conditions for seven days. They were then transferred to uncontaminated flowing water after that period through 60 days after hatching. They found the maximum no-effect concentration under these conditions to be between 100 and 500 ppb, and recommended that 100 ppb not be exceeded in this type of field situation. Tests were not performed on eggs or on other ages of the young fish to determine their sensitivities to 2,4-D.

Canadian scientists have determined that the 2,4-D butoxyethyl ester LC_{50} for rainbow trout is between 200 and 400 ppb, expressed as an acid equivalent (D. W. Martens, et al. 1980. Toxicity of butoxyethyl ester of 2,4-D to selected salmon and trout. International Pacific Salmon Fisheries Commission. Progress Report No. 40. New Westminster, B. C., Canada).

Considering all this information, a 2,4-D limit of 10 ppb appears to be an acceptable limit to protect trout while providing a reasonable margin of safety. Until new information is brought to our attention, we can assume that this limit will protect other aquatic life also.

The most sensible interpretation of this limit requires a closer focus on the 2,4-D family of compounds, as described in the concluding section.

5. WHAT IS EPA DOING?

5.1 Water Quality Criteria for Phenoxy Herbicides

In its 1972 "Blue Book", EPA recommended a limit for 2,4-D butoxyethanol ester at 4 ppb for protection of aquatic life. The newer (1976) "Red Book" does not give a limit. According to Alan Rubin, Chief of EPA's Criteria Section, Office of Water Regulations and Standards, EPA is now revising all criteria for the phenoxy herbicides and may have their draft recommendations for public comment into the Federal Register by June 1981. The proposed criteria would apply to 2,4-D; 2,4,5-T; and 2,4,5-TP. EPA hopes to have final criteria by the end of 1981. The initial data gathering and review is being done by Syracuse Research Corporation under contract to EPA. On May 13-15, 1981, the Syracuse staff and its own outside peer reviewers will meet and discuss their preliminary data collation. The "magic numbers" may not be decided upon at this meeting. However, shortly thereafter, through a series of communications among the same people, those numbers will be decided upon. The recommendations and supporting rationale will then be sent to EPA. EPA will first conduct an in-house review which will involve review by its national freshwater research laboratory at Duluth. After the in-house review is complete, EPA will solicit public comment via the Federal Register. Subject to EPA approval, Syracuse Research Corporation will be sending me a draft copy of their recommendations to EPA.

Mr. Rubin emphasized that EPA is using a "new methodology" to derive water quality criteria (known to us). The "old methodology" involved finding a concentration that a species was most sensitive to, dividing this concentration by a factor relating chronic to acute toxicity (most commonly 100), and setting that as the water quality criterion. With the new methodology, EPA is not necessarily attempting to protect the most sensitive species. The new philosophy is that "no one organism is the key to the community". EPA is going to look at the "whole community" in setting criteria and this may or may not involve keying into the most sensitive species. Mr. Rubin said, "We are trying to be realistic." He also added that the new methodology is data intensive. If not enough of the right kind of data is available, and this must include both acute and chronic toxicity data, then EPA will issue "summary statements" in place of criteria.

5.2 Data Requirement to Maintain Registration of 2,4-D

In 1979, EPA began a review of potential health effects of 2,4-D. This was initiated because of the controversy surrounding the closely related compound, 2,4,5-T. As a result of this review, EPA concluded that 2,4-D use does not pose an imminent hazard when used according to label directions and that there is no need to remove it from the market ("2,4-D Fact Sheet", April 22, 1980).

At the same time EPA recognized that the majority of the data used to support registration of 2,4-D products had been developed through studies that do not meet today's standards for test protocols (2,4-D products have been in use since the 1940's). EPA concluded that "there are significant information gaps in several areas including cancer-potential, reproductive effects, neurotoxicity, and metabolism in animals". On August 29, 1980, EPA issued an "Order and Notice" to 2,4-D registrants requesting specific toxicological information on 2,4-D. This order was modified and clarified in a subsequent order issued January 27, 1981, (both were issued under authority given to EPA under FIFRA - the Federal Insecticide, Fungicide and Rodenticide Act).

Industry responded to this directive by developing a collaborative study approach that involves 7 registrants (including Dow, the major manufacturer) together with EPA and Agriculture Canada. Report due dates for the eight required studies are listed in the August 29, 1980, order. They range from May 1, 1981, to December 1, 1983.

6. THE SWEDISH EXPERIENCE

Considering the significant amount of environmental chemistry work done in Sweden, I was curious about their regulations on 2,4-D. I called Dr. Soren Jensen, formerly with the Swedish Environment Protection Board in Stockholm. Briefly, he said that Sweden surprisingly is an "undeveloped country" with regard to regulation of chemicals in water. There is, however, a prohibition against direct application of 2,4-D to water.

For a historical perspective on concerns in Sweden over 2,4-D and related herbicides, an article published by the Swedish Institute (an autonomous foundation financed by the Swedish government) is included as Attachment 4. Legal and administrative actions are described on pages 2-3. A brief note on ecological effects appears near the bottom of page 3.

7. DIOXINS IN CANADIAN 2,4-D

The herbicide 2,4-D recently made news in Canada where researchers detected several chlorinated dioxin compounds in 2,4-D formulations. Chlorinated dioxins had been found before in European 2,4-D by other workers, but not to any significant extent. The Canadians found chlorinated dioxins in both 2,4-D ester and amine products, but not in the 2,4-D acid. The detection limit for most isomers was 1 ppb. (Note on terminology: As noted above, the highly toxic dioxin found in 2,4,5-T and 2,4,5-TP is TCDD. TCDD is a chlorinated dioxin compound containing four chlorine atoms at specific locations - the "2,3,7 and 8" positions. One of the dioxins contained in the Canadian 2,4-D contained four chlorine atoms also, but it was not TCDD. The Canadian 2,4-D contained chlorines located at the "1,3,6 and 8" positions. Toxicities of molecules can vary widely depending on the positions of certain atoms such as chlorine. Sometimes TCDD is used to refer to "tetrachloro" dioxins generally or to all chlorinated dioxins. These uses are inaccurate.)

As a result of the recent dioxin findings, considerable concern has been expressed regarding their influence on human health. At this time, there is little chronic toxicity information on the specific dioxin compounds detected in the Canadian 2,4-D. There is little or no information to determine if they might be a problem in the aquatic environment.

Of the chlorinated dioxins (or combinations) identified in the Canadian formulations (2,7/2,8 dichloro-; 1,3,7/1,3,8 trichloro-; 1.3.6.8/1.3.7.9

Although the available toxicity data on the "2,4-D dioxins" have not shown cause for alarm, Canada is taking some regulatory action. There are three reasons for this. First, 2,4-D is used on food crops; second, chlorinated dioxins are chemically related to TCDD although their toxicology is not well defined; and third, the concentrations of di, tri, and tetrachlorodioxins combined reached up to 7.5 ppm in the 2,4-D. The Canadian regulatory action includes (1) banning the sale by manufacturers of the 2,4-D products shown to have dioxins in the highest amounts (greater than 1 ppm), the "iso-octyl" and "mixed butyl" esters; and (2) ensuring that all 2,4-D is essentially "dioxin-free" by 1982. Use of the second 2,4-D type found to contain dioxins, the dimethylamine salt, will continue in Canada. Chlorinated dioxins in those formulations (di, tri, and tetra combined) did not exceed 862 ppb.

With respect to 2,4-D itself, there are apparently no standards or criteria for protection of aquatic life from 2,4-D in Canadian waters. The only standard for 2,4-D in water is 0.1 ppm for drinking water (which is the same as EPA's 2,4-D criterion for potable water in the 1976 Red Book).

(2) "flavor-impairment studies with 2,4-dichlorophenol showed that flesh tainting in fish occurred at substantially lower concentrations than those that produced other adverse effects on plants, fish and invertebrate species."

According to Dr. Frank Gostomski (EPA Office of Water Regulations and Standards, Criteria and Standards Division), the lowest recommended 2,4-dichlorophenol criteria to serve as guidance for protection of freshwater aquatic life are 2020 ppb for acute toxicity, and 365 ppb for chronic toxicity - which is significantly higher than the recommended limit for 2,4-D. These concentrations are referred to in the criteria document. In this document also, a concentration of 70 ppb was noted to harm young rainbow trout. However, Dr. Gostomski stated that the work which produced this information was not conducted according to standard protocol. He added that the study was "unique" and the results difficult to interpret. EPA-supported research is on-going to develop final criteria for 2,4-dichlorophenol.

The lowest water concentration of 2,4-dichlorophenol reported to taint the flavor of fish flesh was 0.4 ppb. The comparable concentration for 2,4-D dimethylamine salt is 50 ppb, an effect which can be reversed in several days if the fish is placed in uncontaminated water. (L. C. Folmer, 1980. Bull. Environ. Contam. Toxicol. 24,217-224).

10. IS THERE A "SAFE" 2,4-D?

The more toxic 2,4-D esters are used to control plants competing with conifers because they are more oil soluble and, therefore, penetrate the leaves better than other formulations. Further, those esters with the shorter chain penetrate more readily than those with longer chains (see Attachment 1). One of the longer chain esters used in the North Coast region is less volatile than the other 2,4-D compounds. The trade-off here is that this ester is both effective and less likely to volatilize and drift into adjacent agricultural areas, e.g., vineyards in Mendocino. Dr. Steven Radosevich, a professor of botany at U. C. Davis, suggested that an oil soluble amine-type of 2,4-D compound would be somewhat less effective in the forest, but much less toxic in the water. This type of change in application practice of herbicide to mitigate adverse effects on water quality requires further investigation. The advantages and disadvantages of the different 2,4-D structures with respect to potential harm to stream life and to humans, and usefulness in the forest should be studied, preferably by the manufacturers wishing to use this chemical in California.

11. 2,4-D CONCENTRATIONS IN NORTH COAST STREAMS

Approximately 75 to 100 "spray unit" analyses have been made for 2,4-D in North Coast waters between 1974 and 1980. (A "spray unit" consists of measurements before, during, and after a spray incident.) The analyses were performed by laboratories under contract to the Regional Board, U. S. Forest Service, Department of Food and Agriculture, and other agencies. Since April 1978, when waste discharge requirements went into effect, 2,4-D concentrations in the water ranged up to 18 ppb (except for one enforcement case where the concentration exceeded this). Most measurements were below 10 ppb. Most analyses since April 1978 have been positive for 2,4-D (but below 10 ppb) when water was sampled during or after the spraying period.

12. OTHER CONSIDERATIONS

As indicated above, contaminants, such as dioxins, complicate interpretations of phenoxy herbicide toxicity. An additional issue with many pesticides that has not been addressed is the toxicity of (1) solvents used to dilute them; (2) "minor" component pesticides that may be mixed with the major constituent; and (3) the combined ingredients constituting the pesticide mix. With respect to solvents, 2,4-D in the North Coast region can be mixed with diesel oil and stove oil. The clarification of the toxicity of this use of petroleum is an issue which needs to be addressed.

13. RECOMMENDED STRATEGY

13.1 The 10 ppb 2,4-D limit should be applied to areas where the toxic 2,4-D esters are used. The areas would include watersheds where only esters are used and where other forms in addition to esters are sprayed. The reason for this latter stipulation is that once the herbicides enter water they "hydrolyze" to common forms. One could not determine in this circumstance if the "parent" compound was, for example, an ester or an amine. The limit should, therefore, be based on total 2,4-D detected in the water. This is easily achieved. The common analytical procedure converts all forms of the 2,4-D herbicide and closely related metabolites to the fundamental 2,4-D acid structure. The measurement is then made on the acid. The 2,4-D used in the North Coast region is the same as that used in the Wyoming experiments - the propylene glycol butyl ether ester. Cutthroat trout, one of the species tested in Wyoming is also found in the North Coast. The relationship between the Wyoming laboratory study and the North Coast field situation is close because both the 2,4-D structure and the fish species were similar.

If no 2,4-D esters were used in a watershed, and only amine salts were, for example, the State Board could consider a water limit somewhat higher than 10 ppb for that watershed. I do not, at present, recommend a specific limit for the North Coast region in this situation for the following reason. The California Department of Food and Agriculture 1980 Pesticide Use Report shows that most of the 2,4-D used on forest and timberland is PGBE ester (20,102 lb.) (Attachment 2). The amount of 2,4-D amine used in 1980 for forest and timberland was only 823 lb. Our preliminary information on 1981 use indicates that the ester will be the predominant form used. If the Wyoming experiments on trout had been done with the amines as well, this would have provided a readily comparable basis for 2,4-D amine. Future onsite studies are needed to determine appropriate limits

13.2 All the laboratory experiments have an element built into them that we should also consider - and this is time. Although a test concentration of 2,4-D can be comparable to a field concentration (e.g., directly after spraying), there is an important difference. The fish, or other organism, in the test situation is held in a container that continually exposes the animal to the same water and toxicant for a period of time. Given that situation, and it is the basis for most aquatic toxicity estimates, the 2,4-D limit requirement should specify a minimum time, perhaps 24 hours, that the 2,4-D must be in the water at the concentration limit.
The 2,4-D concentration to be compared with the 10 ppb limit would be an average of concentrations determined for this period. For example, it could be an average of concentrations determined for two samples taken 24 hours apart.

In the one field simulation experiment described above (with cutthroat and lake trout), the observed no-effect concentration for the young, developing fish was 100 ppb for a 7-day exposure, compared to no-effect concentrations ranging from 24 to 52 ppb for 60 days exposure. Obviously, the longer the exposure time the lower the no-effect concentration. The essential point here is that the limit must be based on measurements made over a period of time. Following good analytical practice, the measurements also should be done at least on multiple (preferably triplicate) water samples at an appropriately certified laboratory.

13.3 A complementary research program is recommended to identify 2,4-D field concentrations which are harmful to California's freshwater aquatic life. The limit would then depend less on data extrapolated from other situations. It could then be modified on the basis of site-specific California experience.

Development of this program would benefit from active public participation and input, particularly representatives from industry, North Coast citizen groups, University of California researchers, as well as state and federal scientists knowledgable in this area.

The proposed program would involve development of field analytical capability for rapid detection of 2,4-D in ambient waters as well as chronic toxicity indicators.

Chronic toxicity measurements will require expertise in fish development and pathology and in environmental chemistry as well as specialized equipment. Much of this is available at the University of California, Davis (UCD) including the Medical School. Some of the people and equipment are already working for us on the striped bass project.

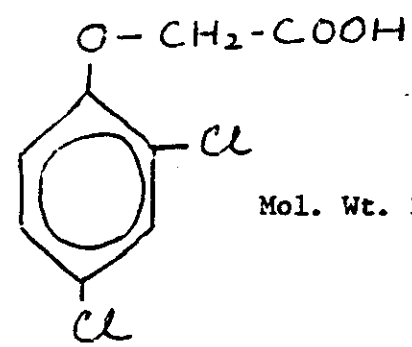
Development of both the analytical capability and the chronic toxicity indicator system would have wide applicability in California. Presently, live fish or dead fish appear to be the only indicators of the health of our streams, except for measurements of certain toxicants. We must, therefore, develop a means to measure chronic toxicity.

Attachments 1 and 2
Attachments 3,4 and Appendix 1 filed with
Technical Services Division

Attachment 1

CHEMICAL STRUCTURES OF 2,4-D FORMULATIONS

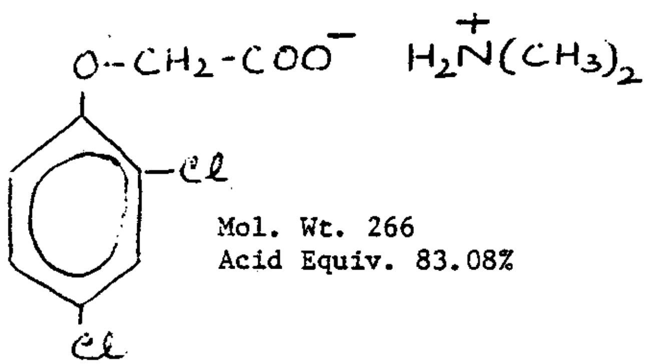
ACID



Mol. Wt. 221

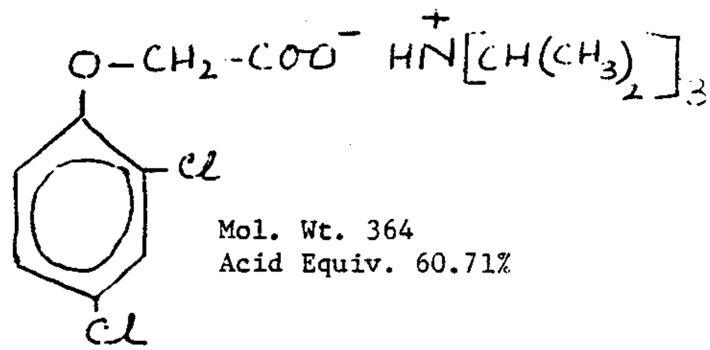
2,4-D Acid

AMINE SALTS



Mol. Wt. 266
Acid Equiv. 83.08%

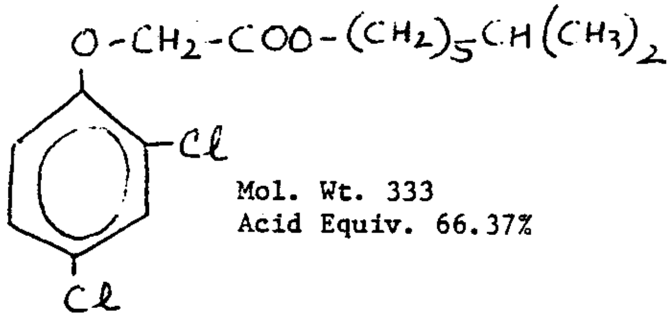
Dimethylamine salt (DMA4)
(Predominantly used salt formulation)



Mol. Wt. 364
Acid Equiv. 60.71%

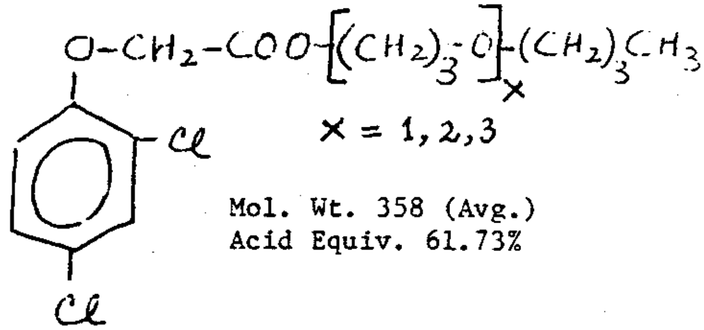
Triisopropylamine salt
(Use reported on forest/timberland)

ESTERS



Mol. Wt. 333
Acid Equiv. 66.37%

Isooctyl ester (HEDANOL)
(Predominantly used ester formulation)



Mol. Wt. 358 (Avg.)
Acid Equiv. 61.73%

Propylene glycol butyl ether ester
(Use reported on forest/timberland)

Attachment 2

TABLE 1

Total Reported Use of Various 2,4-D Formulations in California in 1980

Formulation	Amount Applied (lb)
Salt	771,632
Ester	86,821
Acid	35,976
Total	894,429

Source: CDFA Pesticide Use Report, 1980

TABLE 2

Total Reported Use of Various 2,4-D
Salt Formulations in California in 1980

Salt Formulation	Amount Applied (lb)	Major Use
Dimethylamine	531,682	Wheat, barley, oats
Alkanolamine (Ethanol & Isopropanol)	214,196	Wheat, barley, corn
N-Oleyl-1,3-propylene diamine	13,756	Wheat, barley, corn
Dodecylamine	7,788	Rights of way
Tetradecylamine	1,951	Rights of way
Diethanolamine	1,151	Wheat, barley, turf
Triisopropylamine	823	Forest/timberland
Sodium	285	Asparagus
TOTAL	771,632	

Source: CDFA Pesticide Use Report, 1980

TABLE 3

Total Reported Use of Various 2,4-D Ester Formulations in California in 1980

Ester Formulation	Amount Applied (lb)	Major Use
Isooctyl	33,350	Barley, wheat
Butoxyethanol	23,701	Barley, wheat
		Pasture, conifers
Propylene glycol butyl ether	20,102	Forest/timberland, oats
Propyl	4,577	Orange
Butyl	1,892	Wheat
Butoxypropyl	1,181	Rights of way, wheat
Isopropyl	1,115	Commodity fumigation
2-Ethylhexyl	903	Wheat
TOTAL	86,821	

Source: CDFA Pesticide Use Report, 1980

APPENDIX II

CALIFORNIA STATE WATER RESOURCES CONTROL BOARD

TOXIC SUBSTANCES CONTROL PROGRAM

STAFF REVIEW

OF

ISSUES RAISED REGARDING 2,4-D

AT THE

MAY 19, 1981

PUBLIC HEARING ON

NORTH COAST REGIONAL BOARD

BASIN PLAN AMENDMENT

Prepared by:

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July 1, 1981

Table of Contents

1. BACKGROUND

Toxics staff prepared a previous review (May 18, 1981), of the North Coast Regional Board Basin Plan Amendment to control herbicide discharge. The report dealt with the proposed 2,4,5-T and 2,4,5-TP prohibition, the proposed 2,4-D limit, toxicology of 2,4-D in aquatic systems, experiences of other countries, the significance of dioxin contamination and breakdown products of 2,4-D, and actual 2,4-D concentrations in the north coast streams. With regard to 2,4-D, the staff review supported the proposed 10 ppb, 2,4-D limit with these conditions: (1) the limit would only be applied to the ester form (in areas where 2,4-D esters are used; other forms of 2,4-D, such as the amines, were specifically excluded); (2) the limit would be based on an average concentration for a cumulative time period such as 24 hours; (3) the limit would be expressed as the "acid equivalent" common denominator form of 2,4-D. Staff also recommended that a site specific study be conducted in the North Coast Region to identify 2,4-D field concentrations which do not harm freshwater aquatic life in this region. This report amplifies the conclusions and recommendations of the May 18, 1981, staff report and deals with significant issues raised at the May 19, 1981, hearing.

2. DEFINITION OF TERMS

2.1. Chemical Form of 2,4-D

Of the two major groups of 2,4-D, esters and amine salts, the esters are generally much more toxic than the amines to aquatic life. For one test species of fish (bluegill) which has been exposed to a considerable number of 2,4-D compounds, the ester formulations can be 1,000 times more toxic than the amine. From our review of the literature, the proposed 10 ppb limit can only be meaningfully related to the 2,4-D ester. The original staff recommendation as outlined in the May 18 report (page 10) was "The 10 ppb 2,4-D limit should be applied to areas where the toxic 2,4-D esters are used. The areas would include watersheds where only esters are used and where other forms in addition to esters are sprayed". The last sentence is now restated to read: "The limit will be set for watersheds where esters are used exclusively or as part of the total 2,4-D application".

In view of the fact that propylene glycol butyl ether ester (PGBEE) is one of the most toxic forms of 2,4-D to aquatic life, and is the predominant form of 2,4-D presently used in the North Coast Region, the receiving water quality limit should be based on the toxicology of the PGBEE form.

2.2. "Acid Equivalent" - A 2,4-D Common Denominator

Once the 2,4-D ester enters the water, it begins to transform to the acid. The 2,4-D acid is the common building block of all 2,4-D forms - the "common denominator" (Attachment 1). The rate of transformation of the ester to the acid in the water depends on several environmental conditions as described in Section 5 of this report. If a 10 ppb limit was stipulated based on analysis of the ester, only a fraction of the 2,4-D that was sprayed might be detected. The "total" amount of 2,4-D in the water is more closely approximated if the sample is analyzed for the common denominator acid form. The standard analytical procedure transforms the ester and other 2,4-D forms to the acid.

Some authors express the concentration of 2,4-D in terms of the form that was used (i.e., as the ester). Others express the concentration as the acid equivalent. To standardize our terms of reference, we have, wherever possible, converted 2,4-D concentrations reported in the literature to the acid equivalent.

2.3. Time of Exposure and Toxicological Effect

Chronic toxicity tests identify the ranges of toxicant concentrations that are harmful to organisms as well as the "no-effect" concentrations. These tests are conducted over periods of time that encompass development of one or more life stages, (e.g., 21 days for cutthroat trout alevins). We have concluded from a review of the scientific literature that a receiving water limit designed to protect aquatic life from chronic toxicity is more accurately expressed if it specifies a time of exposure. EPA has recommended a time period of 24 hours to minimize the likelihood that pollutant concentrations will reach harmful levels for unacceptably longer periods. This will avoid erroneous conclusions based on analysis of a single grab sample taken at any particular time.

A single number criterion to protect against both acute and chronic toxicity tends to overprotect for acute toxicity and underprotect for chronic exposure. Although most of the chronic toxicity data in the literature are based on gross indicators such as death or size change, subtle effects, such as changes in reproduction rates, ability to compete for food, and avoidance of predation, should not be ignored. Thus, a chronic toxicity criterion acknowledges that our present understanding of aquatic ecosystem interrelationships is limited.

3. METHODS FOR DERIVING 2,4-D WATER QUALITY CRITERIA

The following discussion describes four different approaches that have been developed for determining toxic substance receiving water limits. For each approach, the calculated limit is stated first. This is followed by an explanation of the approach used to derive it.

3.1. Use of General Application Factors

2,4-D Limit: 1.0 ppb 2,4-D PGBEE (0.62 ppb acid equivalent)

EPA's original methodology (1972 Blue Book) for deriving "safe" levels to protect aquatic life from chronic toxic effects was based on multiplying an acute LC50* value for the most sensitive species by 1/100 (an arbitrarily chosen application factor). This calculation gave a concentration that was not to be exceeded for a 24-hour period. Based on this method, the 2,4-D criterion for the most sensitive species (Daphnia magna) is 1 ppb PGBEE (0.62 ppb acid equivalent). This criterion was based on the reported 48-hour LC50 equivalent expressed as immobilization (Sanders, 1970).

3.2. Experimentally Derived Application Factors
2,4-D Limit: 3.4 ppb 2,4-D PGBEE (2 ppb acid equivalent)

Relatively few long-term chronic tests have been run side-by-side with acute toxicity tests. A large data base relating the two kinds of toxicity would produce a range of application factors for a range of toxic substances. An appropriate application factor would then be selected for a toxic substance for which only acute toxicity data is available.

An application factor for 2,4-D was first determined by Mount and Stephan in 1967. They ran both (static) acute and (dynamic) chronic tests on 2,4-D butoxyethanol ester. The concentration of 2,4-D that would kill 50 percent of a minnow test population in 96 hours (96 hr LC50) was determined. They also exposed young minnows to the 2,4-D for approximately 10 months. The data they obtained included (1) the highest 2,4-D concentration that had no effect on growth and reproduction during this period; and (2) the lowest 2,4-D concentration that caused some effect on growth and development. The 10-month chronic toxicity concentration divided by the 96-hour LC50 resulted in an "application factor" of 1/19.

In 1978, a study appeared in the literature that relates more closely to the present issue (Woodward and Mayer, 1978). Although two forms of 2,4-D were used on two species of trout, the experimentally derived application factor using only data from experiments with PGBEE and cutthroat trout was 1/29. Because this information most closely approximates actual field conditions in the North Coast Region, this application factor should be used with this methodology to derive a 2,4-D PGBEE ambient water quality criterion.

As indicated in Section 3.1., the freshwater aquatic species most sensitive of those for which the data is available for 2,4-D PGBEE is Daphnia magna. The concentration of 2,4-D PGBEE causing 50 percent mortality/immobilization is 100 ppb ester (62 ppb acid equivalent). Using the experimentally derived application factor of 1/29 (instead of the arbitrarily chosen factor 1/100), the ambient water quality criterion is 3.4 ppb 2,4-D PGBEE (2 ppb acid equivalent).

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* The LC (lethal concentration) 50 is the concentration of a chemical required to kill 50 percent of the organisms within the time period of the test (most commonly test periods range from 24 to 96 hours).

It should be noted that this calculation uses an application factor based on fish sensitivity to predict a "no-effect" concentration for the most sensitive species - an aquatic invertebrate.

A table of application factors referenced in the literature for protection of aquatic life is given in Attachment 2. The human health safety factor of 1/500 is more stringent than the application factor to protect aquatic life.

Attachment 3, Table 3, describes a derivation of application factors (acute to chronic ratios) from the Mount and Stephan (1967) and Woodward and Mayer (1978) papers.

3.3. No-Effect Level (NOEL) Concentrations
2,4-D Limit: 31 ppb 2,4-D PGBEE (19 ppb acid equivalent)

A receiving water criterion based solely on long-term chronic toxicity data would not include consideration of acute toxicity data and application factors. The published chronic toxicity data most relevant to the north coast issue are those of Woodward and Mayer (1978). This important paper was discussed in the May 18, 1981, staff report. The significance of the raw data relating to early alevin mortality is reviewed in Section 4.

The highest concentration of PGBEE that had no effect on cutthroat trout was 31 ppb (19 ppb acid equivalent). The period of observation for the alevin stage of development was from 22 to 31 days. During the alevin stage, the fish depend upon the yolk sac for nutrition.

Significant alevin mortality began at the next highest concentration of 2,4-D PGBEE: 60 ppb (37 ppb acid equivalent). The highest no-effect concentration is, therefore, between 31 and 60 ppb PGBEE (19 and 37 ppb acid equivalent).

A conservative estimate of the no-effect level would be the highest no-effect concentration used in the experiment: 31 ppb 2,4-D PGBEE (19 ppb acid equivalent). This concentration applies only to the test species. It will not necessarily protect other known and unknown sensitive species of fish and aquatic invertebrates.

3.4. EPA's New Methodology
Maximum Instantaneous Value: 65 ppb 2,4-D PGBEE (40 ppb acid equivalent)
24-Hour Average: 2.8 ppb 2,4-D PGBEE (1.75 ppb acid equivalent which here is rounded off to 2 ppb).

EPA's new methodology for deriving water quality criteria was developed over a period of several years and was recently published in the Federal Register (Nov. 28, 1980, pp. 79341-79347). This development included inputs from four EPA Environmental Research Laboratories, careful consideration of extensive public comments, and review by EPA's Science Advisory Board. The methodology has been used to develop ambient water quality criteria for 14 of the 65 Consent Decree priority pollutants, including DDT and PCB.

Briefly, EPA's new methodology gives a two-numbered criterion:

1. Instantaneous maximum value: This is the Final Acute Value which is developed from acute toxicity data for at least eight different families of aquatic organisms.
2. Twenty-four hour average value: This is the lowest value of:

(i) Final Chronic Value: This is obtained by either of the following two ways depending on the number of chronic toxicity data available.

(a) In the same way as Final Acute Value. This requires chronic toxicity data for at least eight different families of aquatic organisms.

(b) Where sufficient chronic toxicity data are not available, by dividing the Final Acute Value by the Final Acute-Chronic Ratio (which is the geometric mean of the Acute-Chronic Toxicity Ratios for at least three species of aquatic organisms).

(ii) Final Plant Value: This is the lowest plant toxicity value.

(iii) Final Residue Value: This is calculated by dividing the maximum permissible tissue concentration with the product of bioconcentration factor and lipid content of the species.

Sufficient acute toxicity data for 13 species and chronic data for two species of aquatic organisms are available, although requirements that EPA identified for deriving the criteria could not be satisfied in total. The data gaps for 2,4-D PGBEE in the published literature include:

(i) Chronic toxicity data for an aquatic invertebrate. Few standard procedures are available for chronic testing of aquatic invertebrates and PGBEE has not been studied with these procedures.

(ii) Final Plant Value. If a final plant value of less than 2.0 ppb was obtained, it could only affect the 24-hour average limit and only by lowering it. Newton (1977) proposed an irrigation water level of 5 ppb for 2,4-D esters which includes a 5:1 safety factor for certain crops. Aquatic plants, including algae, may be more or less sensitive than these crops.

(iii) Final Residue Value. According to the published literature, 2,4-D does not bioaccumulate to any significant extent.

4. CUTTHROAT TROUT "ALEVIN" MORTALITY VS. 2,4-D DOSE AND TIME

Woodward and Mayer (1978) presented data concerning cutthroat trout mortality and chronic effects during exposure to various forms of 2,4-D, including PGBEE. The mortality figures indicated in the paper were the total observed for the various life stages during the 60-day test period. Mortality began to occur however as early as the fourth day after exposure to 2,4-D for the "alevin" life stage (between egg hatching and the fry stage) (Attachment 4). Even though this experiment was conducted as a long-term chronic test, mortality during the first week in effect represents acute (short-term) data.

The raw data described in Attachment 4 was obtained on June 16, 1981. A review of the data indicated that alevin mortality during the first two weeks of the experiment was not significantly different from the control, except for the highest dose used (77 ppb acid equivalent). Analysis of raw data for lake trout yielded a similar conclusion. California Department of Fish and Game staff have been given a copy of the raw data from this experiment and are conducting an independent statistical analysis.

If significant alevin mortality was found to occur within the first 96 hours of the 60-day test, this information could be used to derive a chronic toxicity criterion, using the appropriate application factor. In view of the lack of significant difference in alevin mortality at all doses tested during the first 96 hours, this information cannot be used to derive chronic toxicity values.

5. INFLUENCE OF pH AND TEMPERATURE ON HYDROLYSIS OF 2,4-D IN WATER

Decomposition of 2,4-D in water involves several processes, the first and foremost of which is chemical hydrolysis. The hydrolysis is pH dependent, being extremely rapid in the alkaline range and relatively slow in the acid range. For example, data from Smith (1972) and Zepp et al (1975) indicate that the half-life for hydrolysis ($t_{1/2}$) of several 2,4-D ester forms is as follows:

Effect of pH on Half-life for Hydrolysis of 2,4-D Esters (Temp. = 28°C)

Ester \ pH	6	9	11.2	13
	$t_{1/2}$			
	(days)	(hours)	(minutes)	(minutes)
Isopropyl	710	17	5	1
n-butyl	220	5	30	1

From kinetic data presented by Zepp et al (1975), the calculated half-life for hydrolysis ($t_{1/2}$) at pH 7.0 (neutral) and 28°C is as follows for a number of 2,4-D esters.

Ester	Half-life at pH 7 (days)
Methyl	4.4
2-Propyl	71
1-Butyl	22
1-Octyl	22
2-Octyl	150
2-Butoxyethyl	2.6
2-Butoxymethylethyl	18

The pH range of various north coast streams is as follows:

Rivers	pH Range
Smith	7.2 - 7.8
Klamath	7.4 - 8.3
Eel	7.4 - 8.3
Redwood Creek	7.2 - 8.4
Other smaller streams	7.0 - 7.6

No pH values below 7.0 have been observed in north coast streams.

The hydrolysis of 2,4-D ester is temperature dependent. As the temperature increases, the rate of hydrolysis increases. The temperature of north coast streams during the spray season is low (10 - 15 $^{\circ}$C). The kinetic data of Zepp et al (1975) for 2,4-D butoxyethyl ester hydrolysis at 47° and 28°C were used to calculate the hydrolysis rate and $t_{1/2}$ of the ester at 10°C. These data are presented in the following table.

Effect of Temperature on 2,4-D Butoxyethyl Ester Hydrolysis (pH 7)

Temperature ($^{\circ}$C)	Hydrolysis Constant (M^{-1} sec^{-1})	Half-life (days)
47	235.0	0.3
28	30.2	2.6
10	5.9	13.6

In view of the above considerations the half-life for hydrolysis of 2,4-D esters in north coast streams would be expected to range from several days to several weeks.

It should be noted that actual residence time of 2,4-D esters in north

Subsequent to the May 18, 1981, hearing, Toxics staff received a copy of a Department of Food and Agriculture (DFA) staff report titled "Humboldt County Phenoxy Herbicides Water Monitoring" by H. Van Cheney (October 20, 1978). The report includes a detailed description of site conditions and analysis of time vs. 2,4-D concentrations during the April-June 1978 spraying operations. Although several rainfall incidents occurred during the test period, Best Management Practices recommended by DFA were observed. Numerous samples were collected for periods of up to 9 hours from several different sites in the spray area. From the data in the report it is possible to calculate (1) the maximum instantaneous values for 2,4-D, (2) the composite average value for the actual sampling period, and (3) the theoretical 24-hour average value. (This value assumes that the lowest measured 2,4-D concentration at the end of the sampling period continues for 24 hours. Sampling intervals for the remainder of the 24-hour period correspond with the last two actual sampling time intervals.)

A summary of this report follows:

Date	Sampling Station	Sampling Duration (Hours)	No. of Samples Collected	2,4-D (ppb) acid equivalent		
				Maximum Instan-taneous	Avg. During Sampling Period	24-hour Average (Calculated)
4/18/78	Simpson Site No. 1 (Sampling Sta. 3)	9	10	1.0	0.26	0.14*
6/23/78	Singley Creek	4.5	10	2.3	0.35	0.15
6/23/78	No Name Creek	7	9	9.0	1.90	1.24**

* Simpson site resampled after 4 and after 34 days. Both samples were below detection limits (0.1 ppb).

** No Name Creek site had initial spraying followed by secondary spraying during a 2-hour interval.

It should be noted that both the instantaneous maximum value observed during the comprehensive sampling program, as well as the calculated 24-hour average value, were well below the 2,4-D acute and chronic criteria derived from EPA's new methodology (Section 3.4. of this report).

Dr. Logan Norris, USDA Forest Service, Corvallis, Oregon, has commented in a letter to the Board dated May 22, 1981, concerning the ratio of instantaneous maximum levels of 2,4-D observed in Oregon streams compared with 24-hour mean concentrations between 1964 and 1980. Dr. Norris has concluded that the actual 24-hour mean concentration "is usually much less than 10 percent of the instantaneous maximum level observed". The DFA data indicate that the 24-hour mean concentration at these sites is less than 15 percent of the instantaneous maximum value.

A report concerning analysis of steelhead trout from Northern California rivers for 2,4-D was received by Toxics staff on June 22, 1981. This report by the Bodega Bay Institute of Pollution Ecology titled "Analysis of 2,3,7,8-TCDD, 2,4-D and 2,4,5-T in Steelhead Trout from Northern California Rivers" was submitted on May 29, 1981, to the California Department of Fish and Game.

Fish from six different sites were collected during October 15-20, 1980, and analyzed for 2,4-D (Attachment 5). The results indicate that for all samples analyzed, 2,4-D concentrations were below detection limits. Detection limits in fish tissue ranged between 0.069 and 1.3 ppb, depending upon the weight of the sample analyzed. In addition all fish samples were analyzed for TCDD (2,3,7,8 tetrachlorodioxin). TCDD concentrations were estimated to be below 10 ppt (<0.01 ppb).

7. OTHER BENEFICIAL USES OF WATER

Professor Michael Newton of Oregon State University, prepared a report for EPA titled "Silvicultural Chemicals and Protection of Water Quality" (EPA Publication No. 910/9-77-036).

In this report, Professor Newton considered the growth regulating properties of 2,4-D on sensitive commercial crops such as grapes, beans, potatoes, and cotton. The report recommends that concentrations of 2,4-D in irrigation water be maintained at lower levels than would be dictated for drinking water or aquatic life protection. The proposed water quality objective (24-hour average) for 2,4-D in irrigation water is 5 ppb. This level is intended to provide a margin of safety of 5:1 below the minimum limits of crop sensitivity.

A common by-product and decomposition product of 2,4-D in water is 2,4-dichlorophenol. This compound has an EPA water quality criterion of 0.4 ppb as a 24-hour average (110 ppb instantaneous maximum) to protect against tainting of fish flesh. Insufficient data has been received from the North Coast Regional Board to establish a firm correlation between levels of 2,4-D PGBEE in water and its breakdown product 2,4-dichlorophenol. From limited data obtained to date the 0.4 ppb limit for 2,4-dichlorophenol would probably not be exceeded if 2,4-D PGBEE did not exceed the maximum concentration in water observed during the April 1981 spraying season (i.e., 12 ppb 2,4-D acid equivalent).

8. CONCLUSIONS

8.1. The PGBEE is the predominant form of 2,4-D presently used in the

8.3. Instantaneous grab samples are sufficient for estimating 2,4-D concentrations in relation to acute toxicity limits. Chronic toxicity limits are time dependent. Samples collected for at least a 24-hour period are required for estimating 2,4-D concentrations in relation to chronic toxicity limits.

8.4. A single number criterion for both acute and chronic toxicity may overprotect for acute toxicity and underprotect for chronic exposure.

8.5. Experimentally derived application factors based on tests of both acute and chronic toxicity are preferred whenever available over general application factors.

8.6. "No-effect level" (NOEL) criteria identify concentrations of toxic substances which do not appear to harm a particular aquatic species during a chronic exposure time. They do not attempt to provide protection for other known or unknown sensitive species of fish, insects and aquatic invertebrates.

8.7. EPA's new methodology is based on a comprehensive approach which aims to protect a wide array of plant and animal species in the aquatic ecosystem. This methodology provides a two-number criterion to distinguish between the need for different levels of protection from chronic and acute toxicity effects.

8.8. The alevin mortality data of Woodward and Mayer (1978) provides valuable information for deriving chronic toxicity criteria and for use with EPA's new methodology. The lack of significant mortality differences between controls and 2,4-D exposed cutthroat trout alevins tested during the first two weeks of the chronic test does not allow calculation of lower chronic toxicity criteria than those described by the authors in their original paper (1978).

8.9. The half-life for hydrolysis of 2,4-D esters in north coast streams would be expected to range from several days to several weeks depending on temperature, pH, and 2,4-D ester form used.

8.10. Since April 1981, most water samples collected by the North Coast Regional Board were found to contain less than detectable amounts of 2,4-D acid equivalent. These data and the field data collected by DFA in 1978 show that the maximum instantaneous value and 24-hour average value calculated according to EPA's new methodology (40 and 2 ppb PGBEE acid equivalent, respectively), can be met if Best Management Practices are followed.

8.11. Analyses of six steelhead trout from Northern California streams showed concentrations of 2,4-D to be below the detection limits ranging from 0.069 to 1.3 ppb. Assuming these trout have been exposed to 2,4-D, the findings tend to support previous experimental findings that 2,4-D does not bioaccumulate to any significant extent in fish tissue.

8.12. The maximum concentration of 12 ppb 2,4-D reported by North Coast Region from the April 1981 spraying season is more than three times

2,4-D Acid Equivalency

The 2,4-D acid form is rarely used for conifer release in forests. The ester form is most frequently used, while the salt form is used only occasionally. The salt and ester forms are bigger molecules compared to the parent 2,4-D acid form.

Acid —(+ base)→ Salt

(Smaller Molecule) | (Bigger molecules)

Unit wt. 1.0. | Unit wt. greater than 1.0

For example: 2,4-D acid —(+ base)→ 2,4-D dimethylamine salt (DMA)

2,4-D acid: Mol. wt. 221 (Unit wt. 1.0)

2,4-D dimethylamine salt (DMA): Mol. wt. 266

($\frac{266}{221}$ or 1.2 unit wt.) (i.e., the molecular weight of this salt is 20% greater than the acid.)

2,4-D acid —(+ alcohol)→ 2,4-D propylene glycol butyl ether ester (PGBEE)

Mol. wt. 358

($\frac{358}{221}$ or 1.6 unit wt.) (i.e., the molecular weight of this ester is 60% greater than the acid.)

If 1 ppb of 2,4-D acid is detected in water, it could have come from either 1.2 ppb of 2,4-D DMA or 1.6 ppb of 2,4-D PGBEE. When water containing 16 ppb of 2,4-D PGBEE is analyzed for by a standard method, 10 ppb of 2,4-D acid will be detected.

Application Factors for Protection of Aquatic Life

Pesticide	Application Factor	Reference
	Arbitrary	
2,4-D esters	1/100	Silvicultural chemicals and Protection of Water Quality (1977)
2,4-D butoxyethanol ester	1/100	Blue Book (NSF, 1972)
Pesticides (in general)	1/100	Environment Saskatchewan

SUMMARY

2,4-D PGBEE (Propylene Glycol Butyl Ether Ester) Ambient Water Quality Criteria Based on EPA's Most Recent Methodology

CRITERIA:

The 2,4-D PGBEE ambient water quality criteria are 1.75 ppb (acid equivalent) as a 24-hour average and the concentration should not exceed 40 ppb (acid equivalent) at any time. Refer to Federal Register, Volume 45, No. 231, pp. 79341 - 79347 for the complete stepwise calculation of the criteria.

1. The acute toxicity values of 2,4-D PGBEE used to calculate the final acute value are given in Table 1. The number of species (N) for which the acute toxicity data are available is 13. Table 2 shows the log mean acute toxicity values of the 13 species arranged from low to high, together with the intervals and cumulative proportion. A plot of the data (Figure 1) from the two mean acute values and cumulative proportions closest to 0.05 log concentration gives the final acute value of 40 ppb (acid equivalent).

2. Table 3 gives the ratio of acute to chronic toxicity available for 2,4-D esters in the literature. The geometric mean of PGBEE ratios gives the final acute-chronic ratio of 22.9. Note that the calculation of this ratio does not include the data for butoxyethanol and butyl esters given in Table 3. If those data were included, the final acute-chronic ratio would be 24.

3. When the final acute toxicity value of 40 ppb is divided by the final acute-chronic ratio, a final chronic value of 1.75 ppb (acid equivalent) is obtained.

4. Data requirements are not completely satisfied:

   (i) Data to calculate the acute-chronic ratio for an aquatic invertebrate is not available.

   (ii) The 24-hour average value here is based on the final chronic value alone, i.e., it does not include the Final Plant Value and the Final Residue Value. However, even with these limitations, the final criteria should be valid. That is, they will never be lower unless the Final Plant Value is less than the Final Chronic Value. The Final Residue Value is not considered because 2,4-D apparently does not bioaccumulate to any significant extent.

TABLE 1

2,4-D PGBEE Acute Toxicity to Aquatic Organisms

N	Species	Exposure Time (hr.)	LC50 ppb (acid equiv.)	Log. LC50	Rank	Reference
	Fish:					
1	Rainbow Trout	48	1100	3.04		Walker (1971)
	" "	"	960	2.98		FWPCA (1968)
	" "	"	1100	3.04		Bohmont (1967)
	" "	"	1100	3.04		Cope (1964)
	Geometric Mean		1060	3.03	5	
2	Bluegill	"	2100	3.32	10	Hughes & Davis (1963)
3	Lake Trout	96	588*	2.77	4	Woodward & Mayer (1978)
4	Cutthroat Trout	"	550*	2.74	3	" "
5	Longnose Killifish	48	4500**	3.65	12	Butler (1965)
6	Redear Sunfish	96	3100**	3.49	11	Walker (1964)
	Crustaceans:					
7	Daphnia	48	62	1.79	1	Sanders (1970)
8	Seed Shrimp	"	197	2.30	2	" "
9	Glass Shrimp	"	1666	3.22	9	" "
10	Scud	"	1604	3.21	8	" "
11	Sowbug	"	1357	3.13	6	" "
	Insect (Stonefly)					
12	*Pteronarcella badia*	96	1481	3.17	7	Johnson & Finley (1980)
13	*Pteronarcys californica*	"	1604	3.21	8	" "

* Geometric mean of 9 acute toxicity values.

** The literature does not indicate ester or acid form.

TABLE 2

Log Mean Acute Toxicity Values Arranged in Ascending Order

N	Species	Log mean Acute Toxicity	Intervals of 0.11 log units	Cumulative Proportion
1	Daphnia	1.79	I	1/13 (0.08)
2	Seed Shrimp	2.30	II	2/13 (0.15)
3	Cutthroat Trout	2.74	III	4/13 (0.31)
4	Lake Trout	2.77		
5	Rainbow Trout	3.03	IV	6/13 (0.46)
6	Sowbug	3.13		
7	Stonefly (*P. badia*)	3.17	V	10/13 (0.77)
8	Stonefly (*P. californica*)	3.21		
9	Scud	3.21		
10	Glass Shrimp	3.22		
11	Bluegill	3.32	VI	11/13 (0.85)
12	Redear Sunfish	3.49	VII	12/13 (0.92)
13	Longnose Killifish	3.65	VIII	13/13 (1.00)

TABLE 3

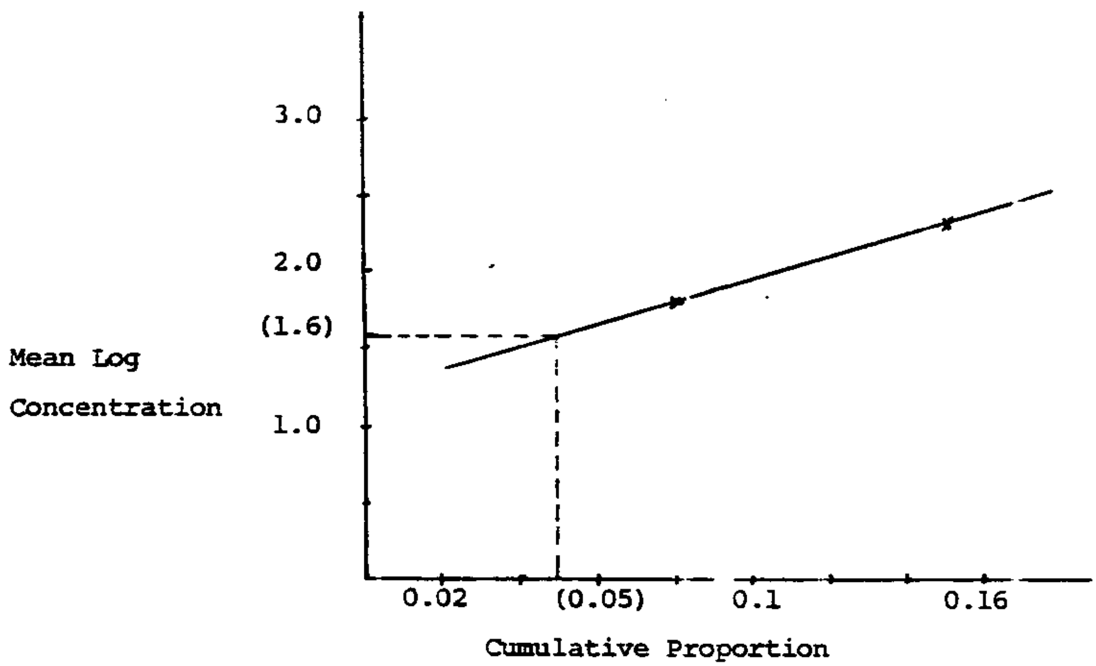
ACUTE TO CHRONIC TOXICITY RATIOS OF 2,4-D ESTERS
CALCULATED FROM PUBLISHED FISH TOXICITY DATA

Ester	Fish	Acute Toxicity (ppb) (A)	Chronic Toxicity (ppb) (B)	Ratio of Acute to Chronic Toxicity (A/B)	Reference
PGBE *	Cutthroat trout	891**	31	28.7	Woodward and Mayer (1978)
	Lake trout	953**	52	18.3	"
			GEOMETRIC MEAN	22.9	
Butyl	Cutthroat trout	730**	24	30.4	"
	Lake trout	845**	33	25.6	"
Butoxyethanol	Minnows	5600	300	18.7	Mount and Stephan (1967)
			GEOMETRIC MEAN	23.8	

*PGBE Propylene glycol butyl ether.

** Each value represents the geometric mean of concentrations derived from 9 tests.

FIGURE 1. Plot of Acute Toxicity Data of 2,4-D PGBEE



Final Acute Value = $10^{1.6}$ or 40 ppb 2,4-D (AE)

ATTACHMENT 4

CUTTHROAT TROUT "ALEVIN" MORALITY (CUMULATIVE)
VS. TIME* AND 2,4-D DOSE
(Number of dead Alevin/50 eggs initially in test) Ref: Woodward & Mayer,
Dose (ppb) as PGBEE and Acid Equivalent (unpublished data)

Time Days from Start of Test	Control Zero	6.5 4 A.E.	16 10 A.E.	31 19,2 A.E.	60 37 A.E.	124 77 A.E.
1	0	0	0	0	0	0
2	0	0	0	0	0	0
3	0	0	0	0	0	0
4	1	0	0	2	0	2
5	1	0	0	2	0	2
6	1	2	0	3	0	2
7	1	2	0	3	0	2
8	1	2	0	3	0	2
9	1	2	0	3	0	3
10	1	2	0	3	0	11
11	1	2	0	3	0	20
12	1	3	0	3	2	37
13	3	3	0	3	4	37
14	3	3	0	3	4	37
15	3	3	0	3	4	40
16	3	3	0	3	4	41
17	3	3	0	3	4	41
18	3	3	0	4	4	41
19	3	3	1	4	7	43
20	3	3	1	5	7	43
21	3	3	1	5	7	43
22	3	7	1	5	7	43
23		10	1	5	7	44
24		10	1	5	7	45
25			1		9	45
26			2		10	45
27					10	45
28					10	45
29					10	45
30					14	45
31					15	[illegible]
% of Total Alevin Dead at End of Test	6	20	4	10	30	90%

ATTACHMENT 5

Results of Analysis for 2,4-D in Steelhead Trout from Northern California Rivers (Expressed as the Acid Equivalent)

(Risebrough et al 1981)

LOCALITY	DATE OF COLLECTION	WEIGHT ANALYZED (grams)	2,4-D (ppb)
Rock Creek Trib. to Klamath	15 Oct/80	71.7	<0.07
Bark Shanty Creek Trib. to Rock Creek	"	64.2	<0.15
Klamath R. at confluence of Rock Creek	"	39.6	<0.21
Klamath R. near mouth	18/Oct/81	44.1	<1.10
Smith River at Jedsmith State Park	19/Oct/80	29.2	<1.30
Klamath River at Iron Gate (Yreka)	20/Oct/80	166.8	<0.44

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APPENDIX III

California State Water Resources Control Board

Toxic Substances Control Program

Staff Review

ISSUES REGARDING THE CHANGE

FROM

2,4-D PROPYLENE GLYCOL BUTYL ETHER ESTER (PGBEE)

TO

2,4-D BUTOXY ETHYL ESTER (BEE)

February 16, 1982

TABLE OF CONTENTS

I. Introduction

The Toxic Substances Control Program prepared a staff review paper on 2,4-D on July 1, 1981. That review stated that ester formulations of 2,4-D can be 1,000 times more toxic than the amine and acid forms. Due to the greatly increased toxicity of the ester formulations, the receiving water quality limits were set for watersheds where esters are used exclusively or as part of the total 2,4-D application. At that time, the propylene glycol butyl ether ester (PGBEE) was the predominant form used in the North Coast Region of California. Thus, the receiving water limits were developed based on the toxicology of the PGBEE form. The maximum instantaneous value of 40 PPB and 24-hour average of 2 PPB were developed using the EPA methodology for deriving water quality criteria (Fed. Reg. Nov. 28, 1980).

On January 25, 1982, Dow Chemical confirmed that it will no longer manufacture the PGBE ester. The registered herbicide Esteron* 99 will now be manufactured and marketed using the butoxy ethyl ester of 2,4-D. Because of this change, the toxicology of the butoxy ethyl ester (BEE) was reviewed. The following is a summary of that review.

*Trademark of the Dow Chemical Company

II. Chemical Form of 2,4-D
(Butoxy ethyl or Butoxy ethanol)

All but two of the papers reviewed were based on the toxicity of 2,4-D butoxy ethanol. The papers by Martens et al (1980) and Alabaster(1969) reported the toxicity of 2,4-D butoxy ethyl ester. The two esters are reported to be one and the same according to L. E. Warren of Dow Chemical (Pers. Comm.) and Jim Sphon of FDA (Pers. Comm.).

III. Persistence in the Environment

The previous staff paper on 2,4-D (July 1, 1981) used data for the butoxy ethyl ester to predict the half-life for hydrolysis of 2,4-D PGBE. 2,4-D BEE data was used because of the lack of such data for the PGBE ester. That paper concluded that the hydrolysis half-life (the time required for one-half of the 2,4-D ester to hydrolyze to the parent acid and an alcohol) in north coast streams would be expected to range from several days to several weeks depending upon temperature, pH, and the ester form used. The hydrolysis product (2,4-D acid) is relatively resistant to chemical degradation and is nonvolatile according to Zepp et al (1975).

The mobility and runoff of 2,4-D BEE should be similar to 2,4-D PGBE because of their somewhat similar chemical structure. Actual runoff and persistence in north coast streams, however, cannot be adequately estimated from the available data. Therefore, this information should be determined as part of a site-specific field study.

IV. EPA Methodology for Deriving Water Quality Criteria

The EPA methodology for deriving water quality criteria was published in the Federal Register (Nov. 28, 1980). This method was used in calculating receiving water limits for 2,4-D esters, as mentioned previously, using the toxicity data for 2,4-D PGBE. A summary of the data requirements of the methodology is as follows:

A. <u>Instantaneous maximum value:</u> This is the Final Acute Value which is developed from acute toxicity data for at least eight different families of aquatic organisms.

B. <u>Twenty-four hour average value:</u> This is the lowest value of:

1. Final Chronic Value: This is obtained by either of the following two ways depending on the number of chronic toxicity data available. The final chronic value should use only the results of flow-through chronic tests in which the concentration of toxicant in the test solutions were measured.

   (a) In the same way as Final Acute Value. This requires chronic toxicity data for at least eight different families of aquatic organisms, including fish and invertebrates.

   (b) Where sufficient chronic toxicity data are not available, by dividing the Final Acute Value by the Final Acute-Chronic Ratio (which is the geometric mean of the Acute-Chronic Toxicity Ratios for at least three species of aquatic organisms).

2. Final Plant Value: This is the lowest plant toxicity value.

3. Final Residue Value: This is calculated by dividing the maximum permissible tissue concentration with the product of bioconcentration factor and lipid content of the species.

V. <u>Data Available from Literature</u>

Acute toxicity data for 19 species and chronic data for 2 species of aquatic organisms are available for 2,4-D butoxy ethyl ester (BEE). These are compiled in Table 1. However, the requirements that EPA identified for deriving the criteria could not be satisfied for the 24-hour average value. The data gaps for 2,4-D BEE in the published literature include:

- No chronic toxicity data for 2,4-D BEE (or PGBEE) are available for aquatic invertebrates.
- Only two of the required minimum of three chronic toxicity tests for three species have been published to date for both 2,4-D BEE and PGBEE.
- Only one of the two chronic toxicity tests used the flow-through method and measured toxicant levels during testing as required by the methodology. This test was reported by Mount and Stephan (1967). The chronic test performed by Martens et al (1980) used a static method with daily renewal of the toxicant. The toxicant level was not measured during testing. This could lead to significant under estimation of the toxic effects. Therefore, the chronic toxicity minimum data base cannot be met.
- Plant toxicity data are not presently available for 2,4-D BEE.

VI. Calculation of Criteria from Available Data

A. Instantaneous Maximum Value

The data presented in Table 1 were used to calculate the instantaneous maximum values of 274 PPB for 2,4-D BEE. The calculated values are shown in Table 2.

B. Twenty-four (24)-Hour Average Value

For discussion purposes, the calculated 24-hour average using the single acceptable chronic test (Mount and Stephan, 1967) is 15 PPB. The 24-hour average value is derived by dividing the instantaneous maximum value by the acute-to-chronic ratio. This test had an acute/chronic ratio of 18.7:1 (Table 3). If both tests were used, the acute/chronic ratio would be 8.6:1 and the calculated chronic value would be 32 PPB (the Martens et al study has an acute/chronic ratio of 4:1).

C. Final Residue Value

A final residue value is calculated by dividing a maximum permissible tissue concentration by an appropriate bioconcentration factor corrected for lipid content. EPA recently established tolerances for 2,4-D in the Federal Register (January 6, 1982, pp. 620-621). These tolerances were established for various agricultural commodities including fish and shellfish. These tolerances are not directly applicable to fish on the north coast since those tolerances were specifically limited to application for water hyacinth or water milfoil control by public agencies. The latter case included the butoxy ethanol ester as used by the Tennessee Valley Authority. The limits for both fish and shellfish are 1 PPM (1000 PPB).

Rodgers and Stalling (1972) reported that whole body residues of 2,4-D were up to 55 times greater than the concentration of 2,4-D BEE in exposure water within 6 hours. The time required for total elimination of 2,4-D residues was up to 120 hours for bluegills and 48 hours for catfish. The EPA methodology requires testing for bioconcentration factors for 28 days or until steady state conditions are achieved. These conditions were not met in this study.

VII. Static Versus Dynamic (Flow-Through) Bioassay Methods Using 2,4-D BEE

All of the acute bioassay tests listed in Table 1 were static with one exception. In static bioassay tests, toxic substances being studied are generally added at the start of the test and not measured or renewed over the test period. In one test (Martens et al) with 2,4-D BEE the substance

[redacted]

in a small aquarium can immediately begin rapid hydrolysis of the ester to the far less toxic acid form of 2,4-D. This process is depicted in Figure 1.

[redacted]

VIII. Comparison of Toxicological Data for BEE and PGBE

Table 4 summarizes the toxicological data which is most directly comparable for both 2,4-D BEE and PGBEE for the following reasons:

1. Reported by the same author in one paper;
2. Same or similar methods and materials; and
3. Same species of organisms preferably in similar condition and life stage.

These data show 2,4-D BEE to have acute toxicity greater than PGBEE for three aquatic species while five other species are less sensitive to BEE than PGBEE. This comparison must be used with caution because of the aforementioned problems with static bioassays.

Table 5 was prepared using data for salmonid fish. These data indicate that 2,4-D BEE may be more toxic to salmonids than PGBEE. Once again, caution must be exercised in making these comparisons because different species, life stages, authors and methods were involved.

IX. Conclusions

1. Rough comparisons of toxicity data indicate that 2,4-D BEE is on the average less toxic than 2,4-D PGBEE to a wide range of aquatic organisms.
2. The 2,4-D BEE ester may be more toxic than PGBEE to salmonids.
3. Calculations based on the EPA methodology indicate that 2,4-D BEE is less toxic than PGBEE.
4. The available data may be inadequate to definitely conclude that 2,4-D BEE is more or less toxic than 2,4-D PGBEE because of the problems with static toxicity tests.

X. Issue

Is the present data base for 2,4-D BEE sufficient to develop instantaneous maximum and 24-hour average criteria now or should the State Board wait until site-specific data from the north coast are available?

Table 1

ate Water Resources Control Board
ACUTE TOXICITY DATA

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'IC	STAT/ DYN. TEST	EXP. TIME (HRs)	LC50 P.P.B. (a.e.)	REFERENCE	COMMENTS
lacustris	S	96	295	Sanders 1969	(T)
irdneri	MS	96	300	Martens et al 1980	(F)-Butoxyethyl-clay form
nchus nerka	MS	96	450	Martens et al 1980	(F)-Butoxyethyl-clay form
chus gorbuscha	MS	96	450	Martens et al 1980	(F)-Butoxyethyl-clay form
nchus kisutch	MS	96	450	Martens et al 1980	(F)-Butoxyethyl-clay form
macrochirus	S	48	640	Inglis & Davis 1972	(F)-Various hardness
		48	670	Alabaster 1969	( )-Butoxyethyl ester
macrochirus	S	48	740	Sanders 1970	(T)
macrochirus	S	96	804	Johnson & Finley 1980	(T)
etes kadiakensis	S	48	940	Sanders 1970	(T)
irderi	S	48	950	Inglis & Davis 1972	(F)-Various hardness
es promelas	D	48	1000	Mount & Stephan 1967	(T)-Eggs-:00% mortality
cys californica	S	96	1070	Sanders & Cope 1968	(F)-Emuls:fied conc.
sis vidua	S	48	1200	Sanders 1970	(T)
sis vidua	S	48	1474	Johnson & Finley 1980	(T)-EC50-Hard water
brevicauda	S	96	1742	Johnson & Finley 1980	(T)
s auratus	S	48	1775	Inglis & Davis 1972	(F)-Various hardness
macrochirus	S	48	2100	Hughes & Davis 1963	(F)-Liquid
brevicauda	S	48	2140	Sanders 1970	(T)
es promelas	S	96	2211	Johnson & Finley 1980	(T)
	S	96	2500	Butler 1965	(T)-EC50
es promelas	S	96	3750	Mount & Stephan 1967	(T)-TLm
magna	S	48	3750	Sanders 1970	(T)-TL50
fasciatus	S	48	3950	Sanders 1970	(T)
fasciatus	S	96	4087	Johnson & Finley 1980	(T)-Hard water
magna	S	96	4288	Johnson & Finley 1980	(T)
	S	48	4490	Butler 1965	(T)
s melas	S	48	4760	Inglis & Davis 1972	(F)-Various hardness
macrochirus	S	48	34500	Hughes & Davis 1963	(F)-Granu es
	S	48	100000	Sanders 1970	(T)

:al

Table 2

State Water Resources Control Board
FINAL ACUTE CALCULATION

2 /16/ 82

LOG LC50	LC50 P.P.B. (a.e.)	0.11 CELL	CUM. PROP.	CELL MEAN	EXP. TIME (HRs)	STAT/ DYN. TEST	TEST ORGANISM	REFERENCE
2.47	295	1	.07	2.474	96	S	Scud	Sanders 1969
2.477	300	1	.07	2.474	96	MS	Rainbow trout	Martens et al 1980
2.653	450	2	.17	2.653	96	MS	Sockeye salmon	Martens et al 1980
2.653	450	2	.17	2.653	96	MS	Pink salmon	Martens et al 1980
2.653	450	2	.17	2.653	96	MS	Coho salmon	Martens et al 1980
2.806	640	3	.3	2.852	48	S	Bluegill	Inglis & Davis 1972
2.826	670	3	.3	2.852	48		Harlequin fish	Alabaster 1969
2.869	740	3	.3	2.852	48	S	Bluegill	Sanders 1970
2.905	804	3	.3	2.852	96	S	Bluegill	Johnson & Finley 1980
2.973	940	4	.47	3.012	48	S	Glass shrimp	Sanders 1970
2.978	950	4	.47	3.012	48	S	Rainbow trout	Inglis & Davis 1972
3	1000	4	.47	3.012	48	D	Fathead minnow	Mount & Stephan 1967
3.029	1070	4	.47	3.012	96	S	Stonefly	Sanders & Cope 1968
3.079	1200	4	.47	3.012	48	S	Seed shrimp	Sanders 1970
3.168	1474	5	.57	3.219	48	S	Seed shrimp	Johnson & Finley 1980
3.241	1742	5	.57	3.219	96	S	Sowbug	Johnson & Finley 1980
3.249	1775	5	.57	3.219	48	S	Goldfish	Inglis & Davis 1972
3.322	2100	6	.7	3.349	48	S	Bluegill	Hughes & Davis 1963
3.33	2140	6	.7	3.349	48	S	Sowbug	Sanders 1970
3.345	2211	6	.7	3.349	96	S	Fathead minnow	Johnson & Finley 1980
3.398	2500	6	.7	3.349	96	S	Oyster	Butler 1965
3.574	3750	7	.93	3.617	96	S	Fathead minnow	Mount & Stephan 1967
3.574	3750	7	.93	3.617	48	S	Waterflea	Sanders 1970
3.597	3950	7	.93	3.617	48	S	Scud	Sanders 1970
3.611	4087	7	.93	3.617	96	S	Scud	Johnson & Finley 1980
3.632	4288	7	.93	3.617	96	S	Waterflea	Johnson & Finley 1980
3.652	4490	7	.93	3.617	48	S	Killifish	Butler 1965
3.678	4760	7	.93	3.617	48	S	Black bullhead	Inglis & Davis 1972
4.538	34500	8	.97	4.538	48	S	Bluegill	Hughes & Davis 1963
5	100000	9	0	0	48	S	Crayfish	Sanders 1970

Table 3

Acute to Chronic Toxicity Ratios of 2,4-D Esters
Calculated from Published Fish Toxicity Data

Ester	Fish	Acute Toxicity (ppb) (A)	Type of Test	Chronic Toxicity (ppb) (B)	Type of Test	Ratio of Acute to Chronic Toxicity (A/B)	Reference
Butoxy ethyl	Fathead minnows	5600	S	300	D	18.7	Mount and Stephan (1967)
	Rainbow trout	300	MS	75	MS	4.0	Martens et al (1980)
PGBE*	Cutthroat trout	891*	S	31	D	28.7	Woodward and Mayer (1978)
	Lake trout	953*	S	52	D	18.3	" "

* Each value represents the geometric mean of concentrations derived from 9 tests.

Legend

S = static
MS = modified static (toxicant was renewed daily)
D = dynamic

Table 4

Comparison of 2,4-D BEE and PGBEE Toxicological Data Derived from Acute Tests which are Directly Comparable[1]

Organism	LC50 BEE	LC50 PGBEE	BEE/PGBEE Ratio	Reference	North Coast species
Scud (*Gammarus lacustris*)	295[2]	1072	3.6	Sanders, H. O., 1969	Yes
Glass shrimp	940	1800	1.9	Sanders, H. O., 1970	Yes
Bluegill	640	660	1.03	Inglis & Davis, 1972	Yes
Bluegill	2100	2100	1.0	Hughes & Stephan, 1967	Yes
Sowbug	2140	1470	0.7	Sanders, H. O., 1970	No
Killifish	4490	3015	0.67	Butler, P. A., 1965	No
Scud (*G. fasciatus*)	3950	1740	0.44	Sanders, H. O., 1970	No
Seed Shrimp	1200	214	0.18	Sanders, H. O., 1970	No
Daphnia	3750	62	0.02	Sanders, H. O., 1970	Yes

1 Test species and conditions were identical.

2 All values are in PPB acid equivalent.

Table 5

Comparison of Acute Toxicity (LC50) to Salmonids of 2,4-D BEE and PGBEE

Organism	LC50 BEE	LC50 PGBEE	Reference	North Coast resident species
Rainbow trout	300 1/		Martens et al, 1980	yes
	950 2/		Inglis & Davis, 1972	yes
		620	Johnson & Finley, 1980	yes
		1100	Walker, 1971	yes
		1100	Cope, 1964	yes
Sockeye salmon	450		Martens et al, 1980	no
Coho salmon	450			yes
Pink salmon	450			yes
Lake trout		588	Woodward & Mayer, 1978	no
Lake trout		680	Johnson & Finley, 1980	no
Cutthroat trout		550	Woodward & Mayer, 1978	yes

1/ All values in PPB acid equivalent

2/ 48-hour LC50

APPENDIX IV

Toxicities of Butoxyethanol Ester and Propylene Glycol Butyl Ether Ester Formulations of 2,4-D to Juvenile Salmonids

by

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SUMMARY

Continuous-flow toxicity tests were conducted to determine acute toxic effects of butoxyethanol ester (BOEE) and propylene glycol butyl ether ester (PGBEE) formulations of 2,4-D on juvenile chinook salmon (Oncorhynchus tshawytscha) and steelhead-rainbow trout (Salmo gairdneri). A chronic toxicity test with chinook salmon egg-to-fry was conducted to determine effects of BOEE on survival and growth. Median lethal concentrations (96-h LC50 values) indicated that PGBEE (313 to 454 ug/l) was slightly more toxic (34%) than BOEE (327 to 601 ug/l). The LC50 values also indicated that chinook salmon were more sensitive than steelhead-rainbow trout and that fry were more sensitive than smolts to the 2,4-D esters. Static tests substantially underestimated BOEE toxicity when compared to dynamic tests. Based on reduced survival and growth of chinook salmon alevins and fry, we estimate the maximum safe chronic exposure concentration under these test conditions to be 40 ug/l BOEE.

Key words: 2,4-D esters; bioassay; acute toxicity; chronic toxicity; Oncorhynchus tshawytscha; Salmo gairdneri

INTRODUCTION

The purposes of this study were to examine the toxicities of butoxyethanol ester (BOEE) and propylene glycol butyl ether ester (PGBEE) formulations of 2,4-D to chinook salmon (Oncorhynchus tshawytscha) and steelhead-rainbow trout (Salmo gairdneri), important salmonids in the north coastal area of California. These herbicide formulations are used in conifer release programs. Off-target movement of these herbicides into forest water bodies is unavoidable, particularly if the materials are applied by air (Norris, 1971). The degree of off-target movement into water can be controlled with the use of buffer strips, anti-drift agents, and favorable weather conditions. There are concerns for the effects of off-target movement of herbicides to fish and aquatic invertebrates. The acute and chronic toxicity data presented in this paper will facilitate establishment of 2,4-D water quality standards needed for the protection of fish and other aquatic organisms.

Although the toxicities of 2,4-D esters to aquatic life have been extensively determined using static tests, none were determined using continuous-flow (dynamic) test conditions with monitoring of ester levels. Because of physicochemical hydrolysis (Que Hee and Sutherland, 1981) and biological hydrolysis (Rogers and Stalling, 1972; Dodson and Mayfield, 1979) of the 2,4-D esters to the less toxic 2,4-D acid by fish, static tests probably underestimated the toxicities of 2,4-D esters. The ability to estimate 2,4-D ester toxicity under known exposure levels is necessary to develop levels which will protect fish and other aquatic organisms.

The trend of toxicology data from static tests of Johnson and Finley (1980), Martens et al. (1980), Woodward and Mayer (1978), Sanders (1970), and Sanders and Cope (1968) suggests that fish are equally or more sensitive to 2,4-D BOEE than aquatic invertebrates, and salmonids are generally the most sensitive group of fish (California Regional Water Quality Control Board-North Coast Region, 1982). This apparent trend would be correct if hydrolysis of BOEE to 2,4-D acid were the same in all tests or was greater in the fish tests. Thus, no-effect concentrations derived from salmonid toxicology data may protect both fish and aquatic invertebrates from BOEE toxicity. The U. S. Environmental Protection Agency (1980) allows for the development of a single water quality criterion value for the protection of fish and aquatic life using either one species or group of aquatic organisms (i.e. salmonids) when it has been demonstrated that they are important (i.e. recreationally or commercially) and the most sensitive to the toxicant. Furthermore, this criterion must protect that group from chronic toxicity.

In this study we estimated 96-h LC50 values for commercial 2,4-D BOEE and PGBEE formulations using two salmonids species and a no-effect concentration for chinook salmon embryos and larvae continuously exposed to BOEE.

MATERIALS AND METHODS

Fish were challenged in continuous-flow toxicity tests with emulsions of commercial 2,4-D ester formulations supplied by proportional diluters (Mount and Brungs, 1967) manufactured from glass, teflon, and stainless steel components and glass predilution systems (Finlayson and Ashuckian, 1979). The formulations are marketed commercially as Esteron 99® Concentrate[1/] (EPA Registration Numbers 464-566-AA [BOEE] and 464-201-AA [PGBEE]) which contain 43.2% BOEE or 44.9% PGBEE active ingredient as acid equivalent (a.e.). Separate 2,4-D ester emulsions were prepared by sonicating the formulations in deionized water for 4 minutes. Stock solutions were checked analytically at the beginning and ending of a test.

The quality of sand-filtered water from the American River for the July 1982 to February 1983 tests was essentially constant: pH 7.0 - 7.2; 16 - 18 mg/l $CaCO_3$ hardness; 32 - 34 mg/l dissolved solids; 17 - 19 mg/l $CaCO_3$ alkalinity; dissolved oxygen above 95% saturation. Temperature varied seasonally between 16 C in July and 8 C in February. Trout fry and smolt and salmon smolt acute tests were conducted at temperatures of 14 to 16 C, salmon egg-to-fry chronic test was conducted at temperatures of 8 to 11 C, and the salmon fry acute tests were conducted at temperature of 9 C.

The chinook salmon fry and smolts and steelhead smolts used in the acute (96-h) tests were obtained 4 days before the tests began from stock at the California Department of Fish and Game's Nimbus Hatchery located on the American River, a tributary to the Sacramento River. The rainbow trout fry were obtained 7 days before tests began from stock at the California

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1/ Dow Chemical Company, Midland, Michigan 48640.

Department of Fish and Game's Hot Creek Hatchery located on Mammoth Creek in the Inyo-Sierra region. All fish were subjected to normal hatchery cultural practices as outlined by Leitritz and Lewis (1979).

Procedures outlined by the American Society for Testing and Materials (1980) and Finlayson and Verrue (1982) were followed for the acute toxicity tests. Acute continuous-flow tests were conducted in 72-l glass troughs with the water volume adjusted to 26 l; 50% water replacement time occurred in 3.0 h. Generally, two tests were conducted simultaneously; one species was exposed to each 2,4-D ester. Two static tests were conducted with steelhead

1N NaOH, cleaned with hot soapy water, rinsed twice with hot water, and then rinsed twice with a mixture (1 + 1) of nanograde acetone and hexane. Samples were collected using glass beakers and deposited in 500-ml borosilicate glass bottles containing 1 ml of 10N NaOH; pH of resulting sample was >12 thus ensuring complete hydrolysis of esters to 2,4-D acid and preserving the sample. Bottles were sealed with teflon-lined plastic caps and kept refrigerated at 4 C until analyzed. Following esteration, total 2,4-D concentrations were determined by gas chromatography with a Ni^{63} electron capture detector (Olson et al., 1978); the detection limit was 5 ug/l.

Water samples (50 to 250 ml) from each trough were collected and analyzed for concentrations of 2,4-D esters at the beginning of each acute test prior to the addition of fish. Additional water samples were collected from the troughs during the test and at its termination. Samples were collected using glass pipets and deposited in borosilicate glass containers containing 50 ml of nanograde hexane. Containers were sealed and vigorously shaken to extract and preserve the esters in the hexane phase. The phases were separated and the sample extracted with a second 50-ml aliquot of hexane. The hexane extracts were then combined and concentrated. The extracts were analyzed for 2,4-D BOEE or PGBEE concentration using the equipment listed above; detection limits for both esters were 5 ug/l a.e. The 2,4-D ester concentrations were stable during storage as determined by repeated analysis.

Chinook salmon eggs used to determine the chronic effects of 2,4-D BOEE on development, growth, and survival were obtained from Nimbus Hatchery. The specific procedures described by Finlayson and Verrue (1980) were used to determine chronic effects. The 50% water replacement time in the troughs was 1.2 h. The 86-day chronic test started on 29 November 1982 with fertilized chinook salmon eggs obtained by dry spawning three adult female and two male fish and ended on 25 February 1983 when the hatched individuals were at the swim-up fry stage. Following fertilization, the eggs were [illegible] Following hardening

Concentrations of total 2,4-D were consistent throughout both the continuous-flow and static tests; these values were used directly in the statistical calculations. Likewise, percent hydrolysis (1 - ester concentration/total 2,4-D concentration x 100) of both 2,4-D esters were consistent throughout the continuous-flow acute tests with trout and salmon fry and the chronic test; these values were also used directly in the statistical calculations. However, hydrolysis of 2,4-D esters fluctuated during the continuous-flow tests with salmon and steelhead smolts. Thus, it was necessary to calculate a mean hydrolysis for the 96-h test period. This was accomplished by approximate integration: measuring hydrolysis at 0, 24, 48, 72, and 96 h from several concentrations and then averaging the interpolated hydrolysis at 12, 36, 60, and 84 h. This procedure was done separately for each 2,4-D ester. The mean hydrolysis value was then applied to the total 2,4-D concentration to estimate 2,4-D ester concentration at the LC50 level. Physicochemical hydrolysis was estimated at the beginning of the test prior to the addition of fish, and biological hydrolysis was estimated as the value of total hydrolysis minus physicochemical hydrolysis when the complete fish loading factor was present. The 2,4-D ester concentrations at the LC50 level for static tests were based on initial concentrations in the aquaria before the fish were added.

RESULTS

Mean water temperatures in the troughs varied seasonally between 8 and 16 C, but varied less than 0.5 C among troughs during concurrent tests. Water temperature during the chronic test varied seasonally from 8 to 11 C. Trough pH varied from 6.9 to 7.3, hardness was 15 to 17 mg/l $CaCO_3$, and dissolved oxygen averaged 90% with a minumum of 75% of saturation.

The 2,4-D ester concentrations of the stock solutions were stable during the tests. Total 2,4-D concentrations in control troughs of all tests were <5 ug/l. Measured total 2,4-D concentrations in toxicant troughs averaged 101 ± 9% (± SD) of expected, based on analysis of stock solutions and known dilution.

Concentrations of 2,4-D esters at the beginning of the continuous-flow acute tests in the absence of fish averaged 79 ± 16% (83 measurements) of expected for BOEE and 62 ± 19% (54 measurements) of expected for PGBEE, based on 2,4-D ester concentrations in troughs and stock solutions and total 2,4-D concentrations in the troughs. Approximately 21 and 38% hydrolysis of BOEE and PGBEE, respectively, to 2,4-D acid had occurred within the 3.0-h 50% water volume replacement time in the troughs (Table I). This suggests that BOEE is twice as resistant to physicochemical hydrolysis as PGBEE under these test conditions. In the chronic test, approximately 5% of BOEE had hydrolyzed to 2,4-D acid within the 1.2-h 50% water volume replacement time in the troughs. The concentration of 2,4-dichlorophenol in the BOEE chronic test was 0.09 ug/l or approximately 0.07% of total 2,4-D concentration. Hydrolyses of 2,4-D esters was variable in the acute tests using salmon and steelhead smolts. The integrated mean hydrolysis of 2,4-D esters during the 96-h testing period was 65% for BOEE and 73% for PGBEE with salmon and

TABLE I

Estimated percent hydrolysis of 2,4-D butoxyethanol ester (BOEE) and propylene glycol butyl ether ester (PGBEE) in continuous-flow tests with different 50% water replacement times, fish loading factors, and temperatures (in parentheses).

	BOEE (%)	PGBEE (%)
Physicochemical Hydrolysis		
Chronic test 1.2-h replacement time (8 - 11 C)	5	-
Acute test 3.0-h replacement time (11 - 16 C)	21	38
Biological Hydrolysis		
0.02 to 0.08 g/l·day fry loading factor (8 - 16 C)	1	1
0.8 to 1.2 g/l·day smolt loading factor (13 - 16 C)	44	35

steelhead. The estimated biological hydrolysis of 2,4-D esters in the tests with smolts was 44 and 35% for BOEE and PGBEE, respectively. Hydrolysis of 2,4-D esters in tests with salmon and trout fry were less variable and approached the values (physicochemical hydrolysis) measured at the beginning of the tests before the fish were added: 22% for BOEE and 39% for PGBEE. It was not apparent that the narrow temperature range (8 to 16 C) affected hydrolysis in the short (1.2 to 3.0 h) water replacement times. Biological hydrolysis of both 2,4-D esters increased with increased fish loading factors.

Survival of controls in acute continuous-flow and static tests ranged from 88 to 100% with a mean of 98%. PGBEE was slightly more toxic than BOEE to chinook salmon and steelhead smolts by 32% and to rainbow trout fry by 39% (Table II). These differences in ester toxicity were significant ($p < 0.05$) in all tests except the chinook salmon smolt tests. Fry were apparently more sensitive to 2,4-D esters than smolts, although these differences were not

cid equivalent) of 2,4-D butoxyethanol ester
using 50% mortality (LC50) to juvenile chinook

BOEE		PGBEE		
EE	Total 2,4-D	n	PGBEE	Total 2,4-D
47)	371(153)			
22)	1,248(262)	2	313(288)	1,159(1,070)
53)	732(8)	2	372(87)	540(54)
120)	1,717(430)	2	454(29)	1,683(108)
300	2,200			
50	3,850			

Table III

Chronic effects of 2,4-D butoxyethanol ester (BOEE) concentrations (ug/l as acid equivalent) on growth and development of chinook salmon (mean values with SD in parentheses).

Concentration		Mortality			Fry, 36 days after hatch		
BOEE	Total 2,4-D	Embryo (%)	Alevin-to-fry (%)	Total (%)	Length (mm)	Weight (mg)	Yolk-sac Size (mm)
0	0	8.8	0	8.8	36(1)	320(40)	2(1)
14(3)	15	7.7	1.3	9.0	36(1)	310(40)	1(1)
24(5)	25	10.8	0	11.0	35(1)	310(40)	2(1)
40(9)	41	8.9	0	8.9	35(1)	330(40)	2(1)
60(16)	62	7.4	4.7 a/	11.8	35(2) b/	300(40)	1(1)
118(26)	124	10.5	47.6 a/	53.1 a/	32(2) b/	300(40)	3(1) b/

a/ Significantly different than controls (x^2, 0.05).

b/ Significantly different than controls (z, 0.05).

alevin-to-fry period was 4.7% and 47.6% for those exposed to 60 and 118 ug/l BOEE, respectively. When compared to controls, growth (length) of salmon to 36 days post-hatch was significantly ($p < 0.05$) reduced in 60 and 118 ug/l BOEE; yolk-sac absorption was significantly slower in 118 ug/l BOEE. Weight of fry at 36 days post-hatch was not a sensitive growth criterion in this test since conversion of yolk to tissue did not result in a detectable difference in body weight; salmon with a yolk-sac size of 3 mm weighed the same as fish with a yolk-sac size of 1 mm. Fry survival and growth were not significantly affected at BOEE concentrations of 40 ug/l or less. Thus, under these test conditions the maximum acceptable toxicant concentration (MATC) of BOEE for chinook salmon egg-to-fry was 40 ug/l. Applying this no-effect concentration with 96-h LC50 values for chinook salmon fry and smolts results in application factors (AF) of 0.12 and 0.10, respectively.

DISCUSSION

The processes of physicochemical and biological hydrolyses of 2,4-D esters to less toxic 2,4-D acid would have caused underestimation of ester toxicity if based upon nominal rather than measured ester concentrations. Physicochemical hydrolysis increased as water replacement time in the troughs increased and biological hydrolysis increased as fish loading factors increased. Physicochemical hydrolysis of BOEE was approximately 5 and 21% with 1.2 and 3.0-h 50% water replacement times, respectively. The half-life of BOEE to 2,4-D acid in water at 28 C has been reported to be 26 days at pH 6 and 0.6 h at pH 9 (Que Hee and Sutherland, 1981). Biological hydrolysis of BOEE was approximately 1% for salmon and trout tests with a loading factor of 0.02 to 0.08 g/l·day and 44% for a loading factor of 0.8 to 1.2 g/l·day. Rodgers and Stalling (1972) and Dodson and Mayfield (1979) had previously reported the ability of fish to rapidly hydrolyze 2,4-D esters. Our tests suggested that salmonid smolts were able to hydrolyze BOEE slightly faster than PGBEE. The ability of the salmon and trout to more rapidly hydrolyze BOEE may account for BOEE being slightly less toxic than PGBEE.

The breakdown of 2,4-D to 2,4-dichlorophenol in water during the chronic test was insignificant (0.07%). This was expected since it has been reported that 2,4-dichlorophenol is not stable and sunlight is needed for its formation from 2,4-D (Que Hee and Sutherland, 1981).

Our static test results substantially underestimated BOEE toxicity to steelhead smolts by approximately 200 to 400% when compared to our continual-flow test results, and the degree of underestimation increased as the loading factor of the static test increased. The underestimation was the result of hydrolysis of BOEE to less toxic 2,4-D acid. During the static tests, BOEE concentrations had decreased to <5 ug/l within the first 24 h of the tests, although total 2,4-D concentrations remained constant. The static test data of Johnson and Finley (1980) and Woodward and Mayer (1978) indicates that lake trout (Salvelinus namaycush) are 70 and 71 times more sensitive to BOEE and PGBEE, respectively, than 2,4-D acid (our analysis). Similar differences between 2,4-D ester and acid toxicity have been reported by Mount and Stephan (1967), Meehan et al. (1974), and Martens et al. (1980).

The continuous-flow 96-h LC50 values clearly indicated that PGBEE was slightly more toxic than BOEE, that chinook salmon were more sensitive than steelhead-rainbow trout, and that fry were more sensitive than smolts to the 2,4-D esters. Although all ester, species, and life-history stage comparisons indicated these trends, those involving smolts were not always statistically significant ($p < 0.05$). This lack of significance can be attributed to the lack of partial mortalities in the smolt toxicity tests which in turn resulted in large LC50 95% confidence limits.

No published data from continuous-flow acute tests with fish and 2,4-D esters are available for comparison with our results. Martens et al. (1980) conducted numerous semi-static (daily renewal) tests with salmonid fingerlings, fry, and smolts with a granular formulation of BOEE 2,4-D (Aqua-Kleen 20®), an aquatic herbicide. They estimated nominal (not measured) 96-h LC50 values (as ug/l a.e.) for sockeye salmon (Oncorhynchus nerka) fingerlings, coho salmon (Oncorhynchus kisutch) fry, and pink salmon (Oncorhynchus gorbuscha) fry at 450, for sockeye smolts at 493, and for rainbow trout fry at 283. This range of LC50 values (283 to 493 ug/l) is similar to our results (327 to 601 ug/l). However, since neither 2,4-D ester or total 2,4-D concentrations were measured during their tests, error could have occurred in estimating 2,4-D concentrations at LC50 levels.

Our 40 ug/l MATC for BOEE approximates MATC values estimated for egg-to-fry tests of cutthroat trout (Salmo clarki) and lake trout chronically exposed to other 2,4-D esters: 19 ug/l a.e. 2,4-D butyl ether ester (BE) and 19 ug/l a.e. 2,4-D PGBEE (Woodward and Mayer, 1978). In our chronic test, significant differences in growth may have occurred at BOEE levels less than 40 ug/l if a greater degree of precision had been used in measuring total toxicity of chemicals is often additive, but synergistic action is rare and is not known to occur at low concentrations near the no-effect level; antagonism of toxic action may occur more frequently than synergism (Finlayson and Verrue, 1982). Another point of view is that additional protection is required to compensate for unknowns when extrapolating laboratory toxicity data to actual aquatic ecosystems. These unknowns include degradation products, joint action of multiple chemical contaminants, different chemical and physical factors, as well as sampling and experimental error from the tests. A safety factor (some fraction of MATC) can be used to provide the additional protection. In other words, predictions based on laboratory data may either overestimate or underestimate effects on aquatic organisms in the environment. This degree of underestimation or over-estimation decreases as the species and conditions used in the tests more closely correspond to the environment in question.

The MATC for BOEE estimated from our chronic chinook salmon egg-to-fry test is below reported levels shown to cause other sublethal effects in salmonids. McBride et al. (1981) reported that BOEE concentrations below the LC50 value (300 to 700 ug/l a.e.) produced reversible stress (internal hypertrophy) in sockeye salmon during static tests at 24 to 96 h; reversible gill pathology was present at higher concentrations (1,000 ug/l a.e.). Martens et al. (1980) challenged sockeye smolts and pink salmon fry to saltwater (28 ^{o}/oo) for 96 h with no mortality after a 24-h static exposure to 540 ug/l a.e. BOEE. Similar results for saltwater challenge tests have been found by McBride et al. (1981) with sockeye salmon smolts: the minimal BOEE concentration required to induce stress is slightly below lethal level and on transfer to an uncontaminated environment, the fish can revert quickly to an unstressed state and survive in sea water. The significance of these studies is confounded by the use of static tests and inadequate toxicant monitoring. However, the importance of these studies is that levels shown to have an effect are approximately one order of magnitude greater than the MATC for BOEE chronic exposure to chinook salmon.

In the study, we found that PGBEE is slightly more acutely toxic to salmonids than BOEE, that chinook salmon are more sensitive to BOEE than steelhead-rainbow trout, and that fry are more sensitive than smolts. Additionally, we found the estimated MATC for BOEE to be 40 ug/l for chinook salmon during continuous egg-to-fry exposure.

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APPENDIX V

STAFF REPORT

MONITORING OF SILVICULTURAL USE OF 2,4-D IN NORTHERN CALIFORNIA

Prepared by Staff of:

State Water Resources Control Board - Toxics Special Project
North Coastal and Regional Water Quality Control Boards
Central Valley and Regional Water Quality Control Boards

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Staff members of the North Coastal and Central Valley Regional Water Quality Control Boards and the State Water Resources Control Board facilitated the work by providing equipment, reviewing the work plan, and commenting on the preliminary and draft final reports.

The U.S. Forest Service as a cooperator in the study contributed greatly to the overall project. Forest Service personnel who provided advice and site information, collaborated on monitoring station location, collected data and water samples, and reviewed the draft final report, were:

Mike Furniss -- Six Rivers National Forest

Dick Jones -- Modoc National Forest

Gene Jensen -- Modoc National Forest

Darrel Ranken -- Shasta-Trinity National Forest

Jerry Anderson -- Shasta-Trinity National Forest

Peter Van Susteren -- Shasta-Trinity National Forest

Bill Moore of Champion International Corporation provided site information and monitoring results for the Whitmore site.

Nancy Richard and Mike Reid, Volunteer State Service Interns, were responsible for the success of Blackhawk site monitoring. They prepared a trail into the site, conducted the steam gauging and water sampling activities, and contributed their time to many other tasks.

Jim Stokes, retiree of Jones & Stokes, Incorporated, contributed his time and facilitated the Blackhawk site monitoring by loaning equipment for use at the monitoring station and by planning the logistics for the Blackhawk station.

Members of the 2,4-D Advisory Committee reviewed the draft final report and provided valuable suggestions for its finalization.

I. SUMMARY

This study was conducted on forest lands in northern California to determine (1) levels of 2,4-D in surface waters during site treatment and subsequent rainfall runoff, (2) whether State water quality objectives were met at all times, and (3) the efficacy of present best management practices (BMPs) in preventing discharge of 2,4-D to surface waters.

Eight sites were selected for study, seven on lands managed by the U.S. Forest Service and one on land owned by Champion Internationl Corporation. Seven of the sites were treated with 2,4-D via helicopter; one was treated manually from the ground. Treatment occurred during the spring, summer and early fall months of 1983. Most of the sites presented particular challenges in controlling 2,4-D discharges, e.g., steep slopes, saturated soils, and numerous water courses in the treated areas that were difficult to see from the air. Sites were representative of the various topographical and climatic conditions occurring in northern California.

Discharge of 2,4-D was controlled by BMPs/guidelines promulgated by the U.S. Forest Service[1] or requirements included in permit terms issued by the Shasta County Agricultural Commissioner[2]. Water monitoring during 2,4-D application and rainfall runoff was done by U.S. Forest Service and/or State staff except for the Champion International site where Champion personnel did the monitoring.

Water sample results from all sites indicated that (1) State water quality objectives were met during 2,4-D application and subsequent rainfall runoff, and (2) 2,4-D discharges from treated areas were either non-detectable or were present at levels reported to be safe for beneficial uses of water (public water supplies and fisheries). Characteristics of study sites and water monitoring results are shown in the following table:

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1 BMPs are shown in Appendix 1. Guidelines are contained in the "Handbook on Aerial Application of Herbicides [6]. In this report the term BMPs is meant to include both BMPs and guidelines.

2 Appendix 2 and 3 show general permit terms and an example of a specific permit for forest use of 2,4-D.

Area	Site	Acres Treated	Month Treated	Maximum 2,4-D Sampled During Treament*	Maximum 2,4-D Sampled During Rainfall Runoff*
Six Rivers	Washington	49	April	<0.1	<0.1
Six Rivers	Blackhawk	426	May	0.6	1.0
Modoc	Long Valley	180	July	0.1	<0.1
Modoc	Bear Camp	120	July	7.0	<0.1
Shasta-Trinity	Hornet Gulch**	38	June	<0.1	0.1
Shasta-Trinity	Gap	90	Sept	<0.1	<0.1
Shasta-Trinity	Hardpan 25	155	Sept	<0.1	<0.1
Champion-Whitmore (Shasta Co.)	Whitmore 17	260	Sept	0.1	<0.1

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* parts per billion
** ground application

One conclusion of this study is that U.S. Forest Service BMPs and Shasta County permit terms effectively controlled 2,4-D discharge to surface waters in and contiguous to the study areas. Even though specific BMPs for buffering (untreated areas) and maximum wind velocity differed among some of the study areas, 2,4-D discharge was similar (low levels or nondetectable) in all areas. Nevertheless, the report presents a rationale and recommendations for an augmentation and standardization of current USFS BMPs and county permit terms to specify minimum buffer widths for flowing and dry intermittent streams as well as maximum wind velocity during 2,4-D application.

Additional conclusions and recommendations are made for buffer marking, monitoring methodology, result reporting, and emphasis/responsibility for future 2,4-D monitoring (see Section VII).

II. INTRODUCTION

A. Silvicultural Use of 2,4-D

Herbicides are a management tool used in silviculture to increase timber and livestock forage yields. The U.S. Forest Service (USFS) reports that the phenoxy herbicide 2,4-D (2,4 dichlorophenoxyacetic acid) is widely used on national forest lands. The chemical selectively inhibits or destroys vegetation that competes with commercially valuable tree and grass species. Management of the competitive vegetation is termed "release" by the USFS. Some 205,000 pounds of 2,4-D were applied manually or by aircraft to release about 117,000 acres in national forests nationwide in fiscal year 1979-80 [1]. The chemical is used mainly in spring and fall months in northern California on national and private forest lands. Use of 2,4-D on private lands was restricted during the past two years in some California counties pending a legal decision.

Prior to a decision on vegetation management for any national forest, the USFS conducts an environmental analysis and issues an environmental analysis report (EAR) in which costs and environmental impacts are compared for various release methods including: (a) manual release (hand cutting), (b) ground application of herbicide[s], (c) aerial application of herbicide[s], and (d) no action. Based on the EAR, the Forest Supervisor selects the release method that is the most cost-effective while protecting environmental resources and public health. One or more release methods may be selected for a given project area, and part or all of the area is subject to a no-action decision. USFS personnel oversee release activities. When herbicides are applied near waterways, USFS personnel routinely monitor downstream surface waters during application. Herbicides are used in accordance with product label restrictions and best management practices (BMPs)[1] developed by the USFS or permit terms issued by county agricultural commissioners. BMPs and permit terms restrict herbicide use relative to weather conditions, terrain, proximity and beneficial uses of surface waters, and application equipment/personnel.

The scope of this study includes several sites in the Six Rivers, Shasta-Trinity, and Modoc National Forests and one site on private land in Shasta County that were treated with 2,4-D during the spring, summer, or fall months of 1983.

B. Concerns with 2,4-D Use

Use of 2,4-D for vegetation management on timberlands has caused widespread concern among regulatory agencies and the public. The chemical can be transported from the target area to streams by wind and water runoff, thus posing a threat to aquatic life and municipal water supplies. Concerns have been voiced most recently by the Humboldt Herbicide Task Force, supervisors of Trinity County, and a number of spokespersons at a Central Valley Regional Water Quality Control Board (CVRWQCB) workshop held in Redding, California, on 25 February 1983. The latter included the Siskiyou Citizens Against Toxic Sprays and the South Feather Watershed Council.

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[1] BMPs are implemented through guidelines contained in Water Quality Management for National Forest System Lands in California (Appendix 1), a USFS document entitled "Handbook on Aerial Application of Herbicides" [6].

The herbicide and its esters can be toxic to fishes and mammals if dosage and exposure periods exceed threshhold levels. The chemicals can also cause taste problems in water supplies. The Environmental Protection Agency (EPA) standard (maximum level) for 2,4-D in domestic water supplies is 100 parts per billion (ppb). Research during 1982-83 by the California Department of Fish & Game (DFG) indicates that the median lethal concentration (96-hour exposure) of the butoxyethanol (BOE) ester of 2,4-D to juvenile stages of chinook salmon and rainbow trout ranges between 327-601 ppb and that the maximum acceptable toxicant concentration for long-term exposure of those species to the BOE ester is 40 ppb [2]. Present analytical detection capability is on the order of 0.1 ppb for 2,4-D as total acid and 1 ppb for 2,4 Dichlorophenol, a 2,4-D breakdown product.

Herbicides from silvicultural operations can enter waterways primarily during application activities (drift or target error) and/or transport from the target area by ensuing runoff. Northern California forest lands and climate pose particular challenges to controlling 2,4-D applications. Steep slopes, numerous drainage courses, saturated soils (particularly in spring months), and high intensity rainfall/runoff increase the potential for applied chemicals to enter aquatic systems as compared with less steep, more arid areas.

Stream monitoring by the USFS and private landowners has been done routinely in northern California in conjunction with 2,4-D applications. The following figures compiled by the North Coast Regional Water Quality Control Board (NCRWQCB) staff show the percent distribution of 2,4-D concentrations in north coast streams as reported in self-monitoring data received from the USFS and private industry during the years 1974 through 1981 [3]:

2,4-D (ppb)	USFS	Private Industry	All Dischargers
<1.0	97 %	83 %	92 %
1.1- 2.0	2	9	4
2.1- 3.0	0.2	2	1
3.1- 4.0	0	0.5	0.2
4.1- 5.0	0.2	0.5	0.3
5.1- 6.0	0	0	0
6.1- 7.0	0.2	1.5	0.6
7.1- 8.0	0	0	0
8.1- 9.0	0.2	0.5	0.3
9.1-10.10	0	1.0	0.3
10 -15.0	0	1.0	0.3
15.1-20.0	0	0.5	0.2
>20.0	0.2	0	0.2
Totals	100%	100%	100%
Total Samples	432	218	650

Such monitoring data indicate that 2,4-D levels believed acutely and chronically toxic to salmonoids are rarely exceeded. However, inadequate monitoring data exist for storm-runoff events after treatment, the period when previously applied 2,4-D would most likely be transported into the aquatic system. Studies by the USDA Pacific Northwest Forest and Range Experiement Station showed that 2,4-D applications during June near Roseburg, Oregon, did not result in detectable stream concentrations of 2,4-D until the following October and November after rainfall events that started in September.

C. State Water Quality Objectives for 2,4-D

III. PROJECT PURPOSE AND OBJECTIVES

A. Purpose and Scope

The overall purpose of this project is to evaluate whether current management practices for 2,4-D use on forest lands in northern California meet water quality objectives for surface waters.

2,4-D was selected as the herbicide to be monitored in the project because: (1) it is a widely used herbicide on forest lands; (2) project resources were insufficient to cover all herbicides; (3) 2,4-D can be viewed as an indicator of the effectiveness of BMPs for control of other herbicides; and (4) its use is viewed with concern by numerous groups and individuals.

The project was directed primarily to USFS lands because of: (1) the greater magnitude of 2,4-D use on those lands at this time as compared with private timberlands, (2) an opportunity existed to evaluate recently developed USFS BMPs and (3) results from USFS lands are transferrable to private lands.

As 2,4-D is applied mainly during spring (April/May) and early fall months (September/October), the project concentrated on 2,4-D use during those months. Runoff containing 2,4-D is more likely from spring applications because of saturated soil conditions, flowing as contrasted with dry drainage courses, and the imminence of rain. However, in areas of local concern where suitable spring applications were not planned, summer and fall applications were monitored.

B. Objectives

Project objectives are to:

1. Monitor 2,4-D applications at sites that exhibit the most likely conditions for occurrence of 2,4-D contamination of surface waters in the Six Rivers, Shasta-Trinity, and Modoc National Forests and selected private forest lands. Conditions include steep terrain, saturated soils, substantive rainfall, relatively large application areas and proximity of spray site to streams;

2. Determine maximum and 24-hour average concentration and mass emission of 2,4-D (as total acid) at selected stream stations during 2,4-D application and ensuing rainy periods when runoff and stream flows increase;

3. Determine concentrations of the 2,4-D breakdown products, 2,4-Dichlorophenol, and any other spray additives (such as petroleum hydrocarbons) at the selected stream stations;

4. Determine whether stream concentrations of 2,4-D at the selected stations achieve Basin Plan water quality objectives; and,

5. Evaluate whether BMPs and attendant guidelines used for 2,4-D application under site conditions are adequate for protection of water quality and public health.

IV. PROJECT SITE CHARACTERISTICS

Eight 2,4-D application sites were monitored during this project. Characteristics of those sites are summarized in Table 1; locatons are shown on Figure 1. Project sites are discussed below under respective national forests and private lands.

A. Six Rivers National Forest - Gasquet Ranger District

1. Washington Site

This site in Del Norte County drains into Siskiyou Fork, which is a tributary to the Middle Fork of the Smith River. The site is drained by a poorly-accessible, first order tributary stream that enters Siskiyou Fork some three miles upstream from the latter's confluence with the Middle Fork Smith River. Siskiyou Fork was flowing at 109 cfs on April 21 at the monitoring station occupied by USFS and state personnel. The slopes of the two sprayed units in the site range from 40%-60% and 60%-80%, respectively; the average slope is 50% and 65%, respectively. The soils of the units are loamy-skeletal, mixed-mesic Typic Haploxerults greater than 50 inches deep and well drained. Soils were considered saturated due to heavy rainfall preceding the application. Major target vegetation included tan oak, madrone, Ceanothus, and huckleberry.

2. Blackhawk Site

This 426-acre unit was previously owned and clearcut/tractor-yarded by a private timber company. USFS acquired the land shortly after harvest and has since reforested the unit. The unit drains into Blackhawk Creek which enters the South Fork Smith River some 20 miles upstream from the latter's confluence with the Smith River (Figure 2). Blackhawk Creek watershed totals 1,088 acres. Blackhawk Creek flows ranged from about 5-13 cfs during April and May of 1983. Stream velocity at that time averaged 2.5 feet per second at the surface and about 1.2 feet per second at mid-depth. The Creek habitat, although marginal for salmonoid production, supports populations of may flies, caddis flies and stone flies that provide food for fishes in downstream waters.

Slope of the sprayed area of the drainage ranges from 10%-75%; average slope is 50%. Drainage follows a general east-west inclination.

Watershed soils are Typic Hapludults of mixed-mesic, loamy-skeletal to fine loamy families, 40-60 inches deep and well drained. Erosion from the unit was extensive following logging, but has since largely stabilized. Abnormal overland flow and slow erosion still occur on many main skid trails.

About 124 inches of rainfall were recorded in nearby Gasquet during the 1982-83 water year. The site's predominant vegetation is conifers, tan oak, madrone, Ceanothus, huckleberry, and alder.

The USFS classified Blackhawk as a high hazard spray site because stream courses are hard to see from the air (shallow declivities), the site has an extensive stream network, and a large area was sprayed in relation to watershed size. Also, runoff potential was high due to the dense road/skid trail network.

Site slope was estimated to range between 50%-60% by the USFS and runoff potential was believed to be moderate. Soils are a dystric xerochrepts, loamy-skeletal, mixed-mesic family with a fractured, cobble substrate having a high infiltration rate.

Major target species were tan oak, vine maple, dogwood, chinquapin, grasses, and forbes.

2. Gap Site - Shasta Lake Ranger District

The 90-acre Gap Site is drained by Gap Creek, tributary to Iron Canyon Reservoir which flows into Iron Canyon Creek, tributary to the Pit River (Figure 5). Iron Canyon Reservoir provides a valuable trout fishery.

Range of site slope was estimated by the USFS to be 60%-90%. Dry weather flow of Gap Creek is 0.25 cfs or less. One live and one dry drainage course were present in the site.

Soils, which are medium depth and gravelly textured, were considered unsaturated during treatment. Target vegetation consisted mainly of bigleaf maple, mountain white thorn, snowbrush, greenleaf manzanita, Site soils are reported by Champion to be a moderately deep, clay loam. Site slope averages about 45% with a maximum slope of some 60%.

Target vegetation for conifer release was primarily deerbrush and greenleaf manzanita.

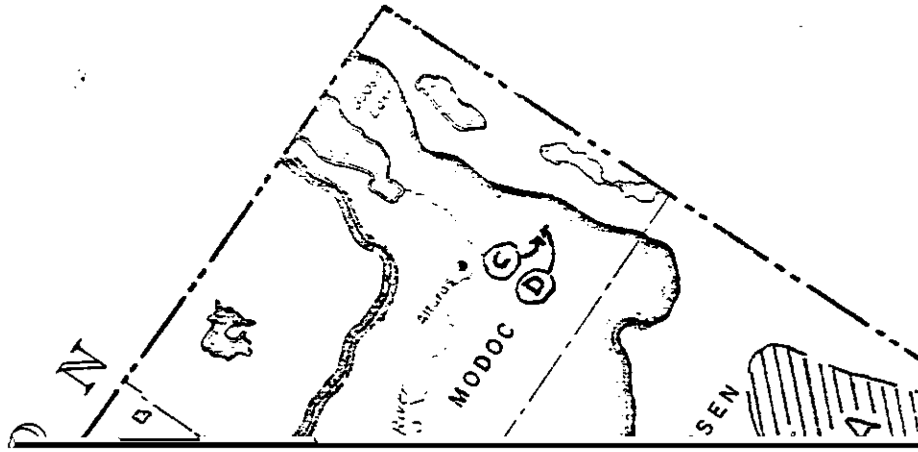

N
C
D
MODOC
SEN
A

Table 1. Site and Application Characteristics of 2,4-D Study Areas

Forest	County	Name of Site	Location of Unit	Acres Sprayed	Area Slope (%)	No. of Drainage Courses in Area	Hours for Drainage Course Flows to Reach Monitoring Station	Monitoring Station & Miles from Closest Portion of Area	Weather During Application	Date/Time of 2,4-D Application
Six Rivers	Del Norte	Washington	S7&8, T17N, R4E	49 (Helicopter)	H Unit: 40-60 Average=50 D Unit: 60-80 Average=65	3	1.45 to 3.95	Siskiyou Fork 2.5 to 3	Cloudy. Wind < 5 mph. Air temp. 47^o-52^oF.	April 21 (0950 to 1137)
Six Rivers	Del Norte	Blackhawk	S17,20&21, T15N, R3E	426 (Helicopter)	10-75 Average=50	15	0.5 to 4.5	Blackhawk Creek 0.15	May 1&2: Cloudy. Wind < 5 mph. Air temp. 48^o-65^oF.	May 1 (0830 to 1228) May 2 (0630 to 1200)
Modoc	Modoc & Lassen	Long Valley	S14&23, T38N, R15E; S25&26, T39N, R15E	180 (Helicopter)	1	1	0.9 to 25	Long Valley Creek 0.25	Cloudy. NW breeze. Air temp. 50^oF.	July 14 (0542 to 0720)
Modoc	Modoc	Bear Camp/ Homestead	S4&5, T38N, R16E; S33, T39N, R16E	120 (Helicopter)	2-10 Average=3	5	0.5 to 2	East Creek 0.5	Clear. NW breeze. Air temp. 52^o-55^oF.	July 14 (0730 to 0830)
Shasta-Trinity	Shasta	Gap	S18&19, T37N, R1W	90 (Helicopter)	60-90	2	0.25 to 1	Gap Creek 0.25	Clear. No wind.	Sept. 6 (0800 to 0930)
Shasta-Trinity	Shasta	Hardpan 25	S25, T37N, R1E	155 (Helicopter)	20-50	3	0 to 0.75	E. Fork Nelson Creek 0.03	Clear. SW wind 3-6 mph.	Sept. 5 (1030 to 1400)
Shasta-Trinity	Shasta	Hornet Gulch	S6, T37N, R1W	38 (Ground application)	50-60	3	4 to 6	Hornet Creek	Clear. Variable intermit. light breeze.	June 24 to June 29
Champion Int'l	Shasta	Whitmore Section 17	S17, T32N, R2E	260 (Helicopter)	30-60 Average=45	5	0.25 to 0.5	Atkin Cr. Trib.-0.25 S. Cow Cr. Trib.-0.2	Clear. Wind up to 5 mph.	Sept. 16 (0753 to 1226)

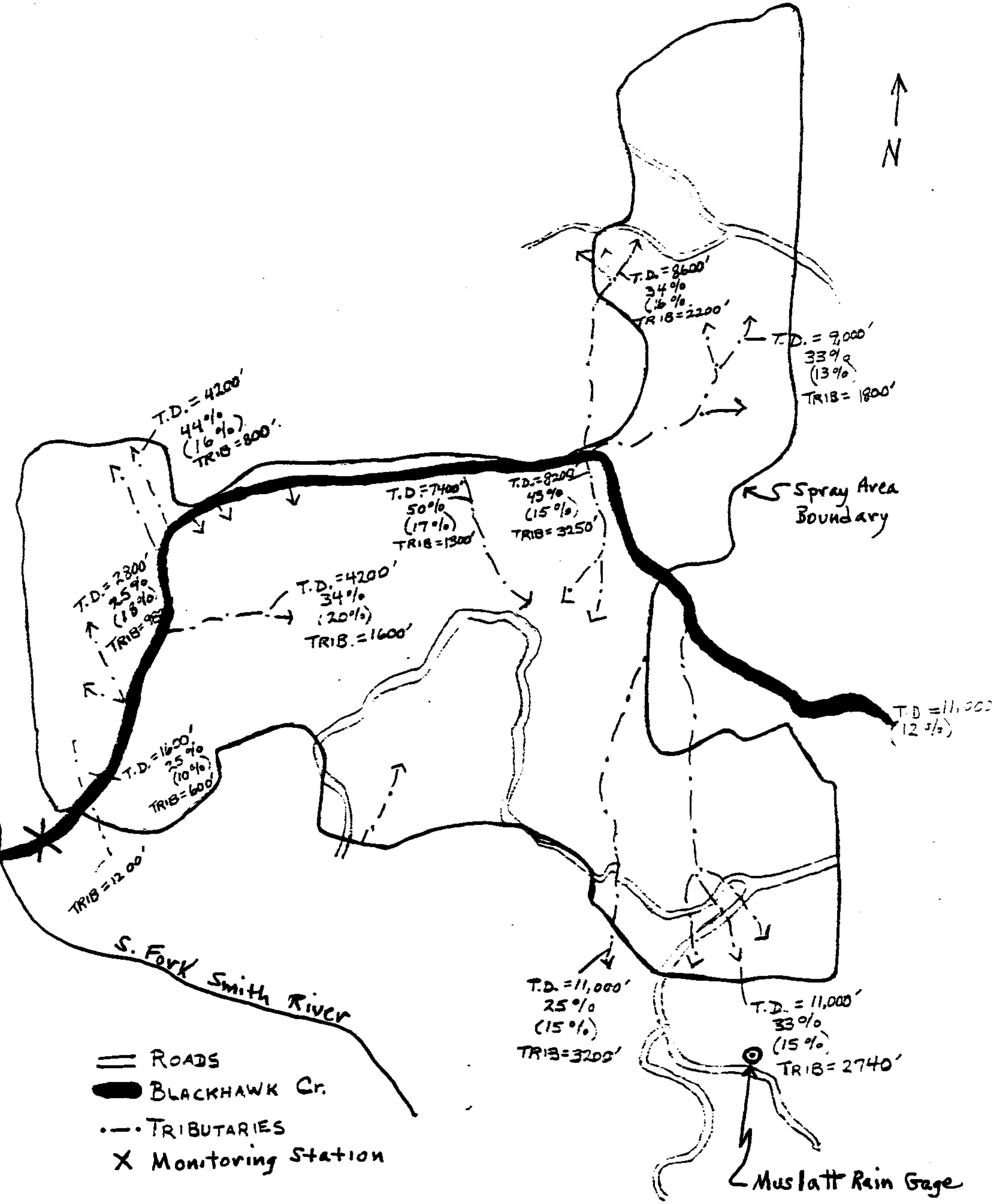
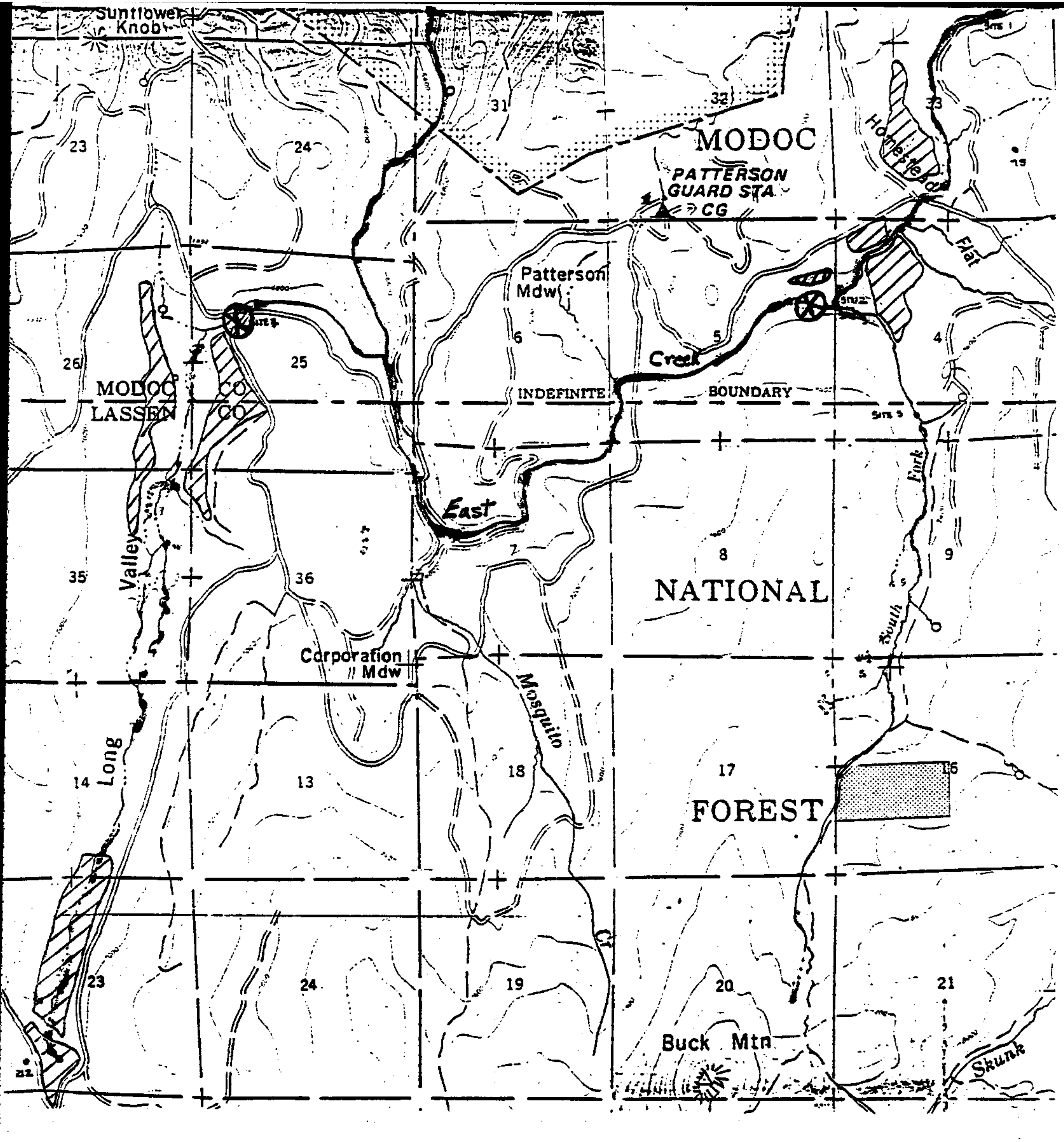
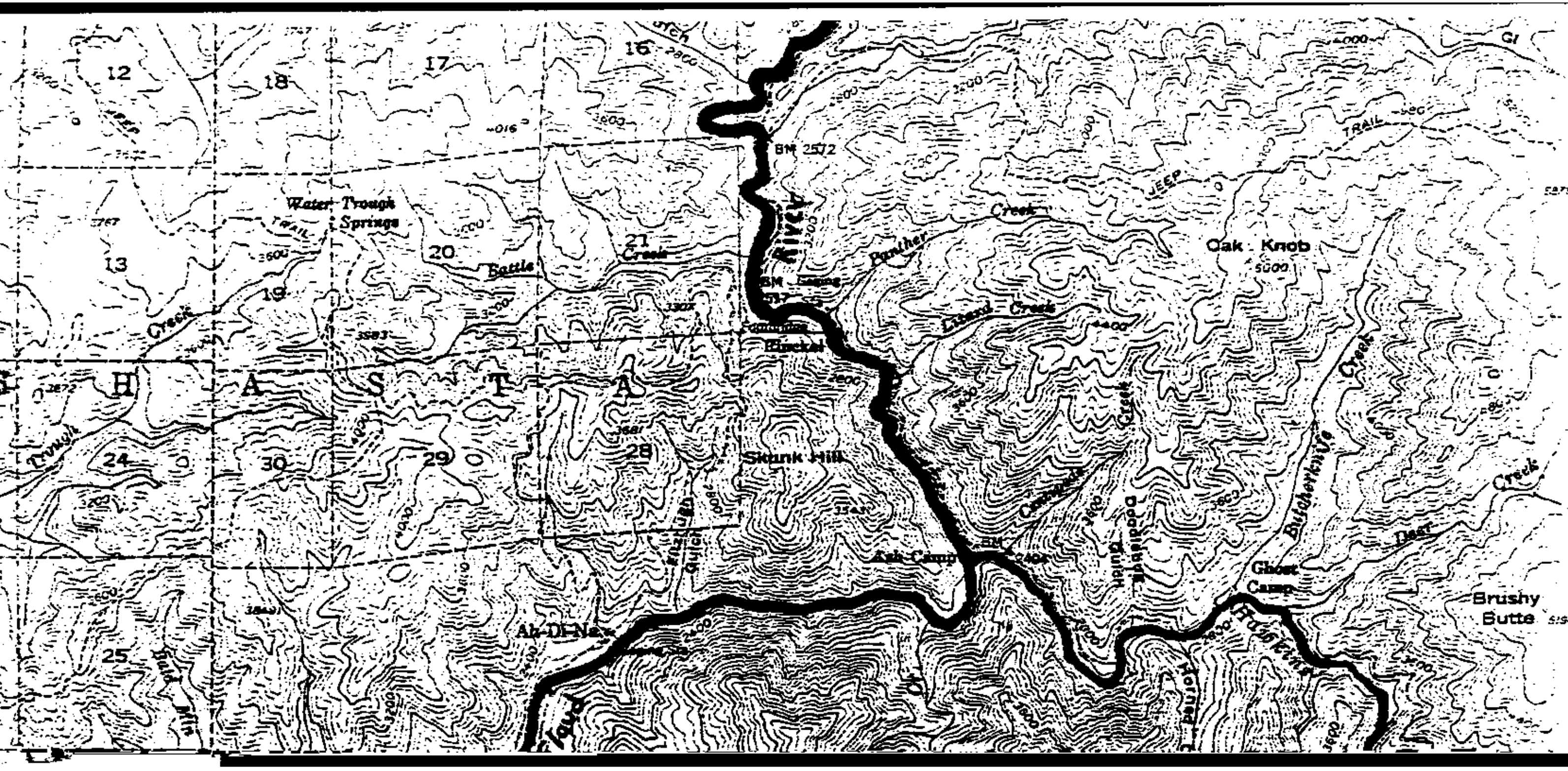


Figure 2. Diagram of Drainage Features in Blackhawk Site and Location of Monitoring Station (USFS map)

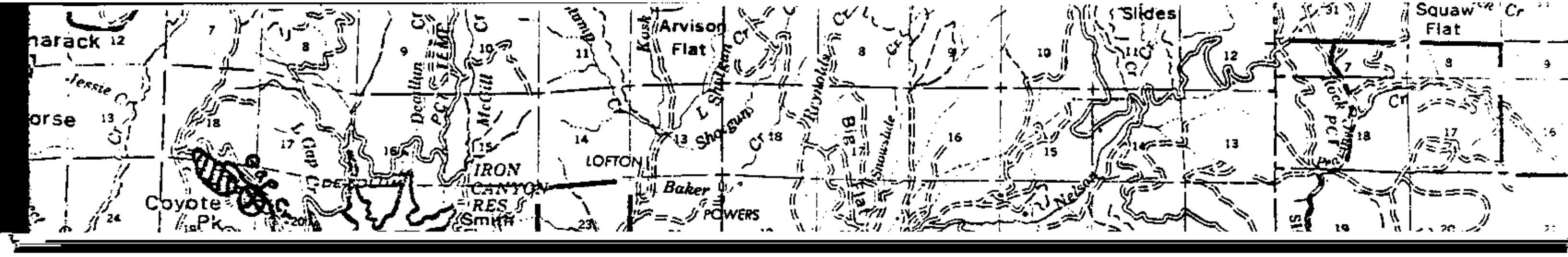


Roads
East Cr. and Tributaries
Sprayed Areas
Monitoring Stations

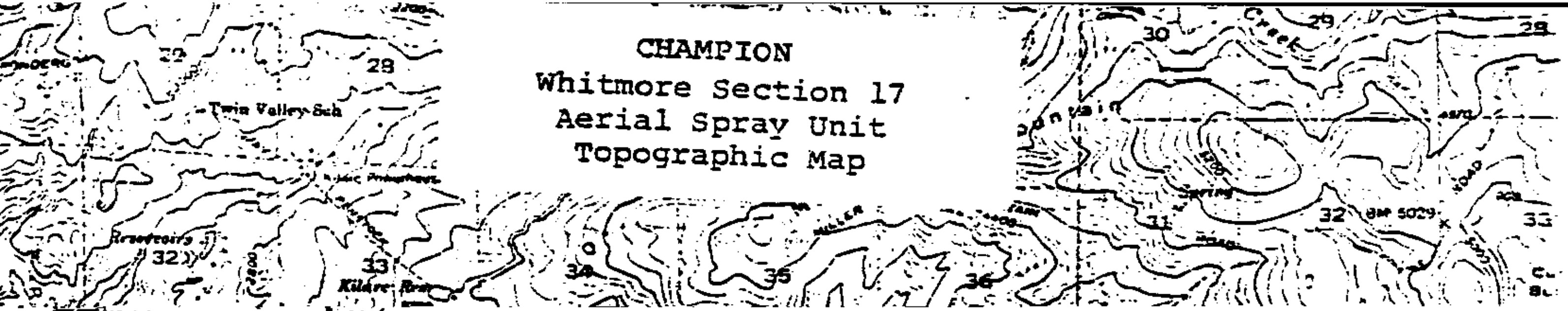
Figure 3. Details of Bear Camp/Long Valley Sites and Location of Monitoring Stations



Water Trough Springs
Battle
Creek
Panther
Lizard Creek
Oak Knob
S H A S T A
Skunk Hill
Hinckel
BM 2572
Ash Camp
Ah-Di-Na
Ghost Camp
Brushy Butte
Deer
Creek
TRAIL
JEEP


Arvison Flat
Slides
Squaw Flat
IRON CANYON RES
LOFTON
Baker
POWERS
Coyote Pk
Smith

CHAMPION
Whitmore Section 17
Aerial Spray Unit
Topographic Map



V. METHODS

A. Herbicide Application

1. Aerial (Helicopter) Application

In this study, all sites were sprayed via helicopter with the exception of the Hornet site which was treated manually from the ground.

A mixture of 2,4-D (BOE ester), adjuvant, and water was prepared adjacent to but outside of the boundaries of each spray site. Fluorescent dye was added to the mixture for the Blackhawk and Washington sites. After transfer to a helicopter, the mixture was applied at rates of from 1.8 to 3 pounds active ingredient 2,4-D per acre. For two sites (Gap and Hardpan 25), six pounds of Dalapon and four pounds of Atrazine per acre were added to the spray mixture.

Standard USFS practices were followed relative to application and equipment; e.g., boom width, jet placement and aperture, flying speed, height, etc. [6]. Single (one swath) coverage was used as opposed to double, criss-cross coverage. On the Blackhawk and Washington sites where dye was included with the herbicide, USFS staff measured for the presence of dye continuously with a fluorometer and obtained water saples periodically at the stgream monitoring station. Usually, wash water from mixing equipment was applied to the spray area.

The following BMPs were followed to control herbicide drift during heli-

Table 2. Drift Control BMPs Followed During Aerial 2,4-D Application

Site	Wind Velocity	Temp.	Hum-idity	Rainfall	Lateral Buffer (From Waterway Midpoint)	Drift Control
Washington	< 5 mph	< 80°F.	> 30%	No spray if raining or 70% chance of rain within next 24 hours.	No spray within 100 feet of each side of live and dry intermittent streams. Buffer borders marked and drift cards placed in buffered areas.	Nozzle size and type, pump pressure, flying height and speed controls, and addition of adjuvant in conformance with Reference 6.
Blackhawk	Ibid.	Ibid.	Ibid.	Ibid.	Ibid.	Ibid.
Long Valley	Ibid.	Ibid.	Ibid.	Ibid.	Ibid., but buffer borders unmarked and drift cards not used.	Ibid., except no adjuvant.
Bear Camp	Ibid.	Ibid.	Ibid.	Ibid.	Ibid., but buffer borders unmarked and drift cards not used.	Ibid., except no adjuvant.
Gap	<10 mph*	No Limit*	No Limit*	Ibid.	No spray within 100 feet of each side of live streams. Buffer borders marked. Drift cards not used.	Ibid., with adjuvant.
Hardpan 25	Ibid.*	Ibid.*	Ibid.*	Ibid.	Ibid.	Ibid., with adjuvant.
Whitmore 17	Ibid.*	Ibid.*	Ibid.*	Ibid.	No spray within 100 feet of each side of live streams and moist areas. Buffers marked. No drift cards.	Ibid., with adjuvant.

*Shasta County Agricultural Commissioner permit conditions.

2. Manual (Ground) Application

This method of treatment (Hornet site only) used backpack tanks and manual spraying of individual plants. Climatic-type BMPs employed were similar to the above aerial application. Fifty-foot buffers (on both sides of live streams) were left untreated.

2. Monitoring Stations Stations for water monitoring were located using the following criteria:

   (a) proximity to the sprayed unit [downstream from the unit boundary, but as close to the boundary as practicable in order to minimize dye tracer or 2,4-D decay],

   (b) accessible without entering the unit during or after 2,4-D application,

   (c) suitable stream section present for flow measurement,

   (d) downstream from the lowest elevation unit, if more than one unit in a watershed was treated, and

In addition to 2,4-D samples, 2,4 Dichlorophenol*, stream hardness, pH and temperature were determined at most monitoring stations prior [redacted] a Hach colorimeter.

2. Stream Flow

At most sites, stream flows were gauged prior to and during 2,4-D treatment as well as during the first runoff following treatment. A calibrated pygmy meter was used for those measurements. A staff gauge was placed at the monitoring station prior to runoff at the Blackhawk and Washington sites; an increase in stage on the staff gauge triggered flow metering and water sampling. Riffle areas with a straight channel and uniform substrate were selected for flow measurement.

D. Sample Disposition and Quality Control

2,4-D and 2,4 Dichlorophenol samples were preserved with NaOH. Within six hours of collection, samples were placed in an iced container and then transported to refrigeration within 48 hours. Chilled samples were delivered to the analytical laboratories within 35 days after collection. Samples remained in the possession of project staff from time of sampling until delivery to analytical laboratories. Precautions were taken during all phases of sample collection, transport, and storage to prevent sample contamination, decay, and adulteration.

For quality control purposes at the Blackhawk site, about 15 percent of the State's 2,4-D/2,4 Dichlorophenol samples were split for analyses by two State-approved contractual laboratories. In addition, results of samples taken by USFS staff were made available for comparison of analytical results.

VI. RESULTS

A. Washington Site (H and D Units)

Forty-nine acres within two units were sprayed on 21 April 1983. Spraying started at 0940 hours and stopped at 1137 hours when rainfall (drizzle) commenced.

State and USFS staff sampled Siskiyou Fork at a common monitoring station for 2,4-D during spraying and the subequent period when time-of-travel studies indicated that 2,4-D could be present. The USFS also operated a fluorometer during the above period; no indicatation of dye was recorded by the fluorometer. Laboratory results of USFS pre-spray and during-spray samples reported no detectable 2,4-D in the samples at an analytical sensitivity of 0.1 ppb.

Stream flow at the Siskiyou Fork monitoring station remained constant until about 1:25 p.m. on 22 April when rainfall which had started at about 11:30 a.m. on that date resulted in runoff and increased flow in Siskiyou Fork. Analyses of samples taken prior to and during the rise in stream flow showed nondetectable levels of 2,4-D as follows:

		Siskiyou Fork				
Date	Time	Estimated Flow (cfs)	Staff Guage (inches)	2,4-D (ppb)	pH	Temp. (°F.)
April 21	0951	109	0	<0.1[1]	7.3	47
	1125			<0.1[1]		
April 22	1325	109	0	<0.1[2]	7.2	46
	1525	>109	0.02	<0.1[2]		
	1725	>109	0.1	<0.1[2]		

Rainfall intensity diminished in the early evening of April 22. During the rainfall event, Siskiyou Fork apparently did not rise above the 0.1 staff guage measurement recorded at 1725 hours. This is assumed because an automatic sampler installed at the station by USFS staff on April 21 had not collected a sample by April 23. The intake height of the sampler was only slightly higher than the 0.1-inch reading on the staff guage. Stream flow higher than 0.1 inch on the guage would have activated the sampler. Inches of rainfall recorded by the USFS at Gasquet for April 21-23 were as follows (rainfall at the Washington Unit may have been higher because its elevation is higher than at Gasquet):

---

[1] USFS samples
[2] State samples

	Time Period			
Date	2400-0600	0600-1200	1200-1800	1800-2400
April 21	0	0	0	0
April 22	0	0.1	1.1	0.5
April 23	0.6	0.5	0.1	0

Siskiyou Fork pH and temperature ranged from 7.2-7.3 and 40°F.-47°F., respectively, during April 21 and 22.

B. Blackhawk Site

About 120 acres of the Blackhawk Unit were sprayed with 2,4-D on May 1 from 0830 hours to 1130 hours. Winds above 5 mph halted spraying at 1130 hours. The remaining 306 acres were sprayed on May 2 from 0630 hours until 1200 hours. State and USFS staff sampled Blackhawk Creek and measured stream flow at a common monitoring station near the Creek's confluence with the South Fork Smith River (Figure 2) before and during spraying. USFS time-of-travel studies (dye injection timing) of Blackhawk Creek and its tributaries indicated that 2,4-D could be present at the monitoring station as soon as one-half hour after spraying started and as long as four and one-half hours after spraying ceased. USFS staff continually monitored Blackhawk Creek with a recording fluorometer during that time period on both May 1 and 2.

The USFS reported a deviation from BMPs on May 2 at 1024 hours when the helicopter sprayed over a live tributary in one swath. From 1058 to 1062 hours, the USFS fluorometer registered the presence of up to 30 parts per trillion of dye at the sampling station. The dye concentration corresponded to an implied 2,4-D concentration of 0.7 ppb. Both the State and USFS sampled for 2,4-D at that time.

Sampling results for pre-spray and spray periods are shown in Table 3. The State's contractual laboratory reported 2,4-D levels of 0.14 and 0.32 ppb at 1122 and 1153 hours, respectively, on May 2 which was from about one-half to one hour after the USFS fluorometer registered the possible presence of dye. No 2,4 Dichlorophenol was measured at a sensitivity of 0.1 ppb. The USFS contractual laboratory reported 2,4-D levels of 0.6 ppb and 0.1 ppb at 1110 and 1122 hours, respectively, and <0.1 ppb at 1153 on May 2.

Runoff sampling was done manually by the State on May 5, 6 and 7 when the first substantive rainfall occurred after 2,4-D application. The USFS automated sampler (ISCO) collected samples during the rise in stream flow which occurred from the evening of May 5 through the early morning of May 6. Sampling results are shown in Table 3 and Figure 7. State results from one laboratory showed a level of 1.0 ppb 2,4-D as stream flows rose during the early morning of May 6 and a level of 0.32 during the late morning of May 6 as stream flows receded. No detectable 2,4-D was measured during the intervening period nor before or after the stream flow rise and fall. Duplicate samples analyzed by the State's quality control laboratory showed a level of 0.19 ppb 2,4-D during the rise in stream flow, a maximum of 1.0 ppb at the crest in stream flow, and less than 0.1 ppb as stream flow decreased. No 2,4 Dichlorophenol was detected in runoff samples.

Table 3. Results of Blackhawk Creek Water Sampling and Gauging

Date	Time	Flow (cfs)	2,4-D (ppb total acid) State Lab 1	2,4-D (ppb total acid) State Lab 2	2,4-D (ppb total acid) USFS	2,4 Dichlorophenol (ppb)	Hardness (ppm as $CaCO_3$)	pH	Temp. ($^oF.$)
May 1	0605				<0.1				
	0825	6.8	<0.1			<0.1	29	7.3	47.5
	0905		<0.1						
	1009		<0.1		<0.1				
	1029		<0.1		<0.1	<0.1			
	1531					<0.1			
May 2	1058	6.4	<0.1		<0.1			7.3	47.5
	1100				<0.1				
	1110				0.6				
	1122		0.14		0.1				
	1140				<0.1				
	1153		0.32		<0.1				
	1522		<0.1						
	1531				<0.1				
May 5	1040	5.4							
	1305	5.5						7.3	47
	1600*				0.1				
	2000*				<0.1				
	2310		<0.1	0.19		<0.1	26		
	2344	5.9						7.3	47.5
	2400*				0.1				
May 6	0010		1.0						
	0049	6.0							
	0112		<0.1						
	0156	5.9							
	0210		<0.1	1.0					
	0307	6.3	<0.1						
	0400*				<0.1				
	0410		<0.1			<0.1	26		
	0458	6.0							
	0510		<0.1						47
	0554	6.1							
	0610		<0.1						
	0710		<0.1						
	0756	6.0							
	0800*				0.1				
	0810		<0.1	0.1					
	0949	5.4						7.3	
	1010		0.32			<0.1			
	1048	5.3							
	1200*				0.1				
	1430		<0.1						
	1500*				<0.1				
	1515	5.8							
May 7	1107	5.3	<0.1						

*Estimated time ± 4 hours. Samples taken with ISCO automatic sampler which was activated by rise in stream flow.

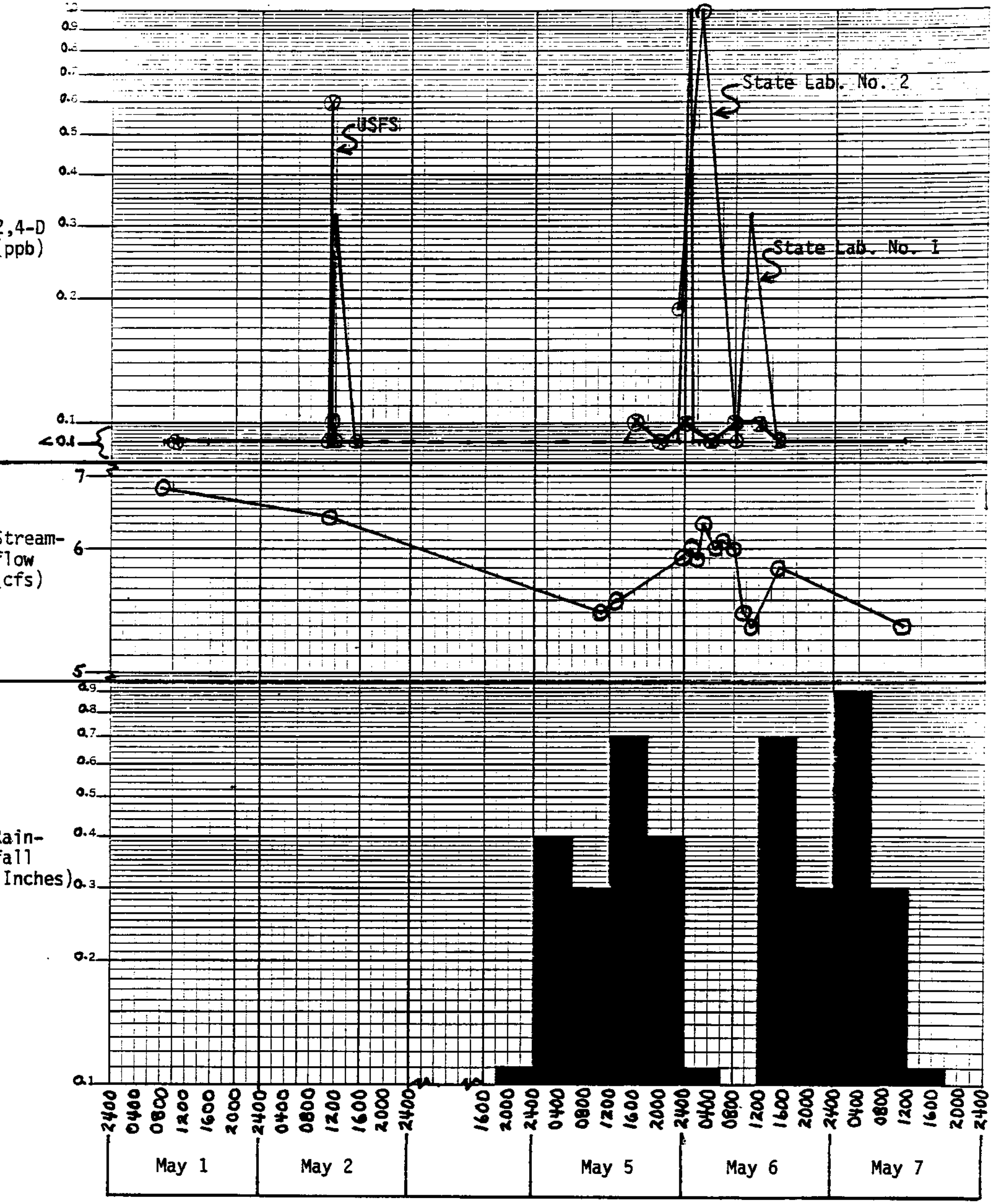


Figure 7. Rainfall, Stream Flow and 2,4-D Levels at the Blackhawk Monitoring Station During Application and Subsequent Runoff

USFS laboratory results for the runoff period verified State results to the extent that levels of 0.1 ppb 2,4-D were measured during the late afternoon of May 5 and the morning of May 6. Timing of USFS samples cannot be reported precisely because the ISCO sampler was activiatd by rise in stream flow rather than by clock.

Stream flows during runoff at the monitoring station increased from 5.36 cfs to a maximum of 6.26 cfs on May 5 and 6.

Rainfall as measured by the USFS at the Muslatt gage totaled 0.1 inch on May 4, 1.8 inches on May 5, 1.1 inches on May 6, 1.3 inches on May 7, and 0.1 inch on May 8 (Figure 7).

Stream pH was 7.3 during the entire sampling period. Stream temperatures ranged from 47°F. to 47.5°F. Stream hardness ranged from 26-29 ppm as $CaCo_3$. Air temperatures ranged from a nighttime low of 45°F. to a daytime high of 65°F. during May 1 to May 7.

C. Long Valley Site

One-hundred eighty acres paralleling the drainage stream were sprayed with 2,4-D at a rate of 2.8 pounds of active ingredient per acre from 0542 to 0720 on July 14. State staff collected grab samples from the drainage course where it passed under County Route 42 during the period that time-of-travel estimates indicated 2,4-D could be present.

Obsevers reported no deviation from BMPs during application, although a variable northwest breeze appeared to occassionally exceed the BMP maximum of 5 mph.

Table 4 lists sampling results. The maximum level of 2,4-D mesured was 0.1 ppb in samples collected 4 and 15 hours after 2,4-D application.

Thunderstorm activity in the Warner Mountains during the period August 14-22 resulted in a rainfall total of 2.4 inches being measured at the National Weather Service station in Jess Valley. The majority of that rainfall occurred on August 19 (1.01 inches) with measurements of 0.2, 0.13, and 0.14 inches on August 20, 21, and 22, respectively. Based on observable runoff in road ditches, the USFS hydrologist for the district surmised that runoff had occurred from the treatment site during the August 19-22 period. Optimum sampling dates for 2,4-D runoff in Long Valley Creek would have been August 20 or 21 as well as August 22, even though stream flows were higher than pre-storm flows present on August 22.

Analysis of a water sample collected by USFS staff at the above station at 1030 on August 22 showed non-detectable levels of 2,4-D (<0.1 ppb) and 2,4

D. Bear Camp/Homestead Flat Site

One hundred twenty acres were sprayed via helicopter with 2.8 pounds of 2,4-D per acre from 0730 to 0830 on 14 July 1983. No deviations from BMPs were reported by USFS personnel or the applicator. Campers in the Bear Camp Flat area contended there was occassional lateral drift of spray to an extent that some seeps and springs within buffered areas were contacted by the spray. State staff estimated that northwest winds occassionally exceeded 5 mph.

A fluorometer was unavailable for monitoring and dye was not used in the spray mix. State staff sampled East Creek and guaged stream flow at a station 200 yards downstream from the confluence of South Fork.

Table 4 and Figure 8 show sampling results. Concentrations of 2,4-D at the monitoring station peaked at 7 ppb about one hour after spraying started. Detectable levels of 2,4-D were present for another five hours after the peak concentration. Time-of-travel estimates indicate that monitoring occurred during the peak runoff of 2,4-D.

Similar to the Long Valley site, thunderstorm activities during the August 19-22 period caused an increase in East Creek flows. Analysis of a USFS sample taken at 1130 on August 22 resulted in non-detectable levels of 2,4-D (<0.1 ppb) and 2,4 Dichlorophenol (<1 ppb). A flow of 5.4 cfs was measured by USFS staff at the sampling time and location. East Creek flows receded during the afternoon of August 22. Subsequent substantive rainfall did not occur in the area until October 23 and 30. Water samples were not taken during that period. As stated for the Long Valley site, optimum sampling time for 2,4-D in East Creek runoff would have been during October 20 and 21 as well as October 22.

The State's contractual laboratory analyzed spiked samples of 2,4-D concurrently with the East Creek/Long Valley Creek 2,4-D samples. Recovery rates of 98 and 100 percent were achieved for spiked samples containing 100 ppb and 0.1 ppb, respectively.

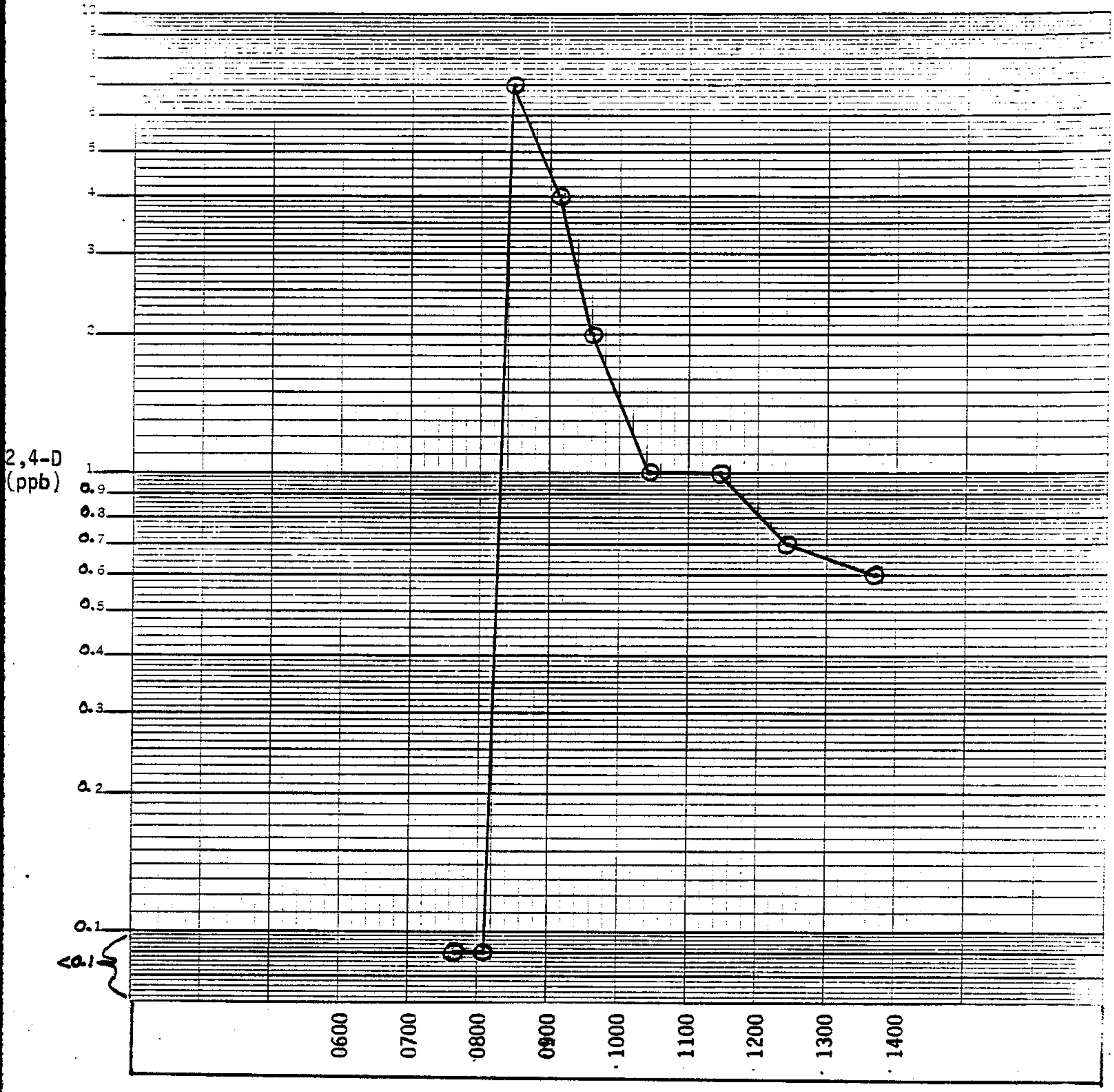


Figure 8. 2,4-D Levels at the East Creek Monitoring Station During Application, 14 July 1983

Table 4. Results of Long Valley and Bear Camp/Homestead Sites Water Sampling and Gauging

Long Valley

Date	Time	Flow (cfs)	2,4-D (ppb)	2,4 Dichloro-phenol (ppb)	pH	Water Temp. (°F.)	Air Temp. (°F.)
7/14/83	0540*		<0.1				
	0640	0.25	<0.1		7.2	48	50
	0740		<0.1				
	0940		0.1				
	2015		0.1				
7/15/83	0630		<0.1				
8/22/83	1130	0.04	<0.1	<1			

Bear Camp/Homestead

Date	Time	Flow (cfs)	2,4-D (ppb)	2,4 Dichloro-phenol (ppb)	pH	Water Temp. (°F.)	Air Temp. (°F.)
7/14/83	Blank**		<0.1				
	0740*		<0.1				
	0805		<0.1		7.6	46	52
	0835		7				
	0911		4				
	0937		2				
	1039	11.5	1				
	1140		1		7.6	51	60
	1240		0.7				
	1345		0.6			60	68
8/22/83		5.4	<0.1	<1			

* Pre-spray samples
** Field blank containing 2,4-D-free water

E. Hornet Gulch Site

The Hornet Site was sprayed with 2,4-D and Glyphosphate (Roundup) with manual backpack sprayers during the period June 24-29, 1983. In this type of operation, herbicide is sprayed onto individual plants. Average application rate was 25 gallons per acre of a mixture containing 3 quarts 2,4-D, 3 quarts Glyphosphate, and 25 gallons of water.

Water monitoring of Hornet Creek was done by USFS staff during each day of the application period pursuant to time of concentration estimates. Nine samples were taken over the six-day period; all samples were analyzed to contain <0.1 ppb 2,4-D. USFS observers stationed in buffer strips reported no spray drift during treatment. None of the spray detection cards placed by the USFS at 50-foot intervals along Hornet Creek showed any evidence of drift.

Light rainfall occurred in the area on August 23 and September 22. Although runoff from the treated area was deemed doubtful, two water samples were taken on August 23 and one was taken on September 22. On October 30 and 31, 0.62 and 1.68 inches of rainfall, respectively, was recorded at McCloud. A stage sampler sampled Hornet Creek automatically on October 30 and a grab sample was obtained at 0900 on October 31. Less than 0.1 ppb 2,4-D was analyzed for all runoff samples except the October 30 sample which was reported to contain 0.1 ppb 2,4-D.

F. Gap Site

The Gap site was sprayed on September 13 from 0800 to 0930 with a mixture of 3.6 quarts 2,4-D (1.8 pounds active ingredient), 6 pounds Dalapon, and 4 pounds Atrazine in 15 gallons of water at a rate of 15 gallons per acre.

USFS staff monitored Gap Creek for 2,4-D pursuant to time of concentration estimates during application of herbicides. The USFS reported no deviation from BMPs. Water samples collected at the Gap Creek monitoring station by USFS staff at 0715 and 0830 on September 13 contained <0.1 ppb 2,4-D.

No subsequent rainfall was reported for the area until light rain started falling late in the day of September 22. On September 23, 0.53 inches was recorded at the USFS Guard Station at Big Bend. Rainfall intensity increased in the early morning hours of September 23 and peaked at about 1100. State staff measured stream flow and collected water samples at the Gap Creek station during the ensuing runoff event on September 23 with the following results:

Time	Flow (cfs)	2,4-D (ppb)	Dichloro-phenol (ppb)	pH	Water Temp. (°F.)
1000	0.26	<0.1	--		
1100	0.46	<0.1	<1		
1220		<0.1	<1	7.8	51
1345	0.46	<0.1	<1		

Stream flow measurement and water sampling were suspended as rainfall waned in the early afternoon. Additional moisture was not recorded for the area until late October and early November. A sample obtained by USFS staff at 1020 on November 10 was analyzed to contain <0.1 ppb 2,4-D.

G. Hardpan 25 Site

This site was sprayed on September 12 from about 1030 to 1400 with a mixture of 3.6 quarts 2,4-D, 6 pounds Dalapon, and 4 pounds Atrazine per 25 gallons of water at a rate of 15 gallons per acre.

USFS staff monitored East Fork Nelson Creek for 2,4-D pursuant to time of concentration estimates during application of herbicides. The USFS reported no deviation from BMPs. Water samples collected at the East Fork Nelson Creek station by USFS staff at 1050 and 1230 on September 12 contained <0.1 ppb 2,4-D.

No rainfall was reported for the area until September 23 when 0.53 inches was recorded at the USFS Guard Station at Big Bend. USFS staff measured streamflow and sampled the East Fork Nelson Creek station on that date. A flow of 2.0 cfs was measured at 1100. A water sample collectd at 1100 contained <0.1 ppb 2,4-D. Measurements and sampling were suspended as rainfall ceased in the afternoon and it was not apparent to the USFS hydrologist that runoff had occurred in East Fork Nelson Creek during the September 22-23 rainfall. Additional rainfall was not recorded for the area until late-October, early-November.

Flows increased at the East Fork Nelson Creek monitoring station on November 1. Water samples taken by USFS staff at 0930 on that date and subsequently at 1230 on November 10 contained <0.1 ppb 2,4-D.

H. Whitmore 17 Site

Champion Internationl Corporation treated this site with 1.8 pounds per acre of active ingredient 2,4-D on September 16 from 0753 to 1226. An adjuvant to increase spray drop size and control drift was added to the spray mixture.

Shasta County Agricultural Commission permit terms were followed; no deviation from those terms was reported during treatment.

Champion employees monitored treatment and obtained water samples from two stations, one on each of the tributaries draining the treated area. During the period 1027 to 1242 a maximum level of 0.1 ppb 2,4-D was analyzed in samples from Station 2. Analysis of Station 1 samples resulted in levels of <0.1 ppb 2,4-D.

No rainfall was reported for the Whitmore area subsequent to treatment until September 23 when 2.5 inches was recorded at the California Department of Forestry Fire Station. Champion employees noted an increase in flow and sampled Stations 1 and 2 at 1200 and 1028, respectively, at what was judged to be the crest in runoff from the treatment site. Analysis of those samples resulted in levels of <0.1 ppb 2,4-D.

Significant additional rainfall did not occur in the Whitmore area until October 23 and 24. Water samples were not taken during that time with the assumption that any 2,4-D amenable to runoff from the treatment site would have entered the drainage courses during the September 23 runoff event.

VII. CONCLUSIONS AND RECOMMENDATIONS

A. Adequacy of Best Management Practices for 2,4-D Use

At the sites monitored in this study, USFS BMPs/guidelines and County Agricultural Commissioner permit terms prevented 2,4-D in surface waters from exceeding State water quality objectives during application and subsequent rainfall runoff. USFS BMPs and Shasta County permit terms appeared adequate for controlling 2,4-D runoff under adverse conditions, i.e., large percentage of the watershed area sprayed, steep slopes, near-saturated soils at some sites, presence of numerous live and intermittent streams in the sprayed area that were difficult to see from the air, and substantial rainfall relatively soon after spraying.

Width of buffer zones (no-spray areas) and the decision to spray or not to spray over dry (but intermittent) drainage courses are flexible under current USFS BMPs and County permit terms. Results from all aerially-sprayed sites demonstrated that requiring 100-foot buffers along both sides of flowing streams is an effective practice in meeting State water quality objectives during 2,4-D application. Runoff of 2,4-D from sites where dry intermittent stream courses were sprayed was no greater than from sites where both flowing and dry stream courses were buffered and left unsprayed. However, most 2,4-D spraying occurs during spring and fall months when rainfall/runoff is likely soon after 2,4-D use. Therefore, it appears prudent and justifiable to buffer intermittent stream courses at sites where downstream waters provide a public water supply or valuable fishery, fishing, or other beneficial use(s) that can be affected by the herbicide.

Buffered areas of less than 100 feet on each side of the stream course were not used at the study sites; therefore, it is not possible to predict 2,4-D levels in surface waters if narrower buffers had been used. Because of public concern and the efficacy of 100-foot buffers demonstrated in this study, buffer strips of at least 100 feet on each side of the stream course appear justified.

Tracer dye in the spray mix and fluorometric capability proved to be a valuable monitoring tool in the Blackhawk operation; water samples could be taken when the fluorometer indicated the presence of dye and therefore the presence of 2,4-D.

Along with buffered areas in the spray site, wind velocity during spraying appears to be a critical factor influencing drift of 2,4-D into surface waters. USFS BMP guidelines suggest that in most instances herbicide should be applied during wind velocities ranging from 2-10 mph. County permit terms curtail application if wind velocities exceed 8-10 mph. A 5 mph maximum wind velocity was followed at the Blackhawk site resulting in a maximum measured level of 0.6 ppb 2,4-D in the drainage stream during site spraying. In that situation it was observed that the helicopter inadvertantly sprayed over the stream in one swath. The same BMP (5 mph) was to have been followed at the

Bear Camp site, but the State observer was convinced that wind gusts occasionally exceeded 5 mph and a camper in the area claimed lateral drift of the spray mixture. In that situation a maximum of 7.0 ppb 2,4-D was measured in the drainage stream during spraying. It is unknown whether the higher 2,4-D level at Bear Camp was caused by wind drift or by the helicopter inadvertantly spraying one of the streams in the sprayed area. Nevertheless, the demonstrated efficacy of restricting spraying to times when wind velocity is 5 mph or less is a strong argument for incorporating that value in USFS BMP guidelines and county permits.

Recommendations: A.1. As applied to aerial 2,4-D sites which contain surface waters or which are contiguous to surface waters that provide a ublic water supply, fishery, or other beneficial use(s) that can be affected by the herbicide, BMP guidelines and County Agricultural Commissioner permit terms should be revised and standardized to call for (a) no less than 100-foot buffers along both sides of flowing and dry intermittent streams, and (b) wind velocities of no greater than 5 mph during 2,4-D application.

A.2. The SWRCB should request the State Department of Food and Agriculture to adopt USFS BMPs/guidelines (as revised in recommendation A.1.) for implementation by County Agricultural Commissioners.

A.3. A non-toxic dye tracer and fluorometer should be used routinely in all aerial 2,4-D applications where on-site contiguous surface waters provide a public water supply, fishery, or other beneficial use(s) that can be affected by the herbicide.

B. Adherence to BMPs During 2,4-D Application

Monitoring results indicated that BMPs were followed during this study except for two instances. During the Blackhawk operation the helicopter sprayed over a live stream on one swath. During the Bear Camp treatment a stream was sprayed inadvertantly or spraying occurred during wind velocities that exceeded the 5 mph BMP guideline. Resultant 2,4-D measured at the monitoring stations was less than the level of present numerical water quality objectives. Water quality objectives were met during 2,4-D application and during the initial rainfall after application at all study sites.

Recommendations: B.1. Entities responsible for 2,4-D use should ensure that buffered areas are easily identifiable.

B.2. Applicators should fly spray sites in advance of 2,4-D application to confirm the location of buffered areas.

C. 2,4-D Runoff from Application Areas

Monitoring detected 2,4-D levels >0.1 ppb only at the Blackhawk station during rainfall runoff.

Maximum discharge levels of 2,4-D from the Blackhawk site were 0.6 ppb during spraying and 1.0 ppb during the ensuing rainfall. Measurable 2,4-D was present for about 45 minutes during spraying on May 2. Measurable 2,4-D occurred during an approximate 20-hour period on May 5 and 6 when the first post-spray rainfall occurred. Highest 2,4-D levels coincided with the initial rise in stream flow and maximum stream flows during the 20-hour period. Maximum 2,4-D levels and stream flow proceeded maximum rainfall by about four hours, which is about the maximum travel time of water through the sprayed areas. No measureable 2,4-D was present in runoff during the second rainfall event that proceeded spraying (from mid-day June 6 until mid-day June 7). This would indicate that (1) 2,4-D subject to mobilization was carried out of the sprayed area during the initial rainfall, and (2) monitoring after an initial, substantive rainfall would be unproductive under conditions similar to the Blackhawk situation. With the variation in laboratory results (see Table 3), it would not be meaningful to estimate the mass emission of 2,4-D from the sprayed site. It is also not practical to report a 24-hour average 2,4-D concentration for Blackhawk Creek during the May 5 and 6 runoff. Sample results indicate the 2,4-D level did not exceed 1.0 ppb during that period.

It is possible that rainfall runoff containing 2,4-D may have been present at the Bear Camp station prior to sampling that occurred on August 22. Water samples and flow measurements of East Creek were not taken during the August 19-21 period when substantial rainfall occurred. Whether the majority of rainfall percolated into the soil or resulted in overland flow during that period cannot be determined confidently. Surface soils were dry and, therefore, conducive to percolation prior to the rainfall period. Runoff did appear to be occurring on August 22 when sampling results indicated that East Creek contained non-detectable levels of 2,4-D.

The 2,4-D breakdown product, 2,4 Dichlorophenol, was not measured at detectable levels downstream from four treatment sites before, during, or after spraying. This indicates that 2,4 Dichlorophenol monitoring is unnecessary.

Recommendations: C.1. Numerical water quality objectives relating to silviculture and 2,4-D should be adjusted to control the maximum concentration of 2,4-D in receiving waters rather than the average concentration.

C.2. Available analytical funds should be used for parameters other than 2,4 Dichlorophenol.

D. Efficacy of Monitoring Program

The monitoring program appeared adequate to meet project objectives. 2,4-D was detected when present (with the possible exception of runoff at the Bear Camp site) and it is unlikely from the monitoring results that any large, short-duration "slug" of 2,4-D missed being sampled. Additional 2,4-D samples and more split samples (for comparative laboratory analysis) during the height of runoff would have improved monitoring results.

Recommendations: D.1. Post-2,4-D application monitoring should focus on the initial rise and crest of stream flow draining the sprayed area.

D.2. Split 2,4-D samples should be taken every one-half hour during stream rise and crest. One-half of the samples taken over the rise/crest period should be submitted for analysis. If laboratory results show 2,4-D levels of 1 ppb or greater, the remainder of the samples should be submitted for analysis.

E. Laboratory Analyses

Results from three laboratories relative to Blackhawk sampling tended to verify that analytical accuracy and precision are difficult with concentrations of less than 1 ppb 2,4-D. However, as concentrations below 1 ppb are not believed harmful to humans or aquatic life, laboratory accuracy and precision at such levels do not appear critical.

There appear to be no benefits to reporting of 2,4-D concentrations in one-hundredths of parts per billions; tenths of parts per billion is sufficient for the use made of analytical results.

Recommendations: Laboratory clients should:

E.1. Provide the laboratory with duplicate 1-liter samples or one 2-liter sample for those 2,4-D samples believed to be critical;

E.2. Provide the laboratory with spiked samples of 1 ppb and 10 ppb 2,4-D along with other samples to be analyzed at least once per year;

E.3. Direct the laboratory to retain the extracts from all samples for verification analyses if so requested by the client; and

E.4. Request the laboratory to round off the reported 2,4-D concentration to the nearest one-tenth part per billion (microgram per liter).

F. Future 2,4-D Monitoring by Regional Water Quality Control Boards and 2,4-D Applicators

Program results indicate that State water quality objectives are met during 2,4-D application with implementation of BMPs described in this report. Results also indicate that water monitoring should occur routinely in situations where deviation from BMPs could result in 2,4-D introduction to important surface waters. Monitoring and sample analysis by both applicators and regulatory agencies do not appear necessary on a routine basis; the objectives of monitoring can be achieved by applicator self-monitoring, with observation and occasional checking by regulatory agencies. Based on the limited scope of this study, monitoring of runoff following 2,4-D application is necessary only if stream buffering and maximum wind velocity recommended in this report or other existing USFS BMPs are not followed.

Recommendations:

F.1. 2,4-D applicators should monitor water quality routinely during those applications where 2,4-D could enter surface waters that provide a public water supply, fishery or other beneficial use(s) that can be affected by the herbicide.

F.2. Regional Boards should observe and occasionally check monitoring activities associated with 2,4-D application on sites where 2,4-D could enter surface waters that provide a public water supply, fishery or other beneficial use(s) that can be affected by the herbicide.

F.3. Unless USFS BMPs/guidelines and this report's recommendation on buffer width and wind velocity are followed during 2,4-D application, the applicator should monitor water quality during the first runoff from sprayed areas that drains into surface waters that provide a public water supply, fishery, or other beneficial use(s) that can be affected by the herbicide.

F.4. Monitoring activities other than water quality monitoring (including ground observation and spray deposit cards) should be done routinely by the applicator during those applications where there is low risk of 2,4-D discharge to surface waters having high beneficial use.

F.5. The USFS and County Agricultural Commissioners should consult with the appropriate Regional Boards and the Department of Fish and Game for identification of beneficial uses of surface waters within and contiguous to 2,4-D application sites.

F.6. The USFS and Department of Food and Agriculture, through the County Agricultural Commissioners, should routinely notify the appropriate Regional Board in advance of intended herbicide applications.

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3. North Coast Regional Water Quality Control Board Public Report. Proposed Action to Amend the Klamath River Basin and North Coastal Basin Policy and Action Plan for Control of Discharges of Herbicide Wastes from Silvicultural Operations. June 14, 1873, Page 9.

4. State Water Resources Control Board/North Coast Regional Water Quality Control Board. Water Quality Control Plan Report, Klamath River Basin & North Coastal Basin Volume 1, 1975.

5. State Water Resources Control Board/Central Valley Regional Water Quality Control Board. Water Quality Control Plan Report, Sacramento River Basin (5A), Volume 1, 1975.

6. United States Forest Service. R-5 FSH 2109.21 - Handbook on Aerial Application of Herbicides, June, 1983.

7. Zemansky, G. M. Basis for Concern: the Environmental Effects of 2,4-D. Prepared for Friends of the Earth for Presentation at the Washington Association of Wheat Growers 26th Annual Convention, Spokane, Washington. December 8, 1980.

PRACTICE: 5.8 Pesticide Use Planning Process

OBJECTIVE: To introduce water quality and hydrologic considerations into the pesticide use planning process.

EXPLANATION: The Pesticide Use Planning Process (PUPP) is the framework for incorporation of hydrologic considerations contained in BMPs 5.9 through 5.14. An EA/EIS addresses these considerations in terms of impacts and mitigation measures. Project work and safety plans then specify management direction.

IMPLEMENTATION: The ID team evaluates the project in terms of site response, social and environmental impacts and the intensity of monitoring needed. The responsible line officer then prepares an EA/EIS, Project Plan, and Safety Plan. Approval authority for proposed pesticide projects involving 100 acres or less, not restricted by the categories below, and housekeeping-type pesticides (2150.5) is delegated to Forest Supervisors. The FS Field Integrated Pest Management Work Group reviews and approves project proposals involving 2,4-D, direct application to water, insect and disease control, rodenticides, aerial application, or greater than 100 acres for compliance with all established guidelines and procedures. Only the Regional Forester may approve projects involving sodium cyanide and the use of pesticides in Wilderness other than for insect and disease control. Sensitive issues involving TCDD and use of pesticides for insect and disease control in designated Wilderness Areas are reviewed and approved by the WO Integrated Pest Management Work Group/Chief.

RECOMMENDATION: Best Management Practice.

PRACTICE: 5.9 Apply Pesticide According to Label and EPA Registration Directions.

OBJECTIVE: To avoid water contamination by complying with all label instructions and restrictions.

EXPLANATION: Directions found on the label of each pesticide are detailed and specific, and include legal requirements for use.

IMPLEMENTATION: Constraints identified on the label are incorporated into project plans and contracts. For in-service projects, responsibility for ensuring that label directions are followed rests with the Forest Service Project Director who shall be a certified commercial applicator. For contracted projects it is the responsibility of the contracting officer or his designated representative to ensure that label directions are followed.

RECOMMENDATION: Best Management Practice.

PRACTICE: 5.10 Pesticide Application Monitoring and Evaluation

OBJECTIVE: To determine whether pesticides have been applied safely, restricted to intended target areas, and have not resulted in unexpected non-target effects.

To document and provide early warning of possible hazardous conditions resulting from possible contamination of water or other non-target areas by pesticides.

To determine the extent, severity and probable duration of any potential hazard that might exist.

EXPLANATION: This practice documents the placement accuracy, amount applied, and any water quality effects so as to reduce or eliminate hazards to non-target species. Monitoring methods include spray cards, dye tracing, and direct measurement of pesticide in or near water. Type of pesticide, type of equipment, application difficulty, public concern, beneficial uses, monitoring difficulty, availability of laboratory analysis and applicable Federal, State and local laws and regulations are all factors considered when developing the monitoring plan.

IMPLEMENTATION: The need for a monitoring plan is identified during the pesticide use planning process as part of the project EA/EIS. The water quality monitoring plan will specify responsbilities for sample collection. A water quality specialist will evaluate and interpret the water quality monitoring results.

RECOMMENDATION: Best Management Practice.

PRACTICE: 5.11 Pesticide Spill Contingency Planning

OBJECTIVE: To reduce contamination of water by accidental pesticide spills.

EXPLANATION: The Forest Oil and Hazardous Substances Pollution Contingency Plan prepared by each Forest consists of predetermined actions to be implemented in the event of a pesticide spill. The plan lists who will notify whom and how, time requirements for the notification, guidelines for spill containment, and who will be responsible for clean-up.

IMPLEMENTATION: Pesticide spill contingency planning is in the Project Safety Plan. The environmental analysis process provides the means for including public and other agency involvement in plan preparation. The plan will list the responsible authorities.

RECOMMENDATION: Best Management Practice.

PRACTICE: 5.12 Cleaning and Disposal of Pesticide Containers

OBJECTIVE: To prevent water contamination resulting from cleaning or disposal of pesticide containers.

EXPLANATION: The cleaning and disposal of pesticide containers must be done in accordance with Federal, State, and local laws, regulations, and directives. Specific procedures for the cleaning and disposal of pesticide containers are documented in FSM 2157.3, R-5 Operational Guides for Aerial Application of Herbicides, FSH 2109.12, and State and local laws.

IMPLEMENTATION: The Forest or District Pesticide Use Coordinator (Certified Commercial Applicator) will approve proper rinsing and disposal sites and arrange for disposal of pesticide containers when the pesticide is applied by in-service personnel. When the pesticide is applied by a contractor, the contractor is reponsible for proper container disposal in accordance with label directions and Federal, State, and local laws.

RECOMMENDATION: Best Management Practice.

PRACTICE: 5.14 Controlling Pesticide Drift During Spray Application

OBJECTIVE: To minimize the risk of pesticide falling directly into water or non-target areas.

EXPLANATION: The spray application of pesticide is accomplished according to prescription that specifies the following: formulation, windspeed and direction, equipment, droplet size, spray height, temperature, relative humidity, application pattern, terrain, and flow rate.

IMPLEMENTATION: The prescription is prepared by an ID team working with the Forest or District Pesticide Use Coordinator during the project planning part of the environmental assessment process. On in-service projects, the Forest Service Project Director is responsible for ensuring the preventive prescription is followed during application and for closing down application when specifications are exceeded. These responsibilities belong to the Contracting Officer or his designated representative on contracted projects.

RECOMMENDATION: Best Management Practice.

SHASTA COUNTY DEPARTMENT OF AGRICULTURE
2430 Hospital Lane, #40
Redding, CA 96001
(916) 246-5656

2,4-D TIMBERLAND PERMIT CONDITIONS - AIR APPLICATION

EXAMPLE OF SHASTA COUNTY DEPARTMENT OF AGRICULTURE FOREST HERBICIDE PERMIT CONDITIONS

Appendix 3

✓ 1. A pre-application site inspection by the Agricultural Commissioner will be made prior to the application.

✓ 2. No herbicide shall be applied aerially within 100 feet of a "blueline" stream, and herbicide applied within the next 400 feet shall have an approved drift inhibitor incorporated into the spray mixture.

✓ 3. No unauthorized person shall be on the spray or batching site.

✓ 4. The permittee shall maintain an hourly log of wind velocity and direction during the application and submit a copy with the Pesticide Use Report.

✓ 5. Pursuant to Section 2458(a) Admin. Code, discharge of spray material is permitted more than 10 feet above the crop or target and shall be made as close to target vegetation as is deemed reasonable and safe by the pilot.

✓ 6. Helicopters carrying herbicide shall not fly over "blueline" streams if reasonably avoidable.

✓ 7. Spray site boundaries and "blueline" streams within site shall be marked or identified to the satisfaction of the Agricultural Commissioner and pilot and sufficient to permit ready identification by pilot during herbicide application.

✓ 8. No application shall be made when precipitation occurs or the U.S.Weather Bureau predicts a 70 percent or greater chance of rain in the next 24 hours in the area of the application.

✓ 9. The Pest Control Operator must receive a copy of the pesticide permit and its conditions and a copy of the written recommendation prior to the pesticide application.

✓ 10. The Pest Control Operator must submit the Pesticide Use Report to the Agricultural Commissioner.

✓ 11. Food & Agriculture Code Section 12825 and 14006.5 duly considered in issuance of this permit and/or pesticide application.

Permit Conditions Acknowledged: Date: 8/5/83

[signature] III
Permittee/Representative

[signature]
Inspector/Commissioner

APPENDIX VI

Sacramento-San Joaquin Delta

by

SUMMARY AND CONCLUSIONS

In the last few years, mats of floating water hyacinth plants have grown to levels that impair boat navigation in some of the smaller channels of the Sacramento-San Joaquin Delta. SB 3144 requires a program for hyacinth control administered by the Department of Boating and Waterways (DBW). One control strategy being considered is the use of the herbicides 2,4-D DMA (dimethylamine salt of 2,4-D; product name "Weedar 64") and diquat. Limited spraying of those herbicides over 20 acres was conducted in 1982 for test and demonstration purposes. Herbicide spraying will probably be expanded in future years.

The 2,4-D DMA herbicide will likely be the main herbicide used due to relatively low cost and high effectiveness. EPA's present residue limit for drinking water of 100 ppb for 2,4-D DMA appears adequate for protection of drinking water and public health, based on existing knowledge of 2,4-D DMA toxicity. However, gaps in our present knowledge of the carcinogenicity of 2,4-D indicate the advisability of minimizing human intake and exposure.

Water quality data from the 1982 tests indicate: (1) the residue limit will be met for water leaving the spray plot; (2) fish mortality will not occur; (3) some fish may temporarily absorb enough 2,4-D DMA to impart an undesirable taste to their flesh for a few days; and (4) some mortality of aquatic invertebrates on which fish feed may occur within the spray plot only. Rapid breakdown of 2,4-D DMA apparently does not occur in all natural waters. Some studies have indicated persistence up to 6 months. It is recommended that DBW conduct testing to document the actual extent of breakdown in Delta waters.

The EPA residue limit of 100 ppb provides minimal protection for certain broadleaf crops (e.g. grapes) that are particularly sensitive to 2,4-D DMA. A guideline residue limit of 20 ppb would provide adequate protection for sensitive agricultural and domestic plants and an additional margin of safety against

INTRODUCTION

This report describes briefly the history of the water hyacinth problem in the Sacramento-San Joaquin Delta, outlines proposed measures for its control and evaluates the potential water quality effects of herbicides proposed for control. Special emphasis is given to herbicide residue limits in water.

The water hyacinth (Eichhornia crassipes) is a floating freshwater aquatic plant native to tropical South America. Water hyacinth plants can grow and reproduce rapidly, forming dense continuous mats that can hinder navigation and foul fishing gear. On the positive side, water hyacinths remove nutrients and heavy metals from the water (Stephenson et al 1980) and are attractive with their delicate lavender flowers.

The water hyacinth was introduced to the southern United States in the late 1800's and rapidly became a nuisance to navigation in areas of Florida and Louisiana. Since the 1960's hyacinth in those states has been effectively controlled by the U. S. Army Corps of Engineers through programs combining application of the herbicide 2,4-D and introduction of insects that eat hyacinths.

The water hyacinth was introduced to northern California, probably as an ornamental, early in this century. It soon became established in the Sacramento-San Joaquin Delta. Hyacinth mats have been a common sight in remote backwater areas of the Delta for many years. During the last few years however, hyacinth mats have rather abruptly reached nuisance levels in many of the smaller channels of the southern and eastern Delta (Figure 1). Many marinas have become so clogged with hyacinth that navigation (mostly pleasure boats) has been hampered. Hyacinths can foul propellers and clog engine cooling water intakes. The cause of the sudden hyacinth explosion is not documented, but may be related to a series of mild winters in 1979-81. The main channels of major waterways have not yet been greatly affected, and the problem was generally not as severe in 1982 as in 1981.

THE DELTA PROGRAM

The passage of SB 3144 (Attachment 1) by the California Legislature in June 1982 mandated a program for control of water hyacinths in the Delta. The lead agency is the California Department of Boating and Waterways (DBW). DBW has contracted with the Corps of Engineers Waterways Experiment Station, Vicksburg, Mississippi, to develop a long-term control plan, produce an EIR/EIS, and perform control actions. The Corps has much experience controlling water hyacinth in southern states. The control plan and EIR/EIS are scheduled for completion early in 1984. In the interim, control efforts will be conducted as experimental and emergency measures.

Three control strategies are presently proposed by DBW for concurrent use in the program: (1) mechanical harvest or barriers, (2) introduction of hyacinth-eating insects, and (3) herbicides. Harvesting is relatively expensive and

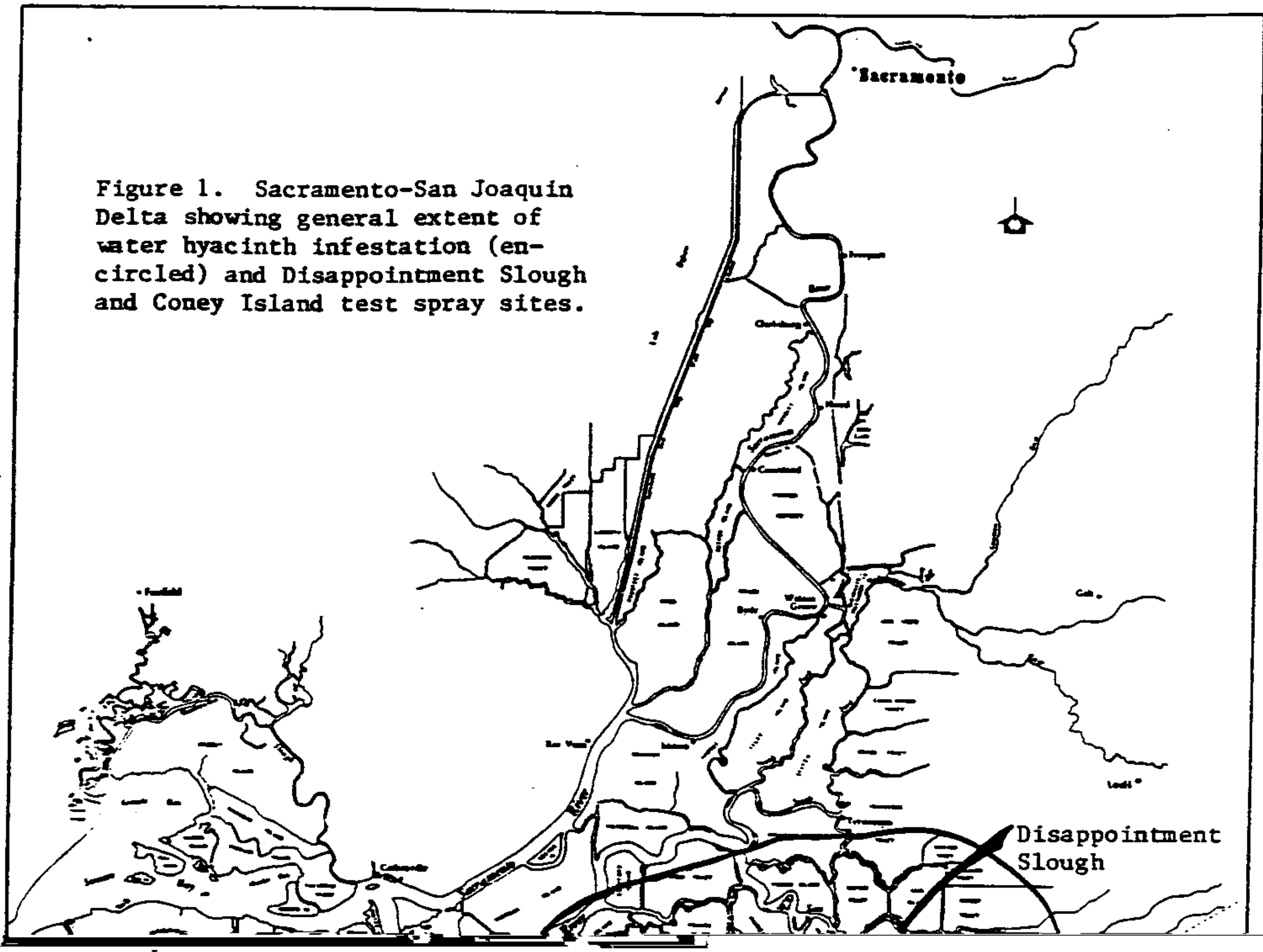


Figure 1. Sacramento-San Joaquin Delta showing general extent of water hyacinth infestation (encircled) and Disappointment Slough and Coney Island test spray sites.

would only be used where immediate removal is necessary, e.g. when hyacinths clog intakes to the Delta-Mendota Canal. Barriers (log booms) would be constructed in selected areas to prevent drifting hyacinth clumps from entering marinas and becoming established. Introduction of hyacinth-eating insects is the strategy least certain of success. Two South American weevils that eat only water hyacinth, Neochetina eichhorniae and N. bruchi, are proposed for introduction to the Delta. Those species have been effective in helping control hyacinths in the southern states; they may greatly reduce the need for herbicides in the Delta if they can survive and reproduce there. Herbicides would be used to kill hyacinths where they have reached nuisance levels (e.g. marinas) and also in more remote areas where mats can grow and plants can break off to drift and infest new areas.

It is probably impossible to eliminate the water hyacinth from the Delta. The goal of the program will probably be to reduce the hyacinth population to a level where only periodic maintenance treatments are necessary.

This year's hyacinth control efforts have been concluded. Hyacinth weevils were introduced in an experimental area in the southern Delta and about 20 acres were treated with herbicides and intensively monitored for water quality effects. This year's efforts were designed to test and demonstrate control technologies rather than achieve significant reductions. Higher levels of herbicide spraying will probably commence next spring, though DBW has no formalized plans yet.

REGISTERED HERBICIDES

The herbicides 2,4-D DMA ("Weedar 64", Union Carbide) and diquat ("Diquat Water Weed Killer", Chevron) have been proposed by DBW and the Corps for hyacinth control. Both herbicides are registered by EPA and the California Department of Food and Agriculture for use in "rivers which are slow moving". The labels for the two herbicides specify dosages to be used, residue limits for uses of treated waters, and some generalized use restrictions to preserve beneficial uses of water. The herbicide glyphosate ("Scout", Monsanto) may soon also be registered for hyacinth control. Glyphosate is the subject of an upcoming report of the State Board's Toxics Program. Aquatic use of glyphosate will be evaluated in a future paper if its widespread use appears likely. For the Delta program, 2,4-D DMA appears to be the herbicide of choice based on cost, effectiveness and use experience. Chemical costs per acre are about $10.00 for 2,4-D DMA and $40.00 for diquat. 2,4-D DMA kills the entire hyacinth plant, but diquat kills only the tissues it contacts, allowing root and stem offshoots to grow and form new plants. Diquat's advantage is its low potential for water quality impacts due to its rapid and irreversible binding to clays and organic matter. If significant use of diquat occurs, it will probably be only in localities where extra water quality protection is desired (e.g. enclosed marinas and areas near agricultural crops sensitive to 2,4-D DMA).

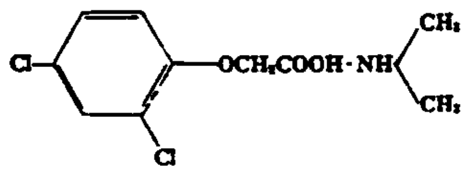
The water quality impacts of 2,4-D DMA and diquat are evaluated below. 2,4-D DMA is examined more closely than diquat because its potential for water quality impacts is higher, its use will be greater, and it is more controversial.

2,4-D DMA

Background and Environmental Fate

2,4-D DMA is the abbreviation for the dimethylamine salt of 2,4-dichlorophenoxyacetic acid. 2,4-D DMA is a related but different compound than the 2,4-D esters used in forestry. 2,4-D DMA and the 2,4-D esters all hydrolize to the parent compound (2,4-D acid). 2,4-D DMA is widely used in agriculture and is present in home use products such as "Weed-B-Gon", "Weed and Feed", and "Turf Builder". 2,4-D compounds are more toxic to broadleaf plants than grasses or conifers. In this paper, all weights of 2,4-D DMA are expressed as 2,4-D acid ("acid equivalent").

The chemical structure of 2,4-D DMA is:



Pure 2,4-D DMA is a white odorless crystalline solid. Its vapor pressure is 10^{-9} torr at 28°C, and it is highly water soluble (300 g in 100 g H_2O at 20°C) (WSSA 1974). Thus, amounts applied in the hyacinth control program will completely dissolve and volatilization from the water will not be significant.

The persistence of 2,4-D DMA in the aquatic environment is variable. Many laboratory experiments have demonstrated complete breakdown in natural waters within a matter of days. Field studies in Florida and Georgia ponds demonstrated degradation to undetectable levels in water, sediment and fish within 3 to 28 days (Gangstad 1978). Some experiments, however, have demonstrated persistence up to 6 months. Apparently, the presence of the proper

TABLE 1. RESIDUES OF 2,4-D DMA (ppb) FOUND IN CONEY ISLAND FIELD TEST JULY 1982. APPLICATION RATE WAS 5.1 POUNDS PER ACRE. DETECTION LIMIT WAS 2 ppb. (ADAPTED FROM ANDERSON, 1982a)

Float Samplers[1/] Within Spray Plot

Sample:	A	B	C	D	E	F	Average
Concentration:	70	51	Not recovered	403	3150	1560	1047

Water Column Samples

Time After Application (Minutes)	Inside Spray Plot	Upstream[2/]	Downstream[2/]
15-20	8,420	59	
	530	20	
	3800	17	
	547		
	168		
	107		
30			5
			4
			2
60-70	702		50
	1389		0
	593		0
90	100		3
	100		4
	157		23

1/ Floating open-top vessels containing 500 ml Delta water.

2/ About 10 to 15 feet outside spray plot.

TABLE 2. RESIDUES OF 2,4-D DMA (ppb) FOUND AT DISSAPPOINTMENT SLOUGH FIELD TESTS, OCTOBER 1982. APPLICATION RATE WAS 4 POUNDS PER ACRE. DETECTION LIMIT WAS 0.1 ppb (SOURCE: DEPARTMENT OF BOATING AND WATERWAYS, UNPUBLISHED DATA.)

Location #	Downstream End of Plot	50 Yards Downstream	Upstream End of Diversion
1	6	8	
	3	0	
	0	0	
	8	0	
2	0	0	0
	0	0	0
	0.5	0	0.6
	0.8	0	13
	0.5	0	
3	0	6	
	4	0	
	0	0	
	0.6		
4	0	0	
	0	0	
	2	0	
	0	0	
	0	0	
	0		

TABLE 3. RESIDUES, IN PPB OF 2,4-D DMA APPLIED AT 3.2 POUNDS PER ACRE FOR CONTROL OF WATER HYACINTH IN RICE IRRIGATION CANALS IN LOUISIANA. (REVISED FROM GANGSTAD 1978)

Time (Days)	Dilution Factor[1/] 0.15 Midplot	0.15 Downstream[2/]	0.18 Midplot	0.18 Downstream[2/]	0.23 Midplot	0.23 Downstream[2/]
0.03	1	1	79	45	1	7
0.06	1	1	1	13	1	1
0.03	1	1	3	3	1	1
2.00	1	1	1	3	1	1

1/ Surface acres treated divided by cubic feet per second flow; e.g., one acre of canal surface treated with a canal flow of 10 cubic feet per second would have a dilution factor of 0.10.

2/ 100 yards downstream.

in Louisiana were lower than residues found in the Delta. The difference is at least partially due to a higher application rate in the Delta. Downstream of the spray plots, residues found in Louisiana were comparable to those found in the Delta.

Drinking Water

The Weedar 64 label requires delaying use of treated water for either (1) three weeks, or (2) until the water contains 100 ppb 2,4-D DMA or less. The U. S. EPA (1976) criterion for 2,4-D in drinking water of 100 ppb is the source of the 100 ppb limit on the Weedar 64 label. The EPA criterion was derived by applying a 1/500 safety factor to the lowest long-term dosage with no ill effects on dogs (8.0 mg/kg/day), assuming a 70 kg person has a daily water intake of 2 liters which contain 20 percent of the total dietary 2,4-D intake. The criterion appears to be appropriately derived. 2,4-D has been found to be teratogenic (cause birth defects) in rodents, but only at levels of about 50 mg/kg and above (DHS/DIR 1980). The drinking water criterion thus appears to protect against teratogenic effects. To date, scientific testing of carcinogenic (causing cancer) effects of 2,4-D has been either inconclusive or inadequate. Additional long-term testing has been required by EPA; unfortunately, the tests will not be complete for about three years (Mountfort pers. comm.). Existing knowledge does not support a lower criterion based on carcinogenicity. In view of the incomplete knowledge, however, it is certainly prudent to minimize human intake of, and exposure to, 2,4-D products.

Conventional domestic water treatment processes apparently have little or no effect in removing 2,4-D from water (Wojtalik et al 1971). Concentrations at domestic water intakes would therefore apply to finished water. The test spray data (Tables 1 and 2) indicate concentrations of 2,4-D DMA leaving spray plots will not exeed the 100 ppb criterion.

Aquatic Life

2,4-D DMA is less toxic to aquatic life than the 2,4-D esters used in forestry. The acute toxicity of 2,4-D DMA ranges from 3300 ppb for Daphnia magna (48-hour EC50) (Sanders 1979) to 542,000 ppb for bluegill (24-hour LC50) (Hughes and Davis 1963). Acutely toxic levels of 2,4-D DMA to fish are typically greater than 100,000 ppb. Rainbow trout demonstrate an avoidance reaction to 1,000 ppb (Folmar 1976). For comparison, 2,4-D butoxyethanol ester (2,4-D BEE) is acutely toxic to glass shrimp at 1,200 ppb and to bluegill at 910 ppb (Sanders 1970).

The Delta field test data indicate 2,4-D DMA residuals from water hyacinth treatments will not approach levels toxic to fish within the spray plots or

Fish present within the spray plot may take up enough 2,4-D DMA or breakdown phenols to impart an objectionable taste to the flesh for a few days after spraying. Water concentrations of 500 ppb impart "inferior" taste and levels of 100 ppb retain "acceptable" taste (Folmar 1980).

Chronic effects (occurring over periods of weeks to years) of 2,4-D DMA on aquatic life appear not to be a threat. Dilution of applied 2,4-D DMA to insignificant levels occurs within a few hours (Tables 1 and 2). If the proper microorganisms are present in Delta waters, biological breakdown probably occurs within a few days. To ensure concerned agencies and the public that breakdown does indeed occur, it is recommended that DBW conduct a simple concentration vs. time test using Delta water in a closed laboratory system.

Insufficient data exist to evaluate effects of 2,4-D DMA on freshwater algae and higher aquatic plants other than water hyacinth. Phytoplankton are generally not sensitive to 2,4-D acid at levels less than 10,000 ppb acid (Voight and Lynch 1974). Avoiding adverse effects on willows and other higher riparian broadleaf plants will depend on the skill and carefulness of the operators. Bulrushes, common in hyacinth-producing areas, are less sensitive to the toxic effects of 2,4-D DMA than broadleaf plants.

Irrigation

The rivers and sloughs of the Delta are boating waterways, are fish and wildlife habitats, and, very importantly, are water delivery channels for agricultural and municipal supplies, both local and distant. Agricultural supplies irrigate crops directly and municipal supplies irrigate home garden crops and a great variety of ornamental plants. Since 2,4-D DMA is an herbicide, its potential to affect farm and home plants is great. The herbicidal effects of 2,4-D compounds are greatest on rapidly growing broadleaf plants, which is why 2,4-D compounds are effective in controlling broadleaf weeds in wheat fields and in controlling brush in newly planted stands of conifers.

Toxicity to farm and home plants in the distant areas of the San Joaquin Valley and southern California appears not to be a threat in view of the plant toxicity data (Table 4) and the rapid dilution of residues (Tables 1 and 2). The main concern is for relatively undiluted residues being directly drawn into Delta farm irrigation systems and local municipal supplies. Concentrations within the spray plots are high enough to injure agricultural crops.

Although the Weedar 64 label residue limit of 100 ppb appears to be generally protective of agricultural crops, recent experiments have shown that concentrations lower than 100 ppb applied over prolonged periods (months) reduced the growth (but not the yield) of grape plants (Comes pers. comm.). The margin of safety between many crop injury thresholds and the label limit is small and there are no toxicity data for the hundreds of domestic garden plants and for some potentially sensitive Delta crops (e.g. sunflowers). It is therefore desirable to have a greater degree of protection for local agricultural and municipal intakes than is provided by the label limit of 100 ppb.

TABLE 4. TOXICITY OF 2,4-D TO IRRIGATED CROPS

	Method	Applied 2,4-D (all forms) ppb	lb/acre	Effect	Ref.
	Furrow	700	0.5	Injury threshold	1
	"	700 - 1500		" "	2
	Sprinkler	100 - 1000		Yield reduction threshold	3
ans	Furrow	7500	2.0	Top growth and root injury (seedlings)	4
	"	7500	2.0	Killed seedlings	5
	Sprinkler	5600	1.0	Increased yield	5
	Furrow	220 - 1100	0.1 - 0.5	Injury threshold	6
	Sprinkler	220 - 2210	0.1 - 1.0	" "	6
	Furrow	10,000	2.7	None	5
	Sprinkler	5800	1.0	None	5
	Furrow	15,200	2.7	Seed quality impaired	5
	Sprinkler	5600	1.0	None	5
	"	220 - 1100	0.1 - 0.5	Injury threshold	6
	Furrow	5510	5.0	Seed quality impaired	6
	Furrow	1100 - 5510	0.5 - 2.5	Injury threshold	6
	Sprinkler	220 - 2210	0.1 - 1.0	" "	6

Clore 1958
8
. comm.
4, in Brooker and Edwards 1975
Carlile 1971, in Brooker and Edwards 1975
1 1973

A water quality limit of 5 ppb for 2,4-D has been suggested in the literature. In an EPA-funded assessment of silvicultural chemicals, Newton (1977) suggested a 2,4-D water quality limit of 5 ppb for protection of irrigation uses. He derived that limit by applying a 5:1 safety factor to the highest 2,4-D concentration having no known phytotoxic effect, which he erroneously cited as 22 ppb from a report by Bruns et al (1973). The maximum no-effect level reported by Bruns et al (1973) was actually 220 ppb; Newton apparently confused 2,4-D data with silvex data in the Bruns report. A water quality limit of 5 ppb thus would be overprotective and possibly not achievable by the water hyacinth control program (Tables 1 and 2).

Presently, the maximum known no-effect level is 100 ppb (Comes pers. comm.). Applying a 5:1 safety factor yields a safe level of 20 ppb. Test data to date (Tables 1 and 2) indicate concentrations 50 yards away and greater from the spray site will not exceed 20 ppb. Thus, the program can generally avoid concentrations greater than 20 ppb from entering intakes by not spraying within 50 yards of the intake. It is recommended that application of 2,4-D DMA in the hyacinth control program be conducted such that concentrations entering agricultural or municipal intakes not exceed 20 ppb. The guideline of 20 ppb is achievable by the program, will protect sensitive crops and domestic plants, and will provide an added margin of safety for protection of public health.

Since 2,4-D DMA is classified by the Department of Food and Agriculture as a "restricted use" material, additional protection for sensitive crops will be implemented by the county agricultural commissioner's permit process. The Weedar 64 label directs that the product shall not be used in irrigation ditches used to sprinkler-irrigate "sensitive crops" such as grapes and tomatoes. This label directive will be implemented by the county agricultural commissioners in issuing permits for spray operations. Federal agencies such as the Corps are exempt from the state permit process. Since DBW is the lead state agency, however, they have agreed to obtain permits for all 2,4-D DMA applications in the Delta that they contract to the Corps.

DIQUAT

Background and Environmental Fate

Central Valley Regional Water Quality Control Board staff has summarized the literature on diquat (Attachment 2). Diquat is of low volatility and highly water soluble; diquat applied for water hyacinth control will completely dissolve;and escape from water to the atmosphere will not be significant. Diquat breaks down readily (weeks) when in solution. Diquat ion rapidly and irreversibly attaches to foliage, organic detritus and clay particles. Attached diquat is highly persistent (years) in the environment. Once attached, diquat is unavailable for further toxic effects on plants or aquatic animals.

Field Test Residues

A test treatment of water hyacinth with diquat was conducted by DBW in coordination with the U. S. Department of Agriculture, Agricultural Research Station, Davis, in June 1982. A one-half acre plot near Coney Island was sprayed and water samples were taken and tested for residues. Float samples within the spray plot averaged 250 ppb diquat immediately after application (Table 5). Only 1 of 6 samples taken within 15 minutes of application had a detectable residue (25 ppb). Of 15 samples taken up to 2½ hours after application, none had detectable residues. The low number of positive findings probably relates to the diquat's tendence to bind to particulate matter, which is generally plentiful in Delta waters.

Drinking Water

The diquat label specifies a drinking water limit of 10 ppb. That limit is based on a long-term, no-observable effect level of 10 parts per million (10,000 ppb) to produce cataracts in rats and appears to be appropriately derived (Federal Register No. 46(3):15281-84). Diquat is effectively adsorbed and removed from water by activated carbon or clay minerals used in some water treatment plants (Zavins 1965 in Calderbank 1972). The test spray data (Table 5) indicate the drinking water limit can be met for water leaving the spray site.

Aquatic Life

Short-term lethal concentrations of diquat to fish range from 20,000 to 90,000 ppb (Attachment 2). The test spray data (Table 5) indicate no short-term threat to fish life. Aquatic invertebrates are more sensitive to diquat than fish; the 24-hour LC50 to Hyalella is 580 ppb. Concentrations in the first few inches of the water column approach that value, but only during the first few minutes after application. It is uncertain whether toxic effects on invertebrates would occur because the exposure period would only be a few minutes, compared to 24 hours in the bioassay. Some invertebrate mortality may occur.

Unlike 2,4-D DMA, diquat is not selectively toxic for certain types of plants. The potential for impacts on bulrushes and other riparian nonbroadleaf nontarget plants is greater for diquat than for 2,4-D DMA.

Chronic effects on aquatic life do not appear to be a problem because diquat is rapidly inactivated after application.

Diquat's persistence is an undesirable characteristic; unforeseen impacts to bottom organisms could occur if diquat use were heavy and buildup of diquat in sediments were to occur.

Irrigation

The diquat label has the same water quality limit for irrigation as for drinking water (10 ppb). That limit appears to protect irrigation uses (Table 6). The field test data (Table 5) indicate there is little danger that water leaving the treatment site will exceed the label limit.

Unlike 2,4-D DMA, a permit from the county agricultural commissioner is not required for aquatic use of diquat. Since use is limited to government agencies, however, some degree of protection of nontarget plants is provided.

TABLE 5. RESIDUES OF DIQUAT, IN PPB, FOUND AT CONEY ISLAND TEST SPRAY SITE, JUNE 1982. APPLICATION RATE WAS 1.5 POUNDS PER ACRE ON A 0.5 ACRE PLOT. DETECTION LIMIT WAS 4 PPB. (ADAPTED FROM ANDERSON 1982b)

FLOAT SAMPLES[1/] WITHIN SPRAY PLOT

Sample:	A	B	C	D	E	F	Average
Concentration:	0	359	482	500	70	105	250

WATER COLUMN SAMPLES

Time After Application (minutes)	Inside Spray Plot	Outside Spray Plot [2/]
15	25	0
	0	0
	0	0
15-150	0x3 samples	0x12 samples

1/ Floating open-top containers containing 500 ml Delta water, collected immediately after spraying.

2/ 10-100 feet outside spray plot.

TABLE 6. TOXICITY OF DIQUAT TO IRRIGATED CROPS

Crop	Method	Applied Diquat ppb	Applied Diquat lb/acre	Effect	Ref.
Corn	Furrow	340,000	60	None	1
Field beans	"	13,600	2.4	Growth suppressed	1
Beans	"	5,000		Injury threshold	2
Corn	"	125,000		" "	2

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1 - Bruns et al 1964, in Brooker and Edwards 1975
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ATTACHMENT 1

Senate Bill No. 1344

CHAPTER 263

An act to add Section 64 to the Harbors and Navigation Code, relating to the control of water hyacinth, making an appropriation therefor, and declaring the urgency thereof, to take effect immediately.

[Approved by Governor June 14, 1982. Filed with Secretary of State June 14, 1982.]

LEGISLATIVE COUNSEL'S DIGEST

agencies of the United States, undertake an aggressive program for the effective control of water hyacinth in the delta and the marsh.

(b) The department is designated as the lead agency of the state for the purpose of cooperating with agencies of the United States and other public agencies in controlling water hyacinth in the delta and the marsh.

(c) The department, other state agencies, cities, counties, and districts are hereby authorized to cooperate with one another and with agencies of the United States in controlling water hyacinth in the delta and the marsh, and may furnish money, services, equipment, and other property to that end.

SEC. 2. Notwithstanding Sections 71.4 and 85.2 of the Harbors and Navigation Code, the sum of one hundred twenty-five thousand dollars ($125,000) is hereby appropriated from the Harbors and Watercraft Revolving Fund to the Department of Boating and Waterways for expenditure during the 1982 calendar year for the following purposes:

(a) The development of a long-range water hyacinth control program in the Sacramento-San Joaquin Delta and the Suisun Marsh, to be undertaken in cooperation with agencies of the United States and other public agencies.

(b) The implementation of a short-term program for the control of water hyacinth until the long-term control program is ready for implementation; provided that the Department of Boating and Waterways shall notify the Department of Finance and the Joint Legislative Budget Committee at least 30 days prior to any expenditure of funds pursuant to this subdivision.

SEC. 3. This act is an urgency statute necessary for the immediate preservation of the public peace, health, or safety within the meaning of Article IV of the Constitution and shall go into immediate effect. The facts constituting the necessity are:

In order that control of water hyacinth can be substantially underway prior to the summer growth season, it is necessary that this act take effect immediately.

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ATTACHMENT 2

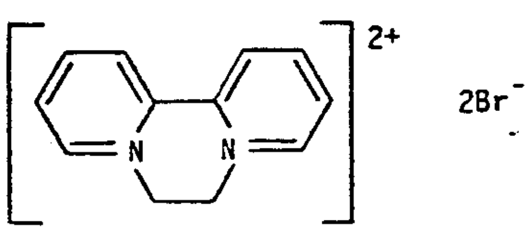
DIQUAT ANALYSIS
Prepared by
Central Valley Regional Board

REGULATORY PICTURE

4/01/68 - Diquat in irrigation waters resulting from application of herbicide to canals and reservoirs for control of submersed and floating weeds. "Do not use [water] for 10 days." - Water Quality Criteria, U.S. Department of the Interior, Federal Water Pollution Control Administration, p. 158.

11/15/72 - "An interim tolerance of 0.01 part per million is established for residues of the herbicide diquat in potable water (calculated as the cation) resulting from the use of its dibromide salt to control aquatic weeds in canals, lakes, ponds, and other potential sources of potable water." - amendment to FFDCA - CFR Title 21, Chapter 1, Subchapter B, Part 121, Subpart D (food additives permitted in food for human consumption) - FR 37, No. 221, p. 24174. This tolerance is presently in effect and applies to all users, both private and public. EPA contends that this criteria will be met if the label directions for the herbicide's use are strictly adhered to.

3/05/81 - Proposed amendment to CFR Title 40, Part 193, Subpart A - Would establish the interim tolerance of 0.01 ppm as permanent and would limit diquat use. Private use would be restricted to "ponds, lakes, and drainage ditches where there is little or no outflow of water and which are totally under the control of the user" of the herbicide. Use in other "slow moving or quiescent " water bodies would be limited to "programs of the Corps of Engineers or other Federal or State or public agencies". In all cases, "the treated water will not be used for animal consumption, swimming, spraying, domestic purposes, or for irrigation for 14 days post treatment or until approved analysis shows that the water does not contain more than 0.01 ppm of diquat ". In addition, "no treatment will be made where commercial processing of fish is practiced." - FR 46, No. 43 pp. 15281-15284.



Diquat

Regulatory:

- EPA Interim Tolerance in potable waters. 1/ 0.01 ppm

Physical Properties:

- Nonvolatile. 3,4,6/
- Completely soluble in water. 2/
- Labile to hydrolysis in the presence of alkaline materials including alkaline waters. 3/
- Stable to chemical decomposition except at a pH greater than 9. 5/

Precautions in use:

- Do not use treated water for animal consumption, swimming, spraying or irrigation within 10 days after treatment. 4/
- Do not use treated water for drinking purposes until 14 days after treatment. 4/
- After application of diquat to water for weed control, residues usually decline to 0.01 ppm or below within 4 to 14 days. 6/
- Regrowth may occur in perennial plants. 4/
- Strip-treating of weed infested waters recommended to reduce the possibility of exhausting oxygen supply available to fish. 10/

Toxicology:

- Entry - ingestion; mist inhalation; minimal skin absorption. 3/
- Concentrate is a skin and eye irritant. 3/
- Acute toxicity -
  oral LD_{50} (rat) 230 mg ion/kg (moderately toxic)
  dermal LD_{50} (rabbit) > 400 mg ion/kg (moderately toxic) 3/
- Chronic toxicity - induces cataracts in rats and dogs; possible liver and kidney damage. 3/
- Unlike paraquat, diquat does not produce pulmonary (lung) toxicity and is not concentrated in lung tissues. 8/
- Diquat may be a weak mutagen. 13/

- Toxicity to the male reproductive system has been inferred (no specifics given). 8/

- Symptoms of injury may be delayed. 4/

Environmental fate:

- Cation is active ingredient. 3/

- Very rapidly absorbed by foliage; very resistant to removal by rain. 3/

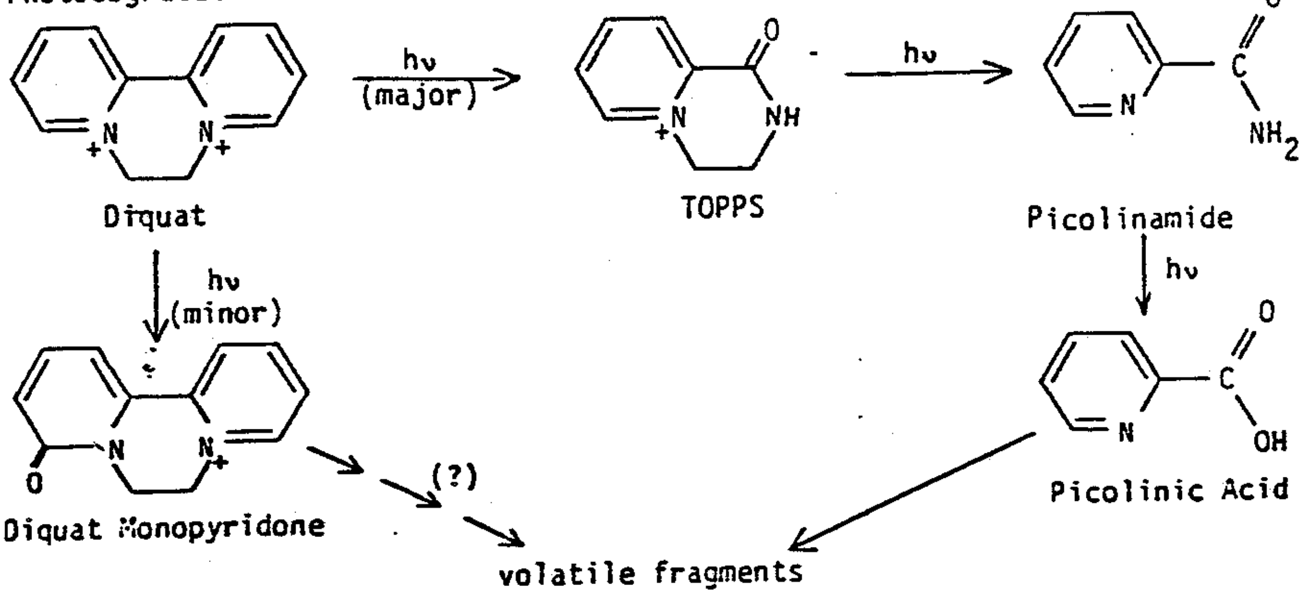
- Metabolic breakdown does not occur in plants. 3/

- Photodegradation on plant surfaces (> 75% loss in 4 days in June). 6/

- Major removal pathway from water - sorption by weeds (concentration); dead weeds sink and carry diquat to sediments where herbicide is transferred to clay particles. 5,6,10/

- High susceptibility to ultraviolet degradation. 3/

- Photodegradation mechanism 6/



- Photodegradation in solution (70% in 3 weeks). 5/

- TOPPS "has a very low oral toxicity to mammals". 7/

- Picolinamide is bacterially degraded. 6/

- Diquat breaks down readily in solution, but degradation is inhibited when bound to clay. 6/

- Longer persistence in clear than in turbid water (27 days vs. 7 days to.

- Long persistence in sediments (years) where it is largely unavailable for microbial decay or to other living organisms. 5,6,8/
- Clay adsorption independent of pH and temperature. 5/
- Desorption of diquat from bottom mud "would not be expecteed to occur". 6/
- Because of strong binding, diquat would not be mobile in soil. 6/
- Faster microbial degradation of plant bound than free diquat. 5/

Impacts on aquatic organisms:

- Diquat is not bioaccumulated or metabolized by fish. 6/
- Threshold toxicity level on blugills, largemouth bass, fathead minnows, channel catfish, and rainbow trout is generally in excess of 10 mg/l. 5/
- Median tolerance limit (TL_{50}) in mg/l 5/

Species	24 hr	48 hr	96 hr
Striped bass	--	--	80
Chinook salmon	29.5	28.5	--
Salmon	--	28.5	--
Rainbow trout	90 11/	20-70	60 11/
Amphipod (Hyalella azeteca)	0.58	0.12	0.048
Brown trout fingerlings	--	--	20.4 16/

- "There is a wide safety margin between the concentration of diquat .... which is toxic to fish in 96-hr. immersion tests and that which is needed for aquatic weed control." 6,10/
- Fingerling brown trout - 5% mortality after 96 hour exposure to 5.5 mg/l. 16/
- Physiological stress shown in 2-year old yellow perch at 1 and 5 ppm. 13/
- Increased incidence of downstream drift of rainbow trout (reduced swimming speed) observed at 0.5 to 5 ppm. 15/
- Diquat could impair downstream migration of yearling coho salmon (smolts) and possibly reduce their survival in seawater. 14/
- Increased mortality of Rana pipiens tadpole embryos on exposure to 100 ppm. 17/
- Developmental toxicity to Daphnia, an important food supply for fish, at 1 ppm (transitory effect). 10/

1/ FR 37, No. 221, p. 24174 (November 15, 1972).

2/ Farm Chemicals Handbood (1981).

3/ Herbicide Handbook of the Weed Science Society of America, 3rd Ed. (1974).

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