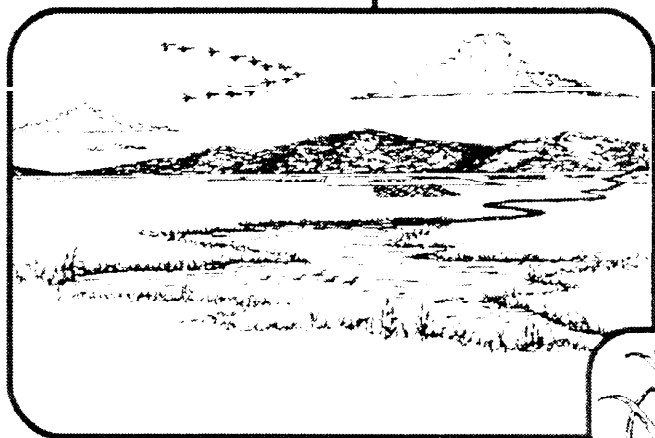
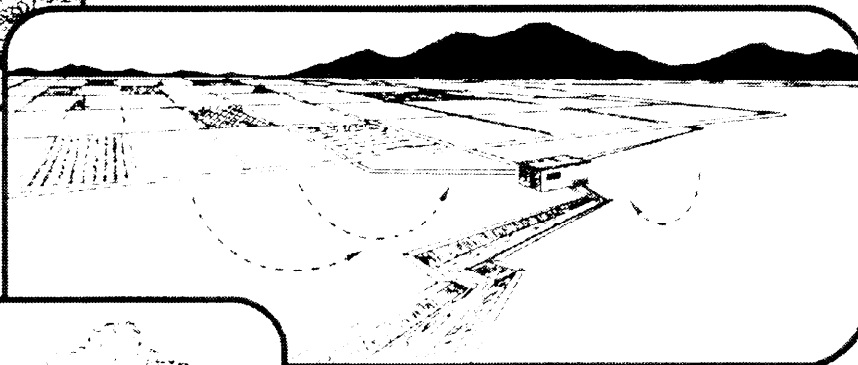
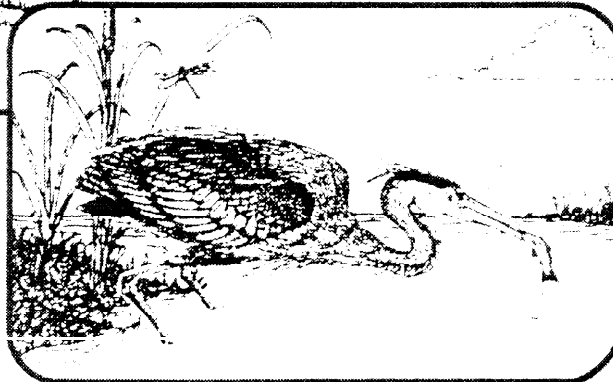


Detailed Study of Water Quality,  
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in the Klamath Basin, California and  
Oregon, 1990-92



**U. S. GEOLOGICAL SURVEY**  
Water-Resources Investigations  
Report 95-4232



U.S. Geological Survey  
U.S. Fish and Wildlife Service  
Bureau of Reclamation  
Bureau of Indian Affairs

# Detailed Study of Water Quality, Bottom Sediment, and Biota Associated with Irrigation Drainage in the Klamath Basin, California and Oregon, 1990-92

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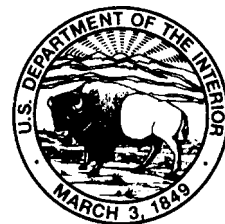
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2020-07

Sacramento, California  
1996



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# CONTENTS

Abstract.....	1
Introduction by <b>Jewel Bennett, Peter D. Dileanis, Thomas Maurer Steven E. Schwarzbach, and Judy Sefchick</b> .....	<b>2</b>
Purpose and Scope.....	3
Approach .....	3
Acknowledgments .....	4
Location .....	4
Geology and Soils.....	4
Klamath Reclamation and Irrigation Project: Changes in Hydrology and Land Use .....	4
Hydrologic Conditions During the Study Period .....	6
Eutrophication in the Upper Klamath Basin.....	7
Pesticide Use on and Near Tule Lake National Wildlife Refuge .....	7
Historic Aquatic Communities of the Klamath Basin.....	9
Invertebrates .....	9
Fish .....	9
Amphibians.....	10
Data Collection and Analysis by <b>Jewel Bennett, Robin Boyer Peter D. Dileanis, John Henderson, Therese Littleton, Dorene E. MacCoy Elizabeth Materna, Thomas Maurer, Deblyn Mead, Meri Moore, Steven E. Schwarzbach, and Judy Sefchick</b> .....	10
Water-Quality Measurements .....	11
Sample Collection and Analysis for Nitrogen, Phosphorus, and Organic Carbon Compounds.....	11
Sampling for Pesticide Analysis and Static Bioassay Tests .....	11
Pesticide Analysis.....	11
Bioassays .....	12
Sediment Sampling and Chemical Analysis .....	14
Sediment Bioassays .....	15
Monitoring Pesticide Drift and Water Quality in Tule Lake National Wildlife Refuge Waterways.....	15
Monitoring the Transport of Acrolein .....	16
Sample Collection and Evaluation of Trace Elements in Resident Biota .....	17
Sample Collection and Evaluation of Organochlorine Residues in Resident Biota.....	17
Analysis for Waterfowl Cholinesterase Activity .....	18
Aquatic Community Surveys.....	18
Benthic Macroinvertebrate Surveys .....	18
Water-Column Invertebrate Surveys .....	18
Fish Community and Health Surveys.....	19
Frog Call Surveys.....	19
Water Quality and Toxicity of Irrigation Drainwater by <b>Jewel Bennett, Robin Boyer, Peter D. Dileanis, Therese Littleton, Dorene E. MacCoy, Thomas Maurer, Meri Moore, Steven E. Schwarzbach, and Judy Sefchick</b> .....	<b>19</b>
Water Quality at Primary Sampling Sites .....	19
Dissolved Oxygen .....	19
pH, Temperature, and Specific Conductance .....	22
Major Ion Chemistry .....	24
Nutrients .....	24
Nitrogen.....	24
Phosphorus.....	27
Organic Carbon.....	29
Pesticides .....	29
Toxicity of Irrigation Drainwater at Primary Sampling Sites.....	34

Microtox® Water Bioassays .....	34
Duckweed (Lemna) Bioassays .....	34
Static Aquatic Invertebrate Bioassays .....	34
Static Fish Bioassays .....	34
Static Frog Renewal Bioassays .....	35
In Situ Aquatic Invertebrate and Fish Bioassays .....	36
In Situ Duckling Bioassays .....	37
Causes of Toxicity in Irrigation Drainwater at the Primary Sampling Sites.. .....	37
Pesticide Drift and Water Quality in Tule Lake National Wildlife Refuge Waterways.. .....	43
Pesticide Drift .....	43
Water Quality .....	44
Transport and Toxicity of Acrolein .....	47
Contaminants and Toxicity in Bottom Sediment by <b>Steven E. Schwarzbach</b> , and <b>Thomas Maurer</b> .....	<b>47</b>
Pesticides in Bottom Sediment .....	47
Arsenic and Mercury in Bottom Sediment .....	49
Bioassay of Sediment Porewater .....	49
Trace Elements and Pesticides in Biota by <b>Steven E. Schwarzbach</b> and <b>Judy Sefchick</b> .....	<b>50</b>
Trace Elements .....	50
Blue-Green Algae .....	50
Aquatic Invertebrates.. .....	50
Fish .....	50
Avian Eggs.. .....	50
Organochlorine Compounds .....	51
Fish and Invertebrates .....	51
Avian Eggs.. .....	51
Sources of Organochlorine Pesticide Contamination in Avian Eggs.. .....	<b>52</b>
Eggshell Thickness Measurements .....	53
Free-Living Waterfowl Cholinesterase Evaluation .....	53
Effect of Irrigation Drainwater on Composition of Aquatic Communities by <b>Jewel Bennett</b> , <b>Robin Boyer</b> , <b>Terese Littleton</b> , <b>Steven E. Schwarzbach</b> , and <b>Judy Sefchick</b> .....	<b>54</b>
Benthic Macroinvertebrates .....	54
Water-Column Invertebrates .....	54
Fish Communities and Fish Health Surveys. ....	54
Frog Populations .....	55
Changes in Aquatic Communities.. .....	56
Summary and Conclusions by <b>Peter D. Dileanis</b> and <b>Steven E. Schwarzbach</b> .....	<b>61</b>
References Cited .....	63

## FIGURES

1-2. Maps showing:	
1. Location of Klamath Basin study area and sampling sites.....	<b>5</b>
2. Location of acrolein monitoring sites, July 13- 15, 1 9 9 2 . . . . .	<b>17</b>
3-4. Boxplots showing:	
3. Concentration of dissolved oxygen at primary sites during periodic monitoring in 1991 and 1992 . . . . .	
4. Concentration of dissolved oxygen at primary sites during continuous monitoring in 1992 .....	22
<b>5-9.</b> Graphs showing:	
5. Mean total nitrogen concentrations in 1991 .....	25
6. Mean total nitrogen concentrations in 1992 . . . . .	26
7. Mean ammonia concentrations in 1991 and 1992 .....	27
8. Mean dissolved organic carbon during 1992 monitoring . . . . .	30
9. Water-quality extremes in 1992, and static and in <i>situ</i> bioassays in 1991 and 1992 . . . . .	41
10. Map showing Tule Lake National Wildlife Refuge leaselands . . . . .	45
11. Graphs showing:	

11. Mean Microtox® EC <sub>50</sub> of sediment porewater in 1992 .....	49
12. Percent frequency of detection of selected organochlorine compounds in white-faced ibis and western grebe eggs collected between 1990 and 1992 .....	52
13. Regression plot of white-faced ibis eggshell thickness and DDE concentrations in eggs collected at the Lower Klamath National Wildlife Refuge in 1991 and 1992 .....	53
14. Water-column invertebrate surveys at primary sites in 1992 .....	57
15. Species composition in fish surveys in 1991 and 1992 .....	58
16. Mean number of calling frogs at individual transects in 1991 and 1992 .....	59
17. Diagram showing historical changes in aquatic communities in the study area .....	60

## TABLES

1. Pesticide use during 1991 and 1992 in the Tulelake Irrigation District .....	8
2. Reporting limits of pesticides in filtered water samples.....	12
3. Samples sent to the National Water Quality Laboratory for pesticide residue analysis, 1991 and 1992.. .....	13
4. Metrics and scoring criteria for the Index of Biological Integrity.. .....	20
5. Percentage of time that dissolved-oxygen concentrations were less than 5 milligrams per liter and th was greater than 9 during periods of continuous monitoring at selected primary sites in 1992 .....	23
6. Summary of water samples with ammonia concentrations greater than the 4-day criteria for protection of aquatic organisms without the presence of sensitive coldwater fish .....	28
7. Ratios of mean available nitrogen to mean dissolved-orthophosphorus concentrations in water samples collected in 1992 .....	29
8. Summary of pesticide detections in water samples collected at primary sites in 1991 and 1992 .....	31
9. Acute toxicity of pesticides used and detected in the study area.. .....	32
10. Results of <i>Xenopus</i> malformation bioassay, 1991.....	35
11. Results of <i>Xenopus</i> mortality and malformation bioassays, 1992.. .....	36
12. Results of <i>Daphnia in situ</i> bioassays in 1991 and 1992.....	38
13. Results of <i>Hyalella in situ</i> bioassays in 1991 and 1992 .....	39
14. Results of <i>Pimephales in situ</i> bioassays in 1991 and 1992 .....	40
15. Toxicity and mortality patterns from bioassay tests in 1991 and 1992 .....	42
16. Methamidophos residues on deposition samplers, and estimated potential water concentrations, 1992 .....	44
17. Water quality and <i>Duphnia</i> survival in Tule Lake National Wildlife Refuge canals and drains during July and August 1992 .....	46
18. Methamidophos application biomonitoring results, 1992 .....	46
19. Field and laboratory analyses of acrolein concentrations in water samples collected July 13-15, 1992.. .....	48
20. Percent survival of <i>Duphnia</i> and fathead minnows before and after application of acrolein.. .....	49
21. Percent frequency of detection and geometric mean concentrations of organochlorine compounds in eggs of white-faced ibis, western grebes, and eared grebes.. .....	52
22. Eggshell thickness of avian eggs collected at Lower Klamath and Tule Lake National Wildlife Refuges, 1990-92.. .....	53
23. Comparison of 1992 <i>Daphnia</i> survival during <i>in situ</i> bioassays.. .....	55
24. Summary of fish Index of Biological Integrity (IBI) scores and aquatic habitat ratings from surveys during 1991 and 1992 .....	55
25. Percentage of samples with abnormalities in each of the fish health index characteristics for each date and sampling site, 1991 and 1992.. .....	56

## CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	By	To obtain
acre	<b>0.4047</b>	hectare
acre	4.047	square meter
acre-foot (acre-ft)	1,233	cubic meter
acre-foot (acre-ft)	0.001233	cubic hectometer
cubic foot per second (ft <sup>3</sup> /s)	0.02832	cubic meter per second
foot (ft)	0.3048	meter
gallon (gal)	3.785	liter
inch (in.)	25.4	millimeter
mile (mi)	1.609	kilometer
mile per hour (mi/h)	1.609	kilometer per hour
ounce, avoirdupois (oz)	28.35	gram
pound, avoirdupois (lb)	4.536	kilogram
square foot (ft <sup>2</sup> )	929.0	square centimeter
square foot (ft <sup>2</sup> )	0.09294	square meter
square mile (mi <sup>2</sup> )	259.0	hectare
square mile (mi <sup>2</sup> )	2.590	square kilometer

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:

$$^{\circ}\text{F}=1.8(^{\circ}\text{C})+32$$

### Vertical Datum

**Sea level:** In this report, “sea level” refers to the National Geodetic Vertical Datum of 1929—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

### Abbreviations

**g, gram**

L, liter

mg/kg, milligram per kilogram

mg/L, milligram per liter

mL, milliliter

mm, millimeter

µg/g, microgram per gram

µg/kg, microgram per kilogram

µg/L, microgram per liter

µg/m<sup>2</sup>, microgram per square meter

µm, micrometer

µS/cm, microsiemens per centimeter at 25 degrees Celsius

AChE, acetylcholinesterase activity (in brain)

ASTM, American Society for Listing and Materials

BIA, Bureau of Indian Affairs

BOR, Bureau of Reclamation

DOI, U.S. Department of the Interior

EC<sub>50</sub>, mean effective concentration, the percent test water that causes a 50-percent decrease in light output by bacteria in Microtox® bioassays.

EPA, U.S. Environmental Protection Agency

FETAX, Frog Embryo Teratogenesis Assay: *Xenopus*  
IBI, Index of Biological Integrity  
LC<sub>50</sub>, median lethal concentration (the concentration at which 50 percent of a population will not survive)  
LD<sub>50</sub>, median lethal dose (the dose at which 50 percent of a population will not survive)  
NIWQP, National Irrigation Water Quality Program  
NOI, Notice of Intent  
NWQL, National Water Quality Laboratory  
NWR, national wildlife refuge  
PACF, Patuxent Analytical Control Facility  
SD, standard deviation  
SE, standard error  
USFWS, U.S. Fish and Wildlife Service  
USGS, U.S. Geological Survey



# Detailed Study of Water Quality, Bottom Sediment, and Biota Associated with Irrigation Drainage in the Klamath Basin, California and Oregon, 1990-92

By Peter D. Dileanis, Steven E. Schwarzbach, Jewel Bennett, and others

## ABSTRACT

The effect of irrigation drainage on the water quality and wildlife of the Klamath Basin in California and Oregon was evaluated during 1990-92 as part of the National Irrigation Water Quality Program of the U.S. Department of the Interior. The study focused on land serviced by the Bureau of Reclamation Klamath Project, which supplies irrigation water to agricultural land in the Klamath Basin and the Lost River Basin. The Tule Lake and Lower Klamath National Wildlife Refuges, managed by the U.S. Fish and Wildlife Service, are in the study area. These refuges provide critical resting and breeding habitat for waterfowl on the Pacific flyway and are dependent on irrigation drainwater from upstream agriculture for most of their water supply.

Water-quality characteristics throughout the study area were typical of highly eutrophic systems during the summer months of 1991 and 1992. Dissolved-oxygen concentrations and pH tended to fluctuate each day in response to diurnal patterns of photosynthesis, and frequently exceeded criteria for protection of aquatic organisms.

Nitrogen and phosphorus concentrations were generally at or above threshold levels characteristic of eutrophic lakes and streams. At most

sites the bulk of dissolved nitrogen was organically bound. Elevated ammonia concentrations were common in the study area, especially downstream of drain inputs. High pH of water increased the toxicity of ammonia, and concentrations exceeded criteria at sites upstream and downstream of irrigated land. Concentrations of ammonia in samples from small drains on the Tule Lake refuge leaseland were higher than those measured in the larger, integrating drains at primary monitoring sites. The mean ammonia concentration in leaseland drains [1.2 milligrams per liter (mg/L)] was significantly higher than the mean concentration in canals delivering water to the leaseland fields (0.065 mg/L) and higher than concentrations reported to be lethal to *Daphnia magna* (median lethal concentration of 0.66 mg/L). Dissolved-oxygen concentrations also were lower, and *Daphnia* survivability measured during *in situ* bioassays was correspondingly lower in the leaseland drains than in water delivery canals.

In static laboratory bioassays, water samples collected at the primary monitoring sites caused toxicity in up to 78 percent of *Lemna minor* tests, in up to 49 percent of *Xenopus laevis* tests, in 17 percent and 8 percent of *Hyalella azteca* and *Pimephales promelus* tests, respectively, and 0 percent in *Daphnia magna* tests. *In situ* exposure at the sites caused mortality in more

than 83 percent of *Pimephales* tests and in more than 41 percent of *Daphnia* and *Hyalella* tests. Much of the observed toxicity appears to have been caused by low dissolved oxygen, high pH, and ammonia. Although water in the study area was toxic to a variety of organisms, no statistically significant differences in the degree of toxicity between sites were observed above or below irrigated agricultural land in any of the bioassays.

Pesticides were frequently detected in water samples collected at the monitoring sites during the 1991 and 1992 irrigation seasons. Among the most frequently detected compounds were the herbicides simazine, metribuzin, EPTC, and metolachlor and the insecticide terbufos. All the insecticides detected were at concentrations substantially below acute toxicity values reported for aquatic organisms.

The herbicide acrolein has been used extensively in the basin to manage aquatic plant growth in irrigation canals and drains. The concentration of acrolein was monitored in a canal near Tule Lake after an application in order to evaluate the potential for the pesticide to be transported to refuge waters. Although acrolein concentrations were toxic to fish in the channels adjacent to Tule Lake, very little of the canal water entered the refuge during the monitoring period.

Organochlorine pesticide concentrations in 25 surficial sediment samples collected in 1990 were below baseline levels commonly found in soils and sediment. Seventeen sediment samples were analyzed for chlorophenoxy acid herbicides and two samples were analyzed for organophosphorus and carbamate insecticides in 1992. No pesticides were detected in any of these samples.

Residues of the trace elements selenium, mercury, and arsenic in algae, invertebrates, fish, and avian eggs revealed no bioaccumulation problems. Concentrations of organochlorine compounds, especially of *p,p'* DDE, were associated with a mean 1 l-percent eggshell thinning in white-faced ibis. However, ibis populations appear to be increasing, and some eggs of ibis were relatively low in DDE concentration. DDE

concentrations in eggs of western grebes were not as high as in the eggs of ibis. Concentrations and types of organochlorine compounds detected in grebe and ibis eggs were highly variable, indicating that the birds were exposed to these compounds outside the basin.

Fish and invertebrates inhabiting drainwater were representative of pollution-tolerant species assemblages. The aquatic communities retained little of their historic ecological structure. Extensive hydrologic modifications and hypertrophic conditions in Klamath Basin waterways have degraded the quality of aquatic habitat and altered aquatic communities.

## INTRODUCTION

In the last several years there has been increasing concern about the quality of irrigation drainwater and its potential effect on human health, fish, and wildlife. In 1983, incidents of mortality, anomalies, and reproductive failures in waterfowl were discovered by the U.S. Fish and Wildlife Service at Kesterson National Wildlife Refuge (NWR) in the western San Joaquin Valley, California, where irrigation drainwater was impounded. In addition, potentially toxic trace elements and pesticide residues have been detected in other areas in western states that receive irrigation drainage.

Because of the concern that problems related to contaminants in irrigation drainwater at the Kesterson refuge might occur in other areas, the U.S. Department of the Interior (DOI) initiated the National Irrigation Water Quality Program (NIWQP) in 1985. The program was designed to determine if irrigation-related problems existed at other DOI constructed or managed irrigation projects, national wildlife refuges, or wetland areas for which the Department has responsibilities under the Migratory Bird Treaty Act, the Endangered Species Act, or other legislation. The program consists of five phases:

- (1) Sites with a potential for problems are identified by evaluating previous investigations and the geological, hydrological, and biological conditions at each site.

- (2) Reconnaissance investigations are initiated at selected sites. Samples of water, sediment, and the biota are collected and analyzed to determine if significant problems exist.
- (3) Detailed studies are done at sites where reconnaissance investigations identified significant problems or found evidence that such problems may exist.
- (4) Remediation is planned for sites with significant problems.
- (5) Identified problems are remediated.

Each of the first three phases are done by study teams of scientists from the U.S. Geological Survey (USGS), the U.S. Fish and Wildlife Service (USFWS), the Bureau of Reclamation (BOR), and the Bureau of Indian Affairs (BIA), with the USGS responsible for overall project management and publication of results. Phases 4 and 5 are led by the BOR. Initially, 20 locations in 13 states were identified and selected for reconnaissance investigations. One of the study areas selected was in the Klamath River Basin in California and Oregon. A reconnaissance investigation was begun in 1988 (Sorenson and Schwarzbach, 1991), and the major findings of that investigation were used as the basis of a detailed study that is the subject of this report.

## PURPOSE AND SCOPE

This report presents the results of a detailed study that was designed to:

- (1) Determine if agricultural chemicals are transported within the Klamath Basin at concentrations acutely or chronically toxic to aquatic invertebrates, fish, or birds.
- (2) Determine the magnitude and extent of water-quality problems related to the highly eutrophic nature of the aquatic system in the study area. Potential problems that were identified in the reconnaissance investigation include low dissolved oxygen, high pH, and toxic concentrations of un-ionized ammonia.
- (3) Confirm the existence of high concentrations of arsenic and mercury in the water, sediment,

and biota of Lower Klamath NWR measured during the reconnaissance investigation and determine possible sources of these constituents.

Sample collection and monitoring began in 1990 and continued throughout the summer irrigation seasons in 1991 and 1992. This report provides descriptive summaries, analysis, and interpretation of data collected during the study. All data used herein have been published in a separate report (MacCoy, 1994).

## APPROACH

Three basic approaches were used to evaluate the effect of drainwater on water quality and biota:

- (1) Water-quality and chemical contaminant monitoring. Measurements were made of chemical/physical characteristics of water and the presence of pesticide and trace-element residues in water, sediment, and biota. Bird eggshell thickness and brain cholinesterase levels also were monitored.
- (2) Toxicity testing. Klamath Basin water was evaluated with a variety of aquatic and sediment bioassay tests. Two types of bioassays were done: laboratory static tests to evaluate the acute toxicity hazard of a drainwater or sediment sample and *in* tests to evaluate the mortality hazard of drainwater under field situations.
- (3) Ambient biological monitoring. Estimates were made of the size of aquatic invertebrate and fish populations, species diversity, and fish health.

Each approach provides different information for evaluation, and each has its own inherent strengths and weaknesses as a tool for understanding the ecological health of an environment (Karr, 1993; Wang, 1994). Monitoring chemical constituents can provide information about the causative agents of potential health threats and biotic impoverishment. The approach is limited, however, by several practical considerations. Monitoring is often restricted to a relatively few times, places, and targeted analytes. In complex and variable systems, such as those found in

the study area, it can be difficult to collect sufficient data to adequately describe the chemical characteristics of the system. Another weakness is that supporting knowledge of the biological importance of detected contaminant concentrations is often limited or nonexistent. When available, criteria for aquatic habitat are often generalized and their relevance to a specific location or time may not be clear.

## ACKNOWLEDGMENTS

Information and logistical support were provided by personnel from the Klamath Basin NWR's, especially Roger Johnson, former Refuge Manager, and personnel from the BOR, especially Bob Davis, Jerry Pyle and Earl Danosky of the Tulelake Irrigation District, Jim Massey and Greg Hermon of the Siskiyou County Agricultural Extension Office, and Les Wright and Maureen Osborne of the Modoc County Agricultural Extension Office provided information about agricultural chemical use in the study area.

The following individuals assisted in the collection and preparation of data: Shane Ridge, Elizabeth Materna, and Derrick Williams of the USFWS; Chetna Acharya, Stephanie Ciccarello, Robin McWilliams, Jesse Overton, Karin Podlesch, and Nina Woodgate from the Student Conservation Association, who volunteered their time and considerable enthusiasm; and Staci Kawaguchi, Darian LaBrie, and Deblyn Mead of the USGS. Stephen Sorenson of the USGS was the project leader during the first 2 years of the detailed study.

In addition to the principal authors, the following individuals contributed text to this report, as indicated in the table of contents: Dorene MacCoy and Deblyn Mead of the USGS; John Henderson, Judy Sefchick, and Thomas Maurer of the USFWS; and Robin Boyer, Therese Littleton, and Meri Moore of the University of Washington, School of Fisheries, Cooperative Fish and Wildlife Research Unit.

## LOCATION

The study area is in the Klamath River Basin on the California-Oregon state border (fig. 1). The region encompasses two watersheds, the Klamath River watershed and the Lost River watershed that formerly terminated in Tule Lake. The Klamath River system in this area includes Upper Klamath, Sheepy, and

Indian Tom Lakes, and the remnants of Lower Klamath Lake in what is now the Lower Klamath National Wildlife Refuges. These areas are about 4,300 ft above sea level and extend in a north and south direction just east of the Cascade Mountain Range. The drainage basin of the Lost River includes Clear Lake, Gerber Reservoir, and Tule Lake sump. The study area encompassed the BOR's Klamath Project and included irrigated agricultural land served by the project, Tule Lake and Lower Klamath NWR's, and channels draining agricultural and refuge lands to the Klamath River.

## GEOLOGY AND SOILS

Tule Lake, Upper Klamath Lake, and Lower Klamath Lake bed occupy basins formed by block faulting and volcanic activity. They are the shrunken remnants of an old pluvial lake that covered an area of 1,096 mi<sup>2</sup> and stretched nearly 75 mi in length during the Pleistocene (Dicken, 1980).

During the Pleistocene, the old pluvial lake was partially filled by sediment and volcanic material carried by runoff from the Cascade Mountain Range. The lacustrine sediment also contained the remains of many varieties of diatoms that grew in the lake and formed deposits on the bottom. Soils from different parts of the basin vary in the amount of diatomaceous material; some contain only a few fragments while others are almost entirely diatomaceous. The heavy soils along the Lost River and in the bottoms of the numerous shallow basins in the area have been formed in part by the weathering of basaltic rock. The area's peat or marsh soils have been formed by the decomposition of bulrushes in shallow lake water and are confined principally to the Lower Klamath Lake bed (Sweet and McBeth, 1908).

## KLAMATH RECLAMATION AND IRRIGATION PROJECT: CHANGES IN HYDROLOGY AND LAND USE

Settlement and agricultural development of the Klamath Basin by western emigrants began in the 1860's. The first crops relied on rainfall (Dicken, 1980), but, by the mid- 1880's, some land was being irrigated from canals and springs along the Lost River (Sweet and McBeth, 1908).

Following the passage of the Reclamation Act in 1902, the DOI investigated the possibilities of large-

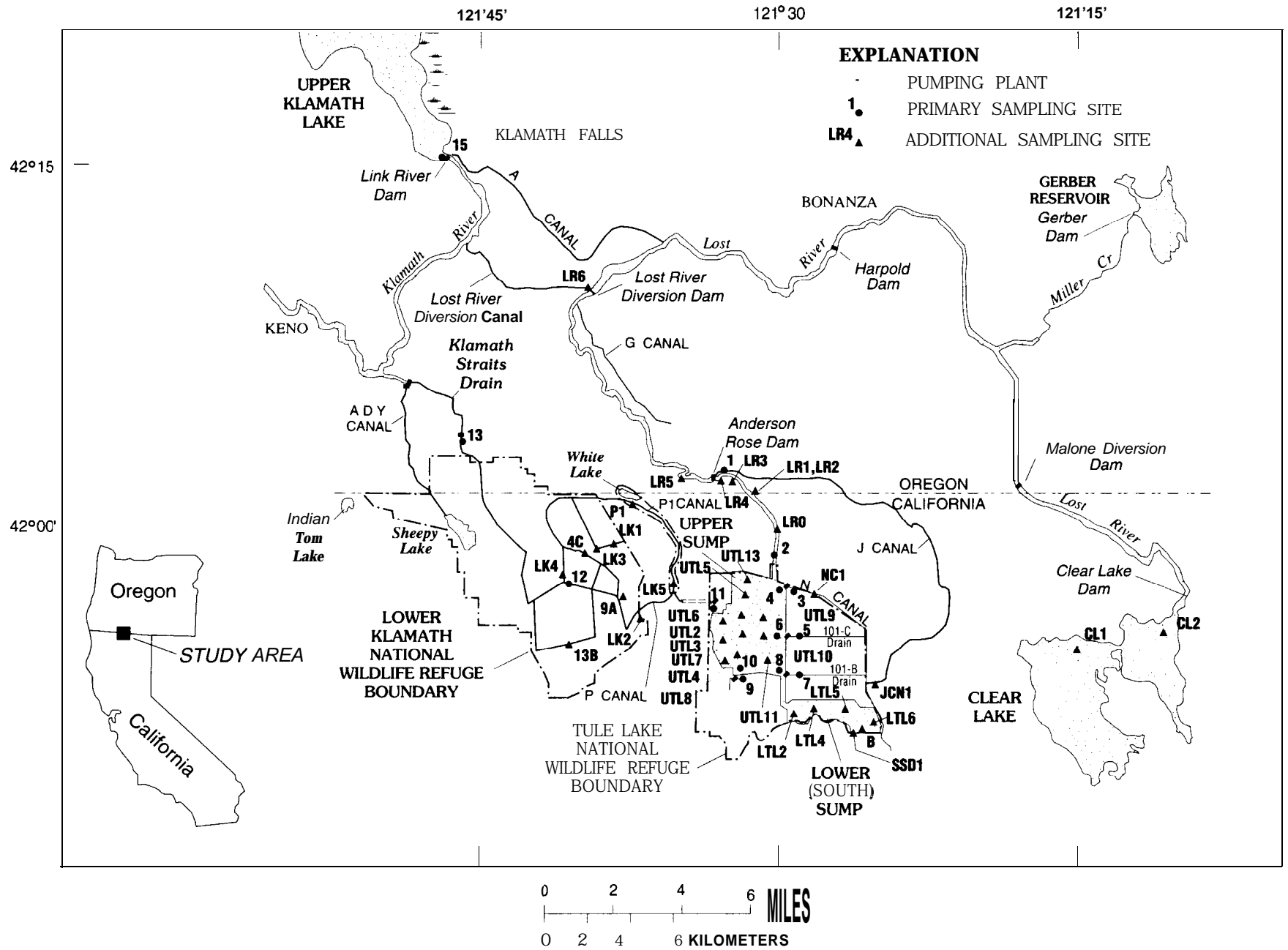


Figure 1. Location of Klamath Basin study area and sampling sites.

scale irrigated agriculture in the basin and approved a plan for development (Boyle, 1987). In 1905, Upper Klamath, Lower Klamath, and Tule Lakes were ceded to the U.S. Government (Dicken, 1980), and in 1906, the BOR began construction of the Klamath Irrigation Project. The project goals were to drain and convert the lakebeds of Lower Klamath and Tule Lakes for agricultural uses, to store and divert water from Clear Lake, Upper Klamath Lake, and the Lost River for irrigation supply, and to control flooding of the newly created farmland (Bureau of Reclamation, 1988). Reclaimed public land was opened for homesteading after 1908, attracting thousands of potential farmers to the basin as the reclamation project proceeded and irrigation service expanded (Pafford, 1971).

When surveyed in 1884, Tule Lake covered an area of 96,000 acres. Although the Lost River was the feeder stream of Tule Lake, periodic flooding of the Klamath River into the Lost River basin also contributed water to the lake (Abney, 1964).

After 1912, water that previously flowed down the Lost River to Tule Lake was impounded in Clear Lake Reservoir or diverted to the Klamath River by the Lost River diversion canal. Tule Lake bed was dried up by 1922 and placed under cultivation (Buettner and Scoppettone, 1991). The present-day Tule Lake sump was created to provide water storage and flood control by diking the lowest areas of the old lake bed and allowing it to refill. Drainage and irrigation return flows from the Klamath Irrigation District, Tulelake Irrigation District, and several smaller irrigation districts accumulate in the sump. Excess water is pumped through a 6,500-ft tunnel in Sheepy Ridge that was constructed in the early 1940's to allow disposal of water from Tule Lake to the Klamath River via the Klamath Straits drain (Bureau of Reclamation, 1975).

The 13,240-acre sump and an additional 17,000 acres of flood-prone land surrounding it were kept in federal ownership and now comprise most of the Tule Lake NWR. Much of the land on the refuge has been available by lease for agricultural production since its conversion.

Before reclamation efforts, Lower Klamath Lake consisted of a 30,000-acre central open-water area that varied in depth from 3 to 11 ft at low water and a 58,000-acre encircling marsh thick with emergent plants (Sweet and McBeth, 1908). Annual flood-

ing of the Klamath and Link Rivers was the principle source of water to the lake and wetlands.

After the construction of levees and a control structure on the Klamath Straits drain, the flow of water to Lower Klamath Lake from the Klamath River was cut off and much of the lake and wetlands drained. Today, Lower Klamath Lake consists of a system of 13 separate and interconnected diked ponds (management units) that encompass several thousand acres within the Lower Klamath NWR. Only a few of these units are permanent, however; the others are periodically drained and used for croplands (Buettner and Scoppettone, 1991). Currently, most water for the refuge is diverted from flows pumped from Tule Lake sump to the Klamath Straits drain but may be restricted by the availability of irrigation drainwater (Bureau of Reclamation, 1975).

Upper Klamath Lake was developed into a source of irrigation water by the construction of a dam in 1917, which raised the level of Upper Klamath Lake by 6 ft to provide a storage capacity in Upper Klamath Lake and Agency Lake of 483,000 acre-ft (Bond and others, 1968). Water stored in Upper Klamath Lake is diverted near the head of the Link River through the "A" canal for irrigation of land south and southeast of Klamath Falls and the Tule Lake/Lower Klamath Lake area. Today, the completed Klamath Irrigation Project serves over 200,000 acres of land and diverts about 400,000 acre-ft of water for agricultural uses (Potter, 1992).

The creation of a productive agricultural region was accompanied by a significant loss of wildlife habitat. Prior to 1900, the Klamath Basin contained greater than 350,000 acres of wetland. Less than 75,000 acres remain today (Adkins, 1970; Klamath River Basin Fisheries Task Force, 1991). Some of the wetlands were inundated for reservoirs, and other lakes and wetlands were drained and reclaimed for farmland. Many of the remaining wetlands and reservoirs are managed by the Fish and Wildlife Service as national wildlife refuges.

## **HYDROLOGIC CONDITIONS DURING THE STUDY PERIOD**

The period of study, 1990-92, represented the last 3 years of a 6-year drought in the region. During the last year of the study, water storage in Clear Lake

and Gerber Reservoirs was the lowest in the irrigation project's history, and water delivery from these sources was curtailed early in the irrigation season. Much of the water used for irrigation came from Upper Klamath Lake in 1992. In a normal water year, as typified by the decades preceding the study, over 1.5 to 1.7 million acre-ft of water is annually diverted from the Klamath and Lost River watersheds. In 1991 and 1992, diversions were down to a little over 800,000 and 600,000 acre-ft, respectively, while water losses due to consumptive use, evaporation, and conveyance loss remained about the same (392,000 and 373,000 acre-ft in 1991 and 1992, respectively).

Irrigated land in the Klamath Basin Project is assigned one of three priority classifications. Land classified as the highest priority received water throughout the irrigation season. Land with the lower two priorities had all or a portion of the expected water supply cut off in July. Little water was pumped from Tule Lake sump to Lower Klamath Refuge in order to maintain high water levels in the sump as mandated for the protection of suckers on the Federal list of endangered species. During the irrigation season of 1992, the Lost River Basin became a closed basin as it had been before the building of the Klamath Project. Water was supplied to Lower Klamath NWR from the Klamath River in 1992 by way of the ADY canal.

## EUTROPHICATION IN THE UPPER KLAMATH BASIN

Eutrophic lakes are characterized by abundant nutrients and high algal productivity. Upper Klamath Lake is a naturally eutrophic lake with a long history of nuisance algal blooms. As early as January 1906, observations were recorded of extensive algal growth in Upper Klamath Lake. At that time, J.B. Lippencot, Supervising Engineer for the Reclamation Service, wrote, "...these waters are filled with some sort of organic matter, either animal or vegetable, so that they have a decided green appearance (Phinney and Peek, 1960)." A party led by G. Kemmerer found eutrophic conditions in Upper Klamath Lake in the summer of 1913 (Kemmerer and others, 1923-24). From the 1930's to 1960's, algal populations shifted from a variety of blue-green algae and diatoms to almost a monoculture of *Aphanizomenon* (Phinney and others, 1959; Phinney and Peek, 1960; Hazel, 1969; Entranco Engineers, 1982). Of the 49 lakes sampled for the

National Eutrophication Survey in July 1971, Upper Klamath Lake ranked third in algal productivity and was one of the 6 lakes characterized as highly productive (Entranco Engineers, 1982).

Upper Klamath Lake is now classified as hyper-eutrophic because of its mono-specific *Aphanizomenon* blooms of long duration and high biomass (Wetzel, 1983). Such changes in phytoplankton diversity and quantity are typical of lakes undergoing a change from eutrophic to hypereutrophic conditions (diatom/green algae dominance to mixed blue-green assemblages to monocultures of blue-green algae) (Wetzel, 1983). The changes in algal species and abundance over the last 50 years appear to be related to increased nutrient availability resulting from agricultural development in the lake basin and possibly fluctuation in lake level since the construction of the Link River Dam (Bortleson and Fretwell, 1993).

Eutrophic conditions have also been noted in other parts of the basin. Buettner and Scopettone (1991) found filamentous algae and *Aphanizomenon* in the study area at Tule Lake, Sheepy Lake, Lower Klamath Lake, ADY canal, and Klamath Straits drain and downstream of the study area at Iron Gate and Copco Reservoirs.

## PESTICIDE USE ON AND NEAR TULE LAKE NATIONAL WILDLIFE REFUGE

Principal agricultural commodities in the basin are small grains, alfalfa hay, potatoes, onions, sugar beets, and pasture for beef cattle and sheep. Irrigation is essential because annual precipitation in the region averages only about 14 in. In addition, because much of the basin is over 2,600 ft in elevation, frost-sensitive crops, like potatoes, are irrigated for emergency freeze protection. In the 1950-60's organochlorine insecticides including DDT, dieldrin, endrin, and toxaphene were heavily used in the basin, and subsequent studies indicated irrigation return flows were the principal source of organochlorine pesticides in Tule Lake sump (Godsil and Johnson, 1968). Today, a wide variety of algicides, fungicides, herbicides, and insecticides are in use in the basin, although organophosphorous and carbamate compounds have replaced the organochlorine insecticides. A list of pesticides used on the agricultural land around Tule Lake during 1991 and 1992 is presented in table 1. Pesticide use data in Oregon were not available.

**Table 1.** Pesticide use during 1991 and 1992 in the Tulelake Irrigation District, Klamath Basin

[Summarized from records in the California Agricultural Agent Offices of Modoc and Siskiyou Counties. Pesticide use in kilograms of active ingredient (kg AI). Compounds in **bold** were included in analyses of samples collected for this study]

Compound	Product name	Function	Crop use	Pesticide use, 1991		Pesticide use, 1992	
				Period of use	kg AI	Period of use	kg AI
Acrolein.....	Magnacide . . . . .	algacide . . . . .	non-crop use . . . . .	June to October	3,431	6-1 to 8-1	2,400
Aldicarb.. ..	Temik .....	insecticide . . . . .	sugar beets .....				59
Carbaryl.....	Sevin XLR .....	. .do .....	. .do .....			5-4 to 6-10	593
Carbofuran..	Furadan 4F.....	. .do .....	alfalfa.. ..	6-15 to 6-21	52	5-1 to ?	150
Chlorothalonil .....	Bravo .....	fungicide . . . . .	potatoes.. ..			6-18 to 8-31	5,071
Chlorpropham .....	Sprout-Nip .....	herbicide . . . . .	. .do .....			5-1	56
Chlorpyrifos .....	Lorsban .....	insecticide . . . . .	sugar beets .....			4-2 to 6-25	1,167
Copper hydroxide.....	Champ Flowable..	fungicide . . . . .					15
Copper hydroxide.....	Champ.....	. .do .....	potatoes.. ..	7-30 to 8-14	1,883	7-21 to 8-12	1,128
2,4-D.. ..	Weedar 64.....	herbicide .....	wheat, barley, oats .....	6-2 to 9-3	7,598	4-28 to 8-28	6,280
2,4-D.. ..	Weed Stroy .....	. .do .....				6-6 to 6-23	75
2,4-D.. ..	Clean Crop.. ..	. .do .....	wheat, barley .....	6-2 to 7-12	1,418	5-30 to 7-27	86
Dicamba .....	Banvel.....	. .do .....	wheat, barley, oats .....	6-2 to 8-11	346	5-2 to 7-15	185
Difenzoquat methyl sulfate .....	Avenge .....	.do.....	wheat, barley .....	6-2 to 7-7	5,292	4-28 to 6-23	2,154
Diquat.. ..	Diquat .....	. .do .....	potatoes.. ..			8-11 to 8-28	68
Disulfoton.. ..	Disyston .....	insecticide . . . . .	wheat, barley .....	7-4 to 8-1	9,015	6-20 to 7-2	5,968
Dithiocarbamate .....	Mancozeb .....	fungicide . . . . .	potatoes.. ..	7- 15 to 8-30	10,734	8-1 to?	46
Dithiocarbamate .....	Dithane .....	. .do .....	. .do .....			7-8 to 8-26	434
Dithiocarbamate magnesium..	Maneb .....	. .do .....	. .do .....			7-27 to 8-27	464
Ethofumesate.. ..	Nortron EC .....	herbicide .....	sugar beets .....			5-1 to ?	33
Ethoprop.. ..	Mocap .....	nematocide....	potatoes.. ..			3-20 to 6-3	4,759
Ethylpropylthiocarbamate (EPTC) .....	Eptam.....	herbicide .....	. .do .....			5-2 to 6-5	1,350
Fluazifop-p-butyl.....	Fus .....	. .do .....	onions .....			5-21 to 6-22	95
Glyphosate.. ..	Protocol.....	. .do .....	beets, potatoes .....				44
Glyphosate.. ..	Round-up .....	. .do .....	onions, beets, potatoes.. ..			4-14 to 8-28	1,609
Iprodione .....	Roval.....	fungicide .....	potatoes.. ..			6-20 to 8-25	2,594
MCPA.....	MCP 4.....	herbicide .....					31
Metaxyl.....	Ridomil .....	. .do .....	potatoes.. ..				271
Metam sodium.....	Vapam .....	. .do .....	. .do .....			4-1 to ?	19,139
Methamidophos.. ..	Monitor.....	insecticide .....	. .do .....			7-17 to 8-10	4,587
Methyl parathion .....		. .do .....	barley, onions, peas, wheat			6- 17 to 8-25	1,520
Metribuzim .....	Lexone .....	herbicide .....	potatoes.. ..			5-28 to 7-31	425
Metribuzin .....	Sencor .....	. .do .....	. .do .....			6-20 to 7- 12	1,253
Paraquat.....	Gramoxone .....	. .do .....	alfalfa.. ..		7	4-27	3
Sethoxydim .....	Poast .....	. .do .....	potatoes.. ..			5-30 to 7-12	350
Sulfur.....	Thiolux .....	fungicide .....	sugar beets .....			8-1 to?	1,743
Thiabendazole .....	Mertect.....	. .do .....					4
Thiophanate-methyl .....	Topps 2.5D.....	. .do .....					362



During the summer months, aquatic vegetation in irrigation waterways (except those on the refuges) is controlled by extensive use of the herbicide acrolein. In 1989, the BOR estimated approximately 339 acrolein treatments were made by the various irrigation districts, treating about 426 mi of waterways (Sorenson and Schwarzbach, 1991). Acrolein is applied by injection into a waterway, with a minimum 5-mg/L target concentration, where it can persist for 2 to 3 days (Sorenson and Schwarzbach, 1991). Acrolein is a preferred aquatic herbicide because of its efficacy and its unique ability to cause aquatic vegetation to disintegrate, relieving the problem of dead vegetation clogging waterways (Meyer, 1971).

## HISTORIC AQUATIC COMMUNITIES OF THE KLAMATH BASIN

### Invertebrates

In 1896, insect larvae and other invertebrates were abundant in Upper Klamath Lake (Evermann and Meek, 1898). During a survey by Kemmerer in July 1913, two species of copepoda (*Diaphanosoma leucht-enbergianum* and *Diaptomus ashlandi*) were the most abundant zooplanktors in the lake (Hazel, 1969). No mention was made of *Daphnia*, which is now the most abundant single genus.

Increased populations of midges became a nuisance to residents near Upper Klamath Lake after 1930. There was some speculation at the time that the increasing number of midges was related to the appearance of vast masses of algae in the lake.

The first comprehensive survey of benthic invertebrates in Upper Klamath Lake occurred in 1964-65 (Hazel, 1969). Benthic organisms ranged from 650 to 1,600 per square foot and consisted primarily of oligochaetes and leeches (Bond and others, 1968).

In 1964, the Federal Water Quality Administration collected macroinvertebrates to determine the effects of irrigation return water on the water quality of the Klamath and Lost Rivers. Eighty-four taxa representing 15 orders were identified; the most prevalent invertebrates were chironomid larvae, oligochaetes, amphipods, isopods, odonates, leeches, and gastropods (Mason and others, 1970).

Collections in Upper Klamath Lake in 1981 and 1982 found the same species dominant as in the 1960's in both the water column and benthic substrate

(Entranco Engineers, 1982). Oligochaetes and leeches were still the predominant benthic organisms, but chironomid counts were substantially below earlier results.

The Klamath Lakes area has been known for its rich endemic mollusk fauna for the past 100 years (T.J. Frest, Deixis Consultants, written commun., 1993). Freshwater mussels were gathered and eaten by the Klamath and Modoc Indians in winter. In 1883, Cope found the most abundant mollusks in Upper Klamath Lake were the freshwater snails, *Planorbis newberryi* and *Lymnaea* spp. (Cope, 1883).

The freshwater mollusk fauna of the Klamath Lakes area has changed over time due to extinctions and local extirpations (Taylor, 1981). In general, species that have declined or disappeared altogether are spring forms that require cold, well-oxygenated, clear water. None are closely associated with dense growths of aquatic macrophytes and none are tolerant of eutrophication, warming, or nutrient enrichment (T.J. Frest, Deixis Consultants, written commun., 1993).

### Fish

The fish fauna of the Klamath Basin is dominated by true freshwater fishes rather than by anadromous forms. Of the 26 fish species that occur in the upper Klamath system today, 14 have been introduced by humans (Moyle, 1976).

Over 100 years ago, in June 1894, the U.S. Fish Commission collected fish near the outlet of Upper Klamath Lake and in the Klamath and Lost Rivers. Fish species included Pacific lamprey, green sturgeon, Klamath largescale sucker, shortnose sucker, Lost River sucker, tui chub, rainbow trout, marbled sculpin, and Klamath Lake sculpin, as well as other species of sculpins, chubs, and suckers (Gilbert, 1898). Upper Klamath Lake was described in 1896 as containing numerous fish of just a few species; trout weighing 8 to 10 pounds were common at this time (Evermann and Meek, 1898). In 1919, residents reportedly observed large suckers and rainbow trout being taken from the mouth of the Lost River (Lewis Foulke, retired rancher, Siskiyou County, in Coots, 1965).

Native fish populations in Upper Klamath Lake have declined greatly in this century; only the tui and blue chub have been commonly captured during systematic netting efforts (Vincent, 1968; Bienz and Ziller, 1987). The predominant fishes today are the introduced fathead minnow and yellow perch. Other introduced forms include the pumpkinseed, sunfish, brown bullhead, and brown trout (Buettner and Scop-

pettone, 1991). Although it is thought that fish were stocked in the Klamath Basin as early as the late 1800's the earliest written stocking records indicate that the Oregon State Game Commission stocked black bass, catfish, and crappie into the Lost River (R. Grenfell, Oregon State Game Commission, written commun., 1970) and largemouth bass, crappie, and yellow perch into Upper Klamath and Agency Lakes (Ziller, 1986) in the late 1930's. Fathead minnows were introduced in the 1970's.

In a survey of Lost River fishes in April 1973, populations of all fish species were small and scattered throughout the system. Chub and bullhead populations were found throughout the Lost River, but bullheads were few in number (Contreras, 1973).

The Upper Klamath Basin contains a surprising diversity of suckers. Upper Klamath Lake with its primary tributaries, the Williamson and Sprague Rivers, and Tule Lake with its primary tributary, the Lost River, provided habitat for hundreds of thousands of suckers as recently as the late 1890's (Williams and others, 1985). Suckers were relied upon as a food source by the Klamath and Modoc Indians (Cope, 1879; Golden, 1969), and at one time, native sucker runs in the Lost River supported a cannery operation (Howe, 1968).

The historic range of the Lost River sucker was the Upper Klamath and Lost River Basins. Lost River suckers and shortnose suckers extended their range into the lower Klamath system following creation of lacustrine habitat by the construction of Copco Reservoir in 1918 (Moyle, 1976). A 1973 survey of the Lost River did not document Lost River suckers in the Lost River, Tule Lake, Lower Klamath Lake, or Sheepy Lake, and found only a distinct population in Clear Lake Reservoir. The shortnose sucker was found only occasionally in the Lost River in 1973 (Contreras, 1973; Koch and Contreras, 1973). Surveys of lake sucker spawners made in 1984 and 1985 (Bienz and Ziller, 1987) produced total population estimates of 2,650 shortnose, 6,990 Klamath largescale, and 11,860 Lost River suckers. In 1988, Lost River and shortnose suckers were listed as federally endangered pursuant to the Endangered Species Act (Williams, 1988). In 1992, 18 shortnose and 21 Lost River suckers were captured in Tule Lake and approximately 100 shortnose suckers were observed spawning at Big Springs above Harpold Reservoir (U.S. Fish and Wildlife Service, 1993).

## Amphibians

Few historic accounts of amphibians in the Klamath Basin exist. In the 1930's large numbers of toads, mainly the western toad (*Bufo boreas*), were seen consuming swarming midges near Upper Klamath Lake (Bonnell and Mote, 1942). In an effort to control midges, thousands of bullfrogs (*Rana catesbeiana*) were stocked in the Lost River from the mid- to late 1930's (R. Grenfell, Oregon State Game Commission, written commun., 1970). By the 1960's bullfrogs were so numerous that a bullfrog hunting season was enacted and is still listed in the Oregon State Sport Fishing Regulations.

Museum records indicate that the tiger salamander (*Ambystoma tigrinum*), Pacific chorus frog (*Pseudacris (Hyla) regilla*), yellow-legged frog (*Rana boylei*), spotted frog (*Rana pretiosa*), western toad, and non-native bullfrog historically occurred in the Klamath Basin (Boyer, 1993). Additionally, the long-toed salamander (*Ambystoma macrodactylum*), Great Basin spadefoot toad (*Scaphiopus intermontanus*), and western leopard frog (*Rana pipiens*) have been observed near the Klamath Straits drain and Lower Klamath NWR (Bureau of Reclamation, 1975).

## DATA COLLECTION AND ANALYSIS

Data collection for this detailed study began in the summer of 1990 with limited sampling of water, sediment, and biota. Extensive monitoring was done throughout June, July, and August in 1991 and 1992. These 13-week monitoring periods represent the peak agricultural irrigation season and summer water conditions. Much of the monitoring effort was directed at 14 sites hereafter referred to as the primary sampling sites (sites 1-13, 15; see fig. 1). These sites were located on major water supply and drainage channels upstream and downstream of irrigated land in the Klamath Reclamation Project service area and in Tule Lake near drainage inputs. Primary sites selected to monitor drainwater were located on large drains that integrated contaminant inputs from a wide area and allowed extensive monitoring with a reasonable number of sampling sites. The primary sampling sites were of four categories: (1) waterways upstream of major drainwater inputs (sites 1, 2, and 15); (2) irrigation return flows to Tule Lake sump (sites 3, 5, 7, and 9); (3) Tule Lake (sites 4, 6, 8, and 10); and (4) downstream of Tule Lake sump and the refuge water system

(sites 11, 12, and 13). Water, sediment, and biota were evaluated at these locations to identify potential gradients in water quality and toxicity along the drainwater system.

Water, sediment, and biota also were evaluated at a variety of other sites in the study area to address specific management practices. During 1992, an additional sampling was done to monitor the acute toxicity of Tule Lake NWR irrigation waterways adjacent to agricultural fields and to determine if drift from aerial insecticide applications entered waterways. Also, a single application of the herbicide acrolein was monitored in 1992 to evaluate the potential for the compound to be transported from its point of application to Tule Lake NWR.

## WATER-QUALITY MEASUREMENTS

In 1991 and 1992, temperature, specific conductance, pH, and dissolved oxygen were measured three times a week at the primary sampling sites 1,2,3,5,7, 9, 11, 12, and 13, with hand-held instruments. In 1992, site 15 was added to the monitoring schedule. These periodic measurements were taken at the beginning, middle, and end of 96-hour *in situ* bioassays being done at the sites and were typically done during the morning hours from 0600 to 1200.

Continuous measurements of water quality were made at selected sites using instruments that automatically recorded dissolved oxygen, pH, specific conductance, and temperature at 15-minute intervals. In August 1991, sites 1,3,7,9, 11, 12, 13, LR5, and LR6 were continuously monitored for 24-hour periods. In 1992, automatic monitors were deployed at selected primary sites concurrent with 96-hour *in situ* bioassays. Sites were randomly selected from each of three site categories according to the schedule shown below:

Dates	Sites with continuous water-quality monitors
June 24-28	2,3,7,12
July 1-5	5,9,11,15
July 15-19	2,3,7,12
July 22-26	3,7,11,15
July 12-August 2	1,5,9,13
August 5-9	2,9,12
August 12-16	3,11,15
August 19-23	1,3,7,13
August 26-30	2,5,9,12

## SAMPLE COLLECTION AND ANALYSIS FOR NITROGEN, PHOSPHORUS, AND ORGANIC CARBON COMPOUNDS

Total nitrogen, nitrate, nitrite, organic nitrogen, total phosphorus, and soluble reactive phosphorus (orthophosphate) were monitored during the study. In August 1991, water samples for analysis of these nutrient compounds were collected every 3 to 4 hours over a 24-hour period at selected sites. The sites included primary sites 1,7, 9, 11, 12, and 13; two additional sites on the Lost River, LR5 and LR6; and a site on the Lower Klamath refuge, 9A. Single samples were also collected at sites 2, 3, and 5. In 1992, samples for nitrogen, phosphorus, and organic carbon analysis were collected monthly during July, August, and September at each of the primary sampling sites and from additional Tule Lake sites (UTL3, UTL5, and UTL7).

## SAMPLING FOR PESTICIDE ANALYSIS AND STATIC BIOASSAY TESTS

In 1991 and 1992, water was collected at sampling sites 1, 2, 3, 5,7,9, 11, 12, and 13 to identify potential gradients in water quality and toxicity along the drainwater system. Site 15 was added in 1992. The water was sampled weekly from each site during June, July, and August (13 weeks) of both years.

A water sample for bioassay and chemical analysis was collected by inserting a chemically cleansed amber 4-L glass bottle into the water column near the surface. The grab sample technique was chosen due to the minimal flow and the well-mixed character of the water within the drainage ditches and canals sampled.

Upon arrival at the field laboratory, approximately 3 L of each water sample was prepared for bioassay by coarse filtration through two layers of 500- $\mu$ m Nitex® screen (to remove vegetation and invertebrates) into a chemically cleansed 4-L clear glass bottle. After the portion for bioassay had been removed, approximately 1 L of water remained in the amber glass bottle and was reserved for pesticide analysis.

## PESTICIDE ANALYSIS

Water samples were prepared for pesticide residue analysis by solid-phase extraction (Sandstrom and others, 1992) in the field laboratory. Analyses were

performed at the USGS National Water Quality Laboratory (NWQL) using gas chromatography and mass spectrometry. The compounds analyzed for and their reporting limits are presented in table 2.

Not all water samples collected and extracted were submitted for analysis. In 1991, samples were selected for pesticide analysis when mortality was observed in the corresponding static bioassay tests. In 1992, up to three water samples per week were selected for analysis if water from a sampled site caused high mortality in that week's static bioassays. Three additional water samples were selected each week in a stratified random manner based upon sample site location category: upstream of Tule Lake sump, return flows to Tule Lake Sump, or downstream of

Tule Lake sump. Samples submitted for analysis are listed in table 3.

## BIOASSAYS

The acute toxicity of Klamath drainwater was tested in static laboratory bioassays using several species of organisms: *Photobacterium phosphoreum* (the Microtox® assay), *Selenastrum capricornutum* (green algae), *Lemna minor* (common duckweed), *Daphnia magna* (a water flea), *Hyalella azteca* (a freshwater amphipod), *Pimephales promelas* (fathead minnow), and *Xenopus laevis* (African clawed frog). The tests were done with undiluted water collected weekly from the water column at each sampling site. Because many water samples had dissolved-oxygen concentra-

**Table 2.** Reporting limits of pesticides in filtered water samples, Klamath Basin

[Compounds in **bold** have records of use in Tulelake Irrigation District during 1991 and 1992. µg/L, microgram per liter; compound in parenthesis is the product name]

Herbicide	Report-ting limit (clg/8.)	Insecticide	Report-ting limit (µg/L)
Alachlor .....	0.003	Azinphos-methyl .....	0.010
Atrazine .....	.002	Carbaryl .....	.05
Atrazine, Desethyl .....	.003	Carbofuran .....	.008
Benfluralin .....	.005	Chlorpyrifos .....	.002
Butylate.. .....	.002	DDE .....	.00
Cyanazine .....	.005	Diazinon .....	.005
Dacthal (DCPA) .....	.002	Dieldrin .....	.002
Diethylanaline, 2,6- .....	.005	Dimethoate .....	.005
(EPTC) .....	.002	Disulfoton (Disyston) .....	.050
Ethalfuralin .....	.003	Ethoprop (Rovokil) .....	.005
Linuron .....	.005	Fonofos (Dyfonate) .....	.005
Metolachlor.. .....	.002	HCH, Alpha.. .....	.010
Metribuzin.. .....	.010	HCH, Gamma (Lindane) .....	.005
Molinate .....	.005	Malathion .....	.010
Napropamide .....	.002	Methyl parathion .....	.005
Pebulate.. .....	.010	Parathion.. .....	.005
Pendimethalin .....	.010	Permethrin (Ambush) .....	.010
Prometon.. .....	.005	Phorate (Timet) .....	.005
Pronamide .....	.010	Propargite (Omite) .....	.010
Propachlor .....	.002	Terbufos .....	.005
Propanil .....	.001		
Simazine .....	.005		
Tebuthiuron .....	.010		
Terbacil .....	.010		
Thiobencarb .....	.002		
Triallate.. .....	.002		
Trifluralin .....	.005		

tions below 5 mg/L all samples for bioassay were gently aerated for approximately 20 minutes to achieve at least 6.0 mg/L dissolved oxygen prior to the introduction of test organisms and continuously thereafter. Duplicate bioassays were done on each water sample, and tests typically began within 4 hours after collection.

Deionized water was used to prepare growth media for the culture and control testing of green algae and duckweed. Bottled spring water (Mt. Shasta Spring Water Co., Klamath Falls, Oreg.) was used for culture and control test water for *Daphnia*, *Hyalella*, *Pimephales*, and *Xenopus*.

MicrotoxB is an acute bioassay test that utilizes a bioluminescent marine bacterium (*Photobacterium phosphoreum*) as the test organism. In 1991, Microtox® analyses were performed on subsamples of the water collected weekly from primary collection sites and prepared for the static bioassay. Detailed methods are described by Microbics Corporation (1988a, b and 1992). Because Microtox® bacteria are sensitive to high pH, water samples that showed any toxicity and had a pH, above 8.0 were retested after a pH correc-

tion. The correction was made using one or two drops of 10-percent hydrochloric acid to lower the pH of the sample to less than 8.0. As a quality assurance check, a 90-mg/L phenol reference toxicant and deionized water samples were used to monitor reagent quality and consistency of test procedures.

Aquatic plant bioassay tests were done in 1992 with common duckweed (*Lemna minor*), using methods described by Wang (1990a, b). Toxicity was assumed if growth was less than 80 percent of controls. Average organism survival at each site was compared to the average survival in control tests with a statistical procedure, the one-tailed t-test. Duckweed has been increasingly recommended for phytotoxicity tests (Wang and Williams, 1988, 1990; Wang, 1990a, b); the tests can be performed on turbid water samples without further preparation (Wang, 1991 a). In addition, it seemed unlikely that individual duckweed plants would be susceptible to herbivory by the very small zooplankton that remained in the coarse filtered water samples. A disadvantage of using duckweed was that little herbicide toxicity data existed for the genus (Wang, 1991 a).

Static laboratory bioassays on *Daphnia* and *Hyalella* (common filter-feeding zooplankton) were done using methods described by Bennett (1994). *Daphnia* used in the static bioassay tests were less than 24 hours old, and *Hyalella* were approximately 7 to 14 days old.

Static laboratory bioassays on fathead minnows were done using methods described by Bennett (1994). Larval fathead minnows were obtained weekly via overnight delivery from Aquatic Research Organisms (Hampton, N.H.) and held at least 12 hours prior to testing to allow for shipping mortality. Larvae used in the bioassays were less than 5 days old.

Static tests were done using the Frog Embryo Teratogenesis Assay: *Xenopus* (FETAX) described by American Society for Testing and Materials (ASTM) (1991). The test uses *Xenopus* embryos, which are transparent, so they can be visually examined for malformation. The FETAX bioassay is a 96-hour static renewal test in which the water being tested is replaced daily. During 1992, a 6-day tadpole static bioassay was done using 7-day-old *Xenopus* larvae (Boyer, 1993). Average organism survival at each site was compared to the average survival in control tests with a one-tailed t-test.

**Table 3.** Samples sent to the National Water Quality Laboratory for pesticide residue analysis, 1991 and 1992, Klamath Basin

Date of sampling	Site no. (fig. 1)
7-03-91	5
7-10-91	2,3,5,7,9,11
7-17-91	5,7,9,11
7-24-91	3,5,7,9,11
8-14-91	3,9
6-03-92	2,5,12,13
6-10-92	1,9,11,15
6-17-92	1,5,7,13,15
6-24-92	2,3,5,7,9,11,12,15
7-01-92	5,7,11,15
7-08-92	1,2,3,5,7,9
7-15-92	2,7,12,13
7-22-92	2,3,11,15
7-29-92	1,3,5,7,9,11) 13
8-05-92	5,7,11,13
8-12-92	2,13,15
8-19-92	1,7
8-26-92	9,13,15

The *in situ* tests done with *Daphnia* and minnows were based upon methods described by Nebeker and others (1984) and other procedures developed for this study (Littleton, 1993; Bennett, 1994). Tests were done weekly at sites 1, 2, 3, 5, 7, 9, 11, 12, 13, and 15 using similar procedures for all species. It was not possible to locate a field control site in a Klamath Basin waterway that was not potentially influenced by water diversion or agricultural inputs. Therefore, during 1991, the survival of *in situ* organisms was compared to the static laboratory control bioassay tests. In 1992, additional attempts were made to estimate the influence of handling and ambient weather conditions on test organism survival. An outdoor control test was done in which duplicate *in situ* chambers were placed outdoors in a 750-L plastic water tank containing potable well water from the Klamath Basin NWR Headquarters. In 1992, the survival of *in situ* organisms was compared to the outdoor controls. Toxicity was assumed if mortality exceeded concurrent references or controls by more than 20 percent. Average organism survival at each site was compared to the average survival in control tests with a one-tailed t-test.

In 1991, 96-hr *in situ* duckling bioassays were done at selected water sampling sites to test for exposure to organophosphorus and carbamate insecticides (Moore, 1993). The duckling test design included monitoring daily growth rates, assessing cold tolerance, and determining brain acetylcholinesterase (AChE) activity. Duckling bioassays were done in June, July, and August at drainwater return flow sites 3, 5, and 7 where insecticide exposure was considered most likely and, beginning with the third duckling test, at site 1, which served as an upstream reference site.

Exposure to acetylcholine-inhibiting compounds can reduce birds' and mammals' ability to regulate their body temperature (Meeter and Wolthius, 1968; Meyers, 1987). Ducklings selected from each *in situ* test group for cold-stress testing were exposed to an ambient air temperature of 042°C and their body temperatures monitored using cloacal thermocouple probes connected to a 12-channel scanning thermocouple thermometer. Birds were tested for 20 minutes or until one or more individuals experienced a 6°C drop in body temperature. Upon removal from the chambers, birds recovered quickly and usually regained normal body temperature within 10 minutes. All ducklings were tested during one evening

and then euthanized. Livers were weighed and heads were frozen for brain AChE analysis. Brain AChE activity for both mallard ducklings and free-living waterfowl collected during the study was determined spectrophotometrically using the methods described by Hill and Fleming (1982).

## SEDIMENT SAMPLING AND CHEMICAL ANALYSIS

Sediment was collected at all primary sites at least once in 1991. In 1992, collections were made six times at primary sites and three or four times at other sites (MacCoy, 1994). Site 4C could only be sampled twice before the site dried up.

Sediment collection was scheduled on Sundays and Mondays at the end of weekly aquatic *in situ* bioassays in order to minimize disturbance of test organisms. Three sediment samples were collected from each site using a petite ponar or Ekman grab sampler. The samples were composited in a stainless steel bucket with a stainless steel spoon. At sites 15 and 13B, sediment was sieved through a 5-mm mesh stainless steel sieve to remove large detritus and gravel. Subsamples for MicrotoxB and organic analyses were placed in 50-mL or 100-mL chemically cleansed glass jars. Subsamples for inorganic constituents were placed in sterilized, 8-oz plastic bags. After each sample was collected, sampling equipment was cleaned in native water at the site, then rinsed with tap water followed by deionized water. All samples were placed on ice in the field. On returning to the lab, MicrotoxB samples were refrigerated at 4°C, and samples for chemical analysis were frozen. Microtox® bioassay was done within 3 days after the sample was collected.

All USFWS analytical procedures are based on U.S. Environmental Protection Agency (1986a, 1991); U.S. Fish and Wildlife Service (1990); Hazelton Laboratories America Inc. (1991); Mississippi State University (1992); and other internal laboratory procedures approved and monitored by the USFWS's Patuxent Analytical Control Facility (PACF) in Laurel, Maryland. Quality control procedures consisting of blanks, spikes, duplicates, and standards were used throughout the analyses, and all data were reviewed and approved for quality control by the PACE

Organic analyses were by Soxhlet extraction with Mini-florisil column clean-up. Extracts were analyzed by gas chromatography and confirmed by mass spectrometry. Chlorophenoxy acid herbicides were analyzed at the Mississippi State University Chemical Laboratory. All other organic analyses were performed by Hazelton Laboratories America Inc., Madison, Wisconsin.

## SEDIMENT BIOASSAYS

MicrotoxB bioassay tests were performed on sediment porewater in 1991 and 1992 using methods described by Microbics Corporation (1988a, b, and 1992). Early porewater extractions in 1991 were by vacuum filtration using a 30-mL syringe and an air stone (Winger and Lasier, 1991). For the remainder of 1991 and all of 1992, porewater extractions were by centrifuge. Corrections for pH were made if the sample showed toxicity and the pH was above 8.0.

A linear regression software package supplied by the Microbics Corporation was used to calculate the EC<sub>50</sub> for the assay. EC<sub>50</sub> is the percent test water that causes a 50-percent decrease in light output by the bacteria.

## MONITORING PESTICIDE DRIFT AND WATER QUALITY IN TULE LAKE NATIONAL WILDLIFE REFUGE WATERWAYS

Pesticide drift and water quality in Tule Lake NWR waterways were monitored in 1992 from mid-July through August, when small grains and potatoes typically receive aerial insecticide applications. Prior to the study, sites were randomly located in shallow waterways adjacent to either small grain or potato fields. The waterways were either drains that contained irrigation water that had drained off a field or canals that contained water being delivered to a field (the source of most canal water was Tule Lake sump). Sites were located at randomly selected distances (between 260 and 1,600 ft) along a waterway. Prior to the study, 176 sites (MacCoy, 1994) were located adjacent to small grain fields, and 66 next to potato fields, reflecting the relative acreage of the two crops.

Chemical applicators in California must submit a Notice of Intent (NOI) to the local County Agricul-

tural Commission Office 24 hours prior to a restricted chemical application. Application must be done within a 4-day period. Monitoring at a site was to begin when an NOI was submitted for that field, with the 24-hour period prior to application serving as a pre-application reference. Monitoring at each site included water quality (temperature, specific conductance, dissolved oxygen, and pH), chemical deposition samplers, and water samples for total ammonia analysis. *In situ* bioassay tests with *Daphnia* were done at all sites monitored. Because the actual spray date within the 4-day window was not known until after it had occurred, *Daphnia* bioassay tests and deposition samplers were replaced every 24 hours until information was obtained that indicated an application had occurred or been missed.

NOI information alone did not provide sufficient notification of upcoming insecticide applications. Despite monitoring 44 sites adjacent to small grain fields, many on multiple days, no sites were actually monitored during a disulfoton application. Methamidophos application monitoring near potato fields during August included obtaining specific information directly from cooperative growers and chemical applicators regarding plans to spray a field. Subsequently, a total of 27 sites adjacent to potato fields were monitored, 15 selected at random and 12 based upon reliable pre-application information. When sufficient pre-application information about a field could be obtained, mallard duckling *in situ* tests were begun on spray day for that field, and pre- and post-spray water samples were collected from the site for pesticide analysis. Six potato field applications were monitored with duckling tests and water-sample collections.

Pesticide deposits onto the edge of the field and drift to the waterway were monitored with deposition samplers, using methods similar to those described by Tome and others (1990, 1992). Water sites had duplicate deposition samplers, each placed approximately 3 ft on either side of the bioassay cages. A single deposition sampler was placed at the edge of the field to document that the crop was sprayed to the edge. Distance from field edge to the waterways averaged 98 ft (range 7-130 ft). Deposition samplers were in place for 24 hours and then collected. Individual samplers were placed in 40-mL amber scintillation vials and frozen before shipment to the USFWS PACF for resi-

due analysis. Laboratory analyses were performed using methods described by USFWS (1989).

Water-quality measurements (dissolved oxygen, pH, water temperature, and specific conductance) were taken when *in situ* test organisms were set out and picked up.

Water samples for total ammonia analysis were collected on the last day that bioassays were done at a site. During the methamidophos spray season, a total of 26 water samples for organophosphorus and carbamate pesticide analysis were collected at primary sampling sites 2, 3, 5, 7, 9, 11 and from six waterway sites after aerial methamidophos applications (the six sites where both *Daphnia* and duckling tests had been done). A water sample was collected in a chemically cleansed 1000mL amber bottle. The pH of the water sample was adjusted, if necessary, to a range of 6.5 to 7.3 with 70 percent nitric acid to stabilize any methamidophos in the water. In addition, quality assurance water samples spiked with methamidophos were submitted using water collected from site 15 (both pH unadjusted and pH adjusted to neutral) and distilled water. Samples were kept at 4°C until analysis at PACF (U.S. Fish and Wildlife Service, 1989).

The *in situ* and reference tests for *Daphnia* and ducklings were done using methods similar to those previously described, except that *Daphnia* tests were placed at a site in the evening and collected after 24 hours, and duckling tests were placed out just prior to sunrise and collected approximately 8 to 10 hours after spraying (Moore, 1993).

## MONITORING THE TRANSPORT OF ACROLEIN

During July 1992, over 100 applications of acrolein were scheduled in the area around Tule Lake (Jerry Pile, Tulelake Irrigation District, written commun., 1992). Concentrations of acrolein downstream of one application point were monitored between July 13 and 15 to determine if measurable levels of acrolein were being transported to drains that can enter the Tule Lake NWR. The presence of acrolein in the water was determined by chemical analysis in the field. Periodic measurements of acrolein concentration were used to determine herbicide levels and period of exposure at different locations along the flow path. *Daphnia* and

fathead minnows were exposed to treated water in the channels before, during, and after the application to evaluate the level of toxicity in downstream water.

The field analysis involved a colorimetric reaction with dinitrophenylhydrazine and quantification with a portable colorimeter. The instruments and reagents for the field analysis were provided by the Magna Corporation, formulators of acrolein. Duplicate samples collected at each downstream location were analyzed by the NWQL for confirmation of the field analysis. Acrolein identification at the NWQL was confirmed by analyzing standard reference materials under the same conditions as the samples, comparing retention times and mass spectra (Donna L. Rose, U.S. Geological Survey, written commun., 1993).

The acrolein application point was located in the J-7 canal (fig. 2) just north of State Highway 39 above the town of Tulelake, California. The canal is a narrow, wadable ditch with several open check dams along the monitored reach. Water flow was measured at 5.1 ft<sup>3</sup>/s at site A2, 0.6 mi downstream of the application point, 1 hour before the application using standard current meter methods (Buchanan and Somers, 1969). No water diversions or inputs into the J-7 canal were observed below the application point, and flow appeared to be steady throughout the monitoring period. Water flowed south in the canal for 2.0 mi downstream of the application point before entering the 44-drain. Very little or no flow was observed in the drain upstream of the canal. The water continued to flow south another 0.35 mi in the drain, where it was pumped into the N canal. The volume of water flowing in the N canal was much larger than the volume pumped from the drain and flowed westward. During the monitoring period, water was not being diverted from the N canal into Tule Lake, although some water from the N canal was entering Tule Lake through leaks in a gated diversion about 0.6 mi west of the 44 drain and 3 mi downstream of the acrolein application point.

Seven sites were chosen for sample collection, and *in situ* bioassay tests were done at four of those sites (fig. 2). On July 12, the day before the monitored application, the first of a series of staggered 24-hour bioassays was begun. Screened cages holding *Daphnia* and fathead minnows were placed at site A2 in the J-7 canal, A4 in the 44 drain, and A6 and A7 in the N canal. The first bioassay was completed and a new



bioassay begun a few minutes before the acrolein application was begun on July 13 at 9:30 a.m. A third bioassay was begun 2 hours after the application, and a fourth was begun 24 hours after the application.

Acrolein applications are preceded by hazing: a small amount of acrolein is released for a brief period to warn or scare away fish from the impending full release. The hazing lasted about 12 minutes. The full application was begun at 9:44 a.m. when approximately 1 gal of the herbicide was injected under pressure into the canal over a period of 50 minutes. This application was designed to result in an instream concentration of approximately 9 mg/L immediately downstream of the application point.

Water sampling began during the acrolein injection. The first samples were collected every 15 min-

utes at site A2. After several hours of monitoring, sampling was continued at sites farther downstream, with occasional samples collected at various locations all along the monitored reach. Fifty-two field tests were done over the monitoring period, and the results were used to select 13 samples for laboratory analysis.

### SAMPLE COLLECTION AND EVALUATION OF TRACE ELEMENTS IN RESIDENT BIOTA

Bird eggs were collected by hand in May, June, and July of 1990, 1991, and 1992 in the Lower Klamath NWR at locations described by MacCoy (1994). All eggs were placed in egg cartons, chilled on ice in the field, and refrigerated upon returning to the lab. Within 48 hours of collection, the egg contents were inspected for gross deformities if embryos were present. Egg contents were then placed in chemically cleansed glass jars and frozen.

Fish were collected at the beginning and end of the field season (June and September or October) in 1991 and 1992. Collections were made by seining, dip netting, and electroshocking. The fish were sorted by species and age (juvenile and adult) and placed in sterilized bags. Samples were placed on ice in the field and frozen at the end of the day.

Dip nets were used to collect waterboatmen and backswimmers. Samples were placed in sterilized bags, placed on ice, and frozen the same day. Blue-green algae were collected using an 80- $\mu\text{m}$  mesh plankton net with about a 24-in. opening. Canal or drainwater was allowed to flow through the net for several minutes until at least 10 g of material were collected. The algae were placed in chemically cleansed glass vials, placed on ice, and later frozen.

Analyses were performed by Environmental Trace Substances Research Center, Columbia, Mo. and Hazelton Laboratories America Inc., using methods described by USFWS (1990).

### SAMPLE COLLECTION AND EVALUATION OF ORGANOCHLORINE RESIDUES IN RESIDENT BIOTA

Bird eggs were collected by hand, and fish were collected using seines and dipnets. Chironomids and leeches were collected using a petite Ponar grab sam-

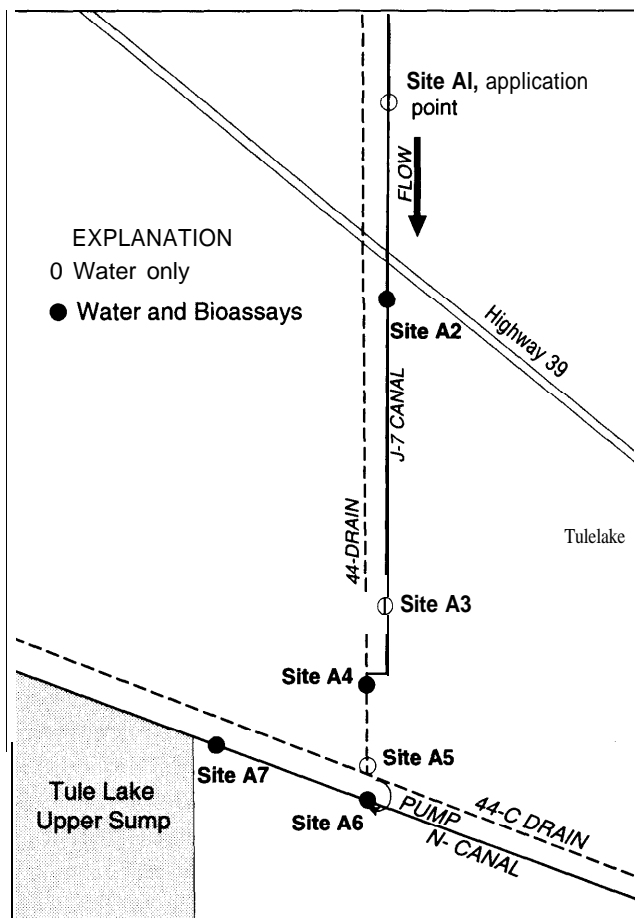


Figure 2. Location of acrolein monitoring sites, July 13-15, 1992, Klamath Basin.

pler. Sediment samples were washed through a 522- $\mu$ m mesh sieve, and the invertebrates were placed in chemically cleansed glass jars, placed on ice, and frozen at the end of the day.

Organochlorine residue analyses were performed by Hazelton Laboratories America Inc. (1991), and Mississippi State University Chemical Laboratory (1991). Eggshell thickness was determined using micrometer measurements as described by USFWS (1990).

## **ANALYSIS FOR WATERFOWL CHOLINESTERASE ACTIVITY**

In 1991 and 1992, wild waterfowl carcasses were opportunistically collected during avian botulism die-offs and their brains analyzed for AChE activity to determine if they had experienced exposure to organophosphorus or carbamate pesticides. Botulism die-offs typically occur during late August or early September of each year, which generally does not coincide with the major pesticide-use period of the year (June-August). Only fresh carcasses or birds that were moribund upon collection were used for these analyses; carcasses were frozen until the brain was prepared for analysis.

## **AQUATIC COMMUNITY SURVEYS**

### **Benthic Macroinvertebrate Surveys**

In 1990, benthic macroinvertebrate samples were collected at 2 sites in Clear Lake, 11 sites in the Tule Lake upper sump, 4 sites in the Tule Lake lower sump, 3 main irrigation waterways that flow into Tule Lake (J canal, N canal, and the South Side drain), 2 sites in the Lost River, 2 sites in the Lower Klamath NWR (in Units 4 and 9), and in the Klamath Straits drain (fig. 1). Each site was sampled once during July and August of 1990.

In 1991, benthic macroinvertebrate samples were collected at primary sampling sites 1, 2, 3, 5, 7, 9, 11, 12, and 13. Each site was sampled once during June, July, and August 1991. In addition, sites 4, 6, and 10 in the Tule Lake upper sump were sampled once in August 1991.

Water-quality measurements were taken at each site prior to sediment collection and included water temperature, dissolved oxygen, specific conductance,

and pH. Sediment samples were collected with a petite Ponar grab sampler using methods described by Britton and Greeson (1987). Three replicate sediment sample grabs were collected at each site during each sampling session. Samples were screened through a 533- $\mu$ m mesh sieve and then placed in wide-mouth containers with 10-percent formalin solution containing Rose Bengal biological stain. Samples were stained to aid distinguishing invertebrates from organic debris. Samples were then rinsed with tap water using a 250- $\mu$ m mesh sieve and preserved in 70-percent ethanol.

Each replicate sample was processed separately throughout the sorting and identification procedures. A binocular dissecting scope at 7 to 10X magnification was used to sort and identify organisms. In most cases, all organisms in a sample were counted and identified. A few sediment samples had a very large number of a single taxa (oligochaetes). In those instances, the oligochaete count was based upon a density per volume estimate using methods recommended by Britton and Greeson (1987). Due to the large number of sediment samples collected during this study, identification to the species level was not practical. Taxa were reported to the family level for Hirundinea, Gastropoda, and Insecta. Groups that require dissection or slide mounting for precise identification were generally reported to order, class, or phylum. Identification was done using taxonomy described by Mason (1968), Pennak (1978); and Merritt and Cummins (1984).

### **Water-Column Invertebrate Surveys**

Invertebrates were surveyed twice a month during June, July, and August 1992 at the 10 primary sites where bioassays were done (sites 1, 2, 3, 5, 7, 9, 11, 12, 13, and 15). Collections were made by duplicate draws of a Student's plankton net (153- $\mu$ m mesh net and 147- $\mu$ m stainless steel mesh plankton bucket) through the entire water column. Handling and subsampling procedures were based on methods described by Plafkin and others (1989) for rapid bioassessment of macroinvertebrates. Annelids were identified to class, crustaceans were identified to order, and mollusks and insects were identified to family using taxonomy described by Merritt and Cummins (1978) and Pennak (1978).

## Fish Community and Health Surveys

Drainwater sites were surveyed to evaluate fish assemblages along the drainwater system. Fish were surveyed in October 1991 and in June and September 1992 at two sites on the Lost River (one below Clear Lake dam and the other below Anderson Rose diversion dam), at site 4 in the northeast corner of Tule Lake (below site 3), and at drainwater sampling sites 3, 7, 11, and 12. Survey procedures were based upon survey methods for rapid bioassessment of fish communities (Plafkin and others, 1989). Collections were made with beach seines using similar collection methods at all sites. The standard collection method was to seine two 330-ft sections of the site, including the shoreline. This method could be applied fairly uniformly at all sites and typically produced several hundred fish. However, in September 1992, site 7 was seined four times to yield a total of only 55 fish. Fish were sorted by species and size, counted, and examined for external abnormalities. The presence of any endangered sucker species was recorded and the fish released.

The fish collections were evaluated by an Index of Biological Integrity (IBI). Fish IBI's typically evaluate the quality of aquatic resources by comparing a sampling site to unimpacted reference sites (Miller and others, 1988; Plafkin and others, 1989). In this study, the upper Lost River site had been selected as a reference site to be surveyed in June and September 1992. One week prior to the June survey, the BOR conducted extensive salvage operations for suckers below Clear Lake dam because of the critically low water conditions due to drought. It is unknown how the salvage operation affected fish species diversity in the downstream survey conducted in June. In addition, that site could not be resurveyed in September because the upper Lost River was reduced to small stagnant pools. As a consequence, results of the fish biosurveys were evaluated by a simplified IBI (table 4) developed to assess a northern California irrigation water system that does not utilize reference site information (Miller and others, 1988). This simplified IBI is used to evaluate the site based upon observed species composition and information about historical fish communities in the waterway being sampled. For this study, the Lost River sites were evaluated by metrics 1 through 6 (table 4) because salmonids were historically present. Because all other survey sites were within constructed waterways, they were more conser-

vatively evaluated by only metrics 1 through 4, which presumes salmonids were never present. A field fish health assessment was done to provide an additional indication of how resident fish populations were responding to the drainwater environment (Littleton, 1993).

## Frog Call Surveys

Frog calls were surveyed during the May-July breeding seasons in 1991 and 1992 to assess the distribution and abundance of frogs on Tule Lake and Lower Klamath NWR's (Boyer, 1993). The frog call methodology was selected because of the large area to survey (Karns, 1986), and aural transect methods have been shown to provide information about relative frog abundance with moderate amounts of time and personnel when compared to other sampling techniques (McDiarmid, 1992).

All shorelines of the refuges accessible by vehicle were surveyed for calling male frogs for 8 weeks. The shorelines were divided into transects of equal length, and random listening points at 1-mi intervals along the transects (Boyer, 1993; MacCoy, 1994, figs. 2 and 3) were surveyed weekly.

## WATER QUALITY AND TOXICITY OF IRRIGATION DRAINWATER

### WATER QUALITY AT PRIMARY SAMPLING SITES

#### Dissolved Oxygen

The EPA's minimum value criterion for ambient dissolved-oxygen concentrations in warmwater habitat is 5.0 mg/L for early life stages and 3.0 mg/L for other life stages (U.S. Environmental Protection Agency, 1986b). For the minimum value criterion to be met, dissolved-oxygen concentrations cannot drop below these values at any time. The State of California has adopted the EPA criteria of 5 mg/L for their Inland Surface Water Plan (California State Water Resources Control Board, 1991).

The range of dissolved-oxygen values measured during periodic morning visits to the primary sampling sites in 1991 and 1992 is presented as boxplots in figure 3. The median dissolved-oxygen value from individual sites was less than the early life stage criterion

**Table 4.** Metrics and scoring criteria for the Index of Biological Integrity (IBI), Klamath Basin, (Miller and others, 1988)

[>. greater than value shown <; less than value shown]

Klamath irrigation drainwater (IBI)			
Metric	Scoring criteria		
	5	3	1
Percent native fishes (by number) ..r.....	>68	35-67	<34
Percent native fish se.....	>68	35-67	<34
Total fish abundance.....	abundant	common	rare
Total fish species:			
First and second order streams.....	3	+ 2	0-1
Third and higher order stream.....	6+	3-5	0-
If salmonids present or historically present: .....			
Juvenile salmonid abundance .....	abundant	common	rare
Sculpin abundance .....	abundant	common	rare

Abundance ratings:

- Abundant- present in all suitable habitats in large numbers
- Common - present in most suitable habitat
- Rare - only occasionally captured or observed

Aquatic Habitat Integrity Classes (parenthetic ranges refer to situations where salmonids were not present):

IBI score	Integrity class	Characteristics
32-35 (18-20)	Excellent .....	Comparable to pristine conditions, exceptional assemblage of species.
26-30 (14-16)	Good.....	Decreased species richness, native species present.
20-24 (11-12)	Fair.,.....	Intolerant and sensitive species absent; skewed trophic structure. Top carnivores and expected species absent or rare; omnivores and tolerant species dominant.
11-18 (7-9)	Poor.....	
<11 (<7)	Very poor.....	Few species and individuals present; non-native species dominant.

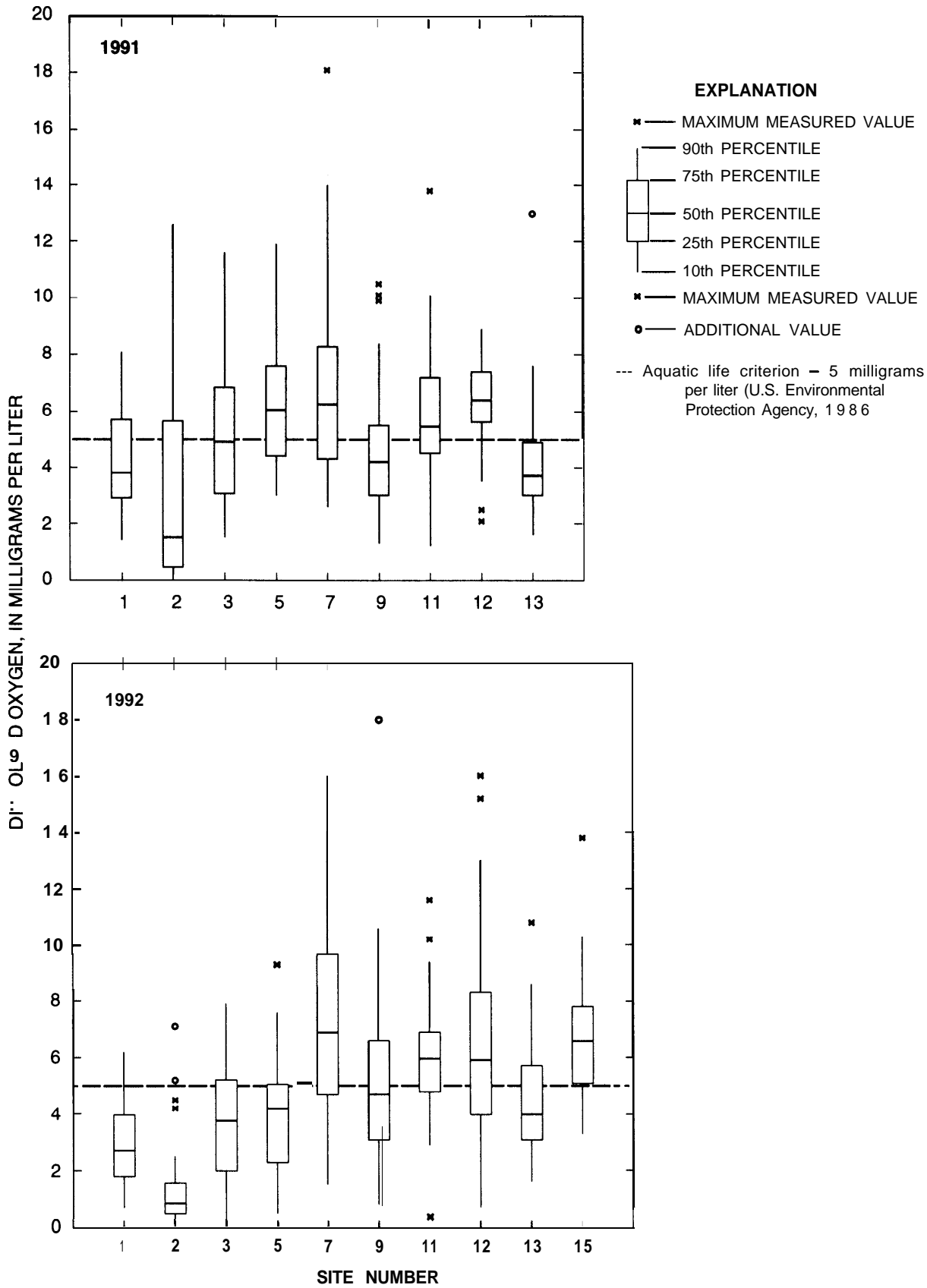
in 5 of the 9 sites monitored in 1991 and in 6 of the 10 sites monitored in 1992. These sites were located upstream of agricultural drains (sites 1 and 2) within drains (sites 3, 5, and 9), and below Tule Lake (site 13). The sites with the lowest medians in both years were sites 1 and 2. Site 7 on irrigation drain 101-B had the highest median values in 1991 and 1992.

Continuous measurements throughout a 24-hour period give a much more complete description of dissolved oxygen in the environment because the full range of daily fluctuation and the length of time that dissolved oxygen is high or low are recorded. In 1991 and 1992, continuous water-quality monitors were deployed at selected sites. Dissolved-oxygen concentrations tended to fluctuate between very high values during daylight hours and much lower values at night,

reaching their lowest levels in the early morning hours. Examples of these diurnal fluctuations are shown by MacCoy (1994).

During August 1991, continuous 24-hour dissolved-oxygen measurements were obtained at eight sites. Concentrations ranged from 0 to 16. mg/L and dropped below the 5. mg/L criterion at four sites (7, 9, LR5, and LR6). Dissolved oxygen was below the 5.0mg/L criterion from 0 to 46 percent of the time.

Dissolved-oxygen data from the 96-hour continuous measurements obtained in 1992 are summarized in figure 4. Values ranged from 0 to 19. mg/L and conditions in which dissolved-oxygen concentrations were below the early life criterion existed at least part of the time at all sites (table 5). The criterion was exceeded at upstream sites 1 and 2 more than at any



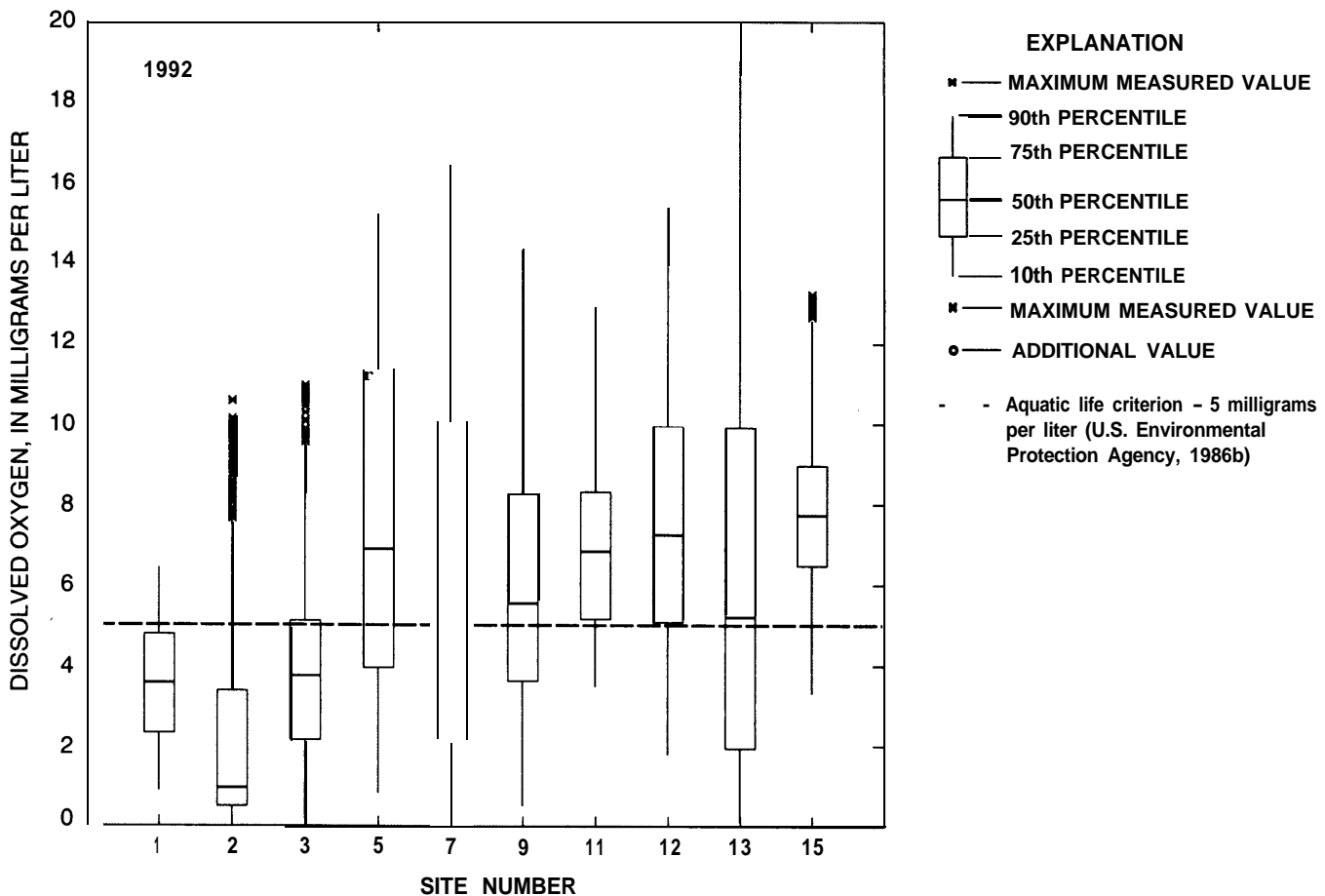
**Figure 3.** Concentration of dissolved oxygen at primary sites during periodic monitoring in 1991 and 1992, Klamath Basin. Aquatic life criterion is 5 milligrams per liter (U.S. Environmental Protection Agency, 1986b).

others. Critically low dissolved-oxygen concentrations were a problem at virtually all sites monitored during 1991 and 1992, with the exception of site 15 at Upper Klamath Lake.

### pH, Temperature, and Specific Conductance

Because of the relatively large biomass of photosynthesizing and respiring organisms in eutrophic systems such as the Upper Klamath River and Lost River Basins, the pH is controlled largely by biological processes. Diel patterns of photosynthesis cause pH to rise and fall along with dissolved-oxygen concentrations (MacCoy, 1994). The EPA criterion for pH for the protection of freshwater aquatic life is a range between 6.5 and 9.0 pH units (U.S. Environmental Protection Agency, 1986b).

In 1991 and 1992, more than 760 periodic measurements of pH were made during morning visits to the primary sampling sites. The percentage of measurements that exceeded pH 9 varied from 0 to 49 percent in 1991 and from 0 to 65.2 percent in 1992. The pH criterion was exceeded at some time during both years at all primary sampling sites, but most frequently at sites 11, 12, and 15, upstream and downstream of agricultural drains. These sites also had the highest median pH of all the primary sampling sites. The criterion was exceeded less than 7 percent of the time in the lower reaches of the Lost River and agricultural drains, but between 29 and 67 percent of the time at Tule Lake and Lower Klamath refuges and 55.6 percent at site 15 in Upper Klamath Lake. Median pH in 1991 and 1992 at the primary sampling



**Figure 4.** Concentration of dissolved oxygen at primary sites during continuous monitoring in 1992, Klamath Basin. Aquatic life criterion is 5 milligrams per liter (U.S. Environmental Protection Agency, 1986b).

sites was similar (pH 8.4 and 8.1, respectively) despite differences in water flow patterns between the two years. The record of pH during continuous water-quality monitoring is similar to measurements described above. The criterion was exceeded the

greatest number of times at sites 11, 12, 13, and 15, whereas water at sites located on drains was rarely above pH 9 (table 5).

In 1991, periodic measurements of temperature at the primary sampling sites ranged from 11 .0 to

**Table 5.** Percentage of time that dissolved-oxygen concentrations were less than 5 milligrams per liter and that pH was greater than 9 during periods of continuous monitoring at selected primary sites in 1992, Klamath Basin [mg.L, milligram per liter]

Site no. (fig. 1)	Period of monitoring	Total number of hours monitored	Percent of time dissolved oxygen less than 5 mg/L		Percent of time pH greater than 9	
			Each week	Each site	Each week	Each site
1	July 29 to Aug. 2	96.3	97	79	0	0
	Aug. 19-23	96.3	60		0	
2	June 24-28	96.3	68	83	6	2
	July 15-19	94.5	89		0	
	Aug. 5-9	94.5	100		0	
	Aug. 26-30	70.5	74		0	
3	June 24-28	95.0	84	73	0	0
	July 15-19	95.0	78		0	
	July 22-26	96.3	65		0	
	Aug. 12-16	93.8	59		0	
	Aug. 19-23	96.3	80		0	
5	July 1-5	96.3	34	36	0	0
	July 29 to Aug. 2	93.5	43		0	
	Aug. 26-30	45.0	33		0	
7	June 24-28	96.3	36	44	0	0
	July 15-19	95.0	44		0	
	Aug. 12-16	95.0	61		0	
	Aug. 19-23	89.3	53		1	
9	July 1-5	94.8	36	41	0	4
	July 29 to Aug. 2	96.0	70		0	
	Aug. 26-30	90.8	15		13	
11	July 1-5	96.3	15	22	34	78
	July 22-26	96.3	52		100	
	Aug. 12-16	95.5	0		100	
12	June 24-28	96.3	30	24	29	70
	July 15-19	95.5	9		50	
	Aug. 5-9	94.8	50		100	
	Aug. 26-30	96.3	7		100	
	July 29 to Aug. 2	94.8	56	49	21	48
13	Aug. 19-23	96.3	41		74	
	July 1-5	96.3	0	4	100	96
15	July 22-26	96.3	1		100	
	Aug. 12-16	92.5	12		88	

28.0°C, with a mean of 18.8°C. In 1992, maximum temperatures were slightly higher, up to 3.1°C, but the 1992 mean of the sites monitored both years was about one degree cooler. Ambient temperatures at the primary sampling sites did not significantly increase or decrease as water moved downstream through the irrigation system. Because the majority of periodic measurements were taken in the morning hours when temperatures were at or close to daily minimums, average daily temperatures and maximum daily temperatures may be higher than reported here. Data from the continuous monitors in 1991 and 1992 averaged 23.0 and 21.8°C, with ranges of 17.1 to 28.8 and 13.3 to 31.3°C, respectively (MacCoy, 1994).

In 1991, specific conductance measurements ranged from 117 to 2,440  $\mu\text{S}/\text{cm}$  and had a mean of 575  $\mu\text{S}/\text{cm}$ . In 1992, values were somewhat lower with a range of 102 to 1,870  $\mu\text{S}/\text{cm}$  and a mean of 485  $\mu\text{S}/\text{cm}$ . Mean specific conductance was lowest in water-supply canals above irrigated land and increased at sites located on agricultural drains. Specific conductance at Tule Lake sampling sites was variable. This variability reflects the different sources of water entering the lake and indicates that the lake is not well mixed and that water quality is subject to local inputs. The highest mean conductance and the highest individual measurements were in the Klamath Straits drain at Lower Klamath NWR (site 12) in 1991. Water at this site was composed of agricultural drainwater and drainwater from refuge land that had probably been recirculated for irrigation a greater number of times. In 1991 water in the Klamath Straits drain below the refuge (site 13) had lower conductance than on the refuge at site 12. This was most likely due to additions of better quality drainwater from land irrigated with water diverted from the Klamath River and delivered through the ADY canal. In 1992, mean specific conductance was reduced at site 12 due to the unavailability of Tule Lake water and the increased use of irrigation water from the Klamath River. With the exception of site 12, there was little difference in mean specific conductance at the primary sampling sites between 1991 and 1992 despite the changes in water flow during the two irrigation seasons.

### Major Ion Chemistry

In 1992, water at 17 sites was monitored for major ion concentrations three times between July and

September. The water entering the irrigation system had low concentrations of dissolved salts. Mean chloride concentrations averaged 4.5 mg/L at site 15 and 5.7 mg/L at site 1. Sulfate concentrations averaged 3.7 mg/L at site 15 and 12.4 mg/L at site 1. These values are near or below lower 25th percentile of baseline values for western U.S. rivers derived from the National Stream Water Quality Accounting Network (NASQAN) (Smith and others, 1987). Chloride concentrations increased as water moved through the irrigation system. Concentrations at site 9 and several sites in Tule Lake increased approximately fivefold compared to upstream reference sites. The highest concentrations were between the baseline 50th and 75th percentile, above the median but not unusually high. Sulfate concentrations, on the other hand, rose over tenfold at many sites, and the mean concentrations at 6 of the 17 sites were over the baseline's 75th percentile.

Inputs of sulfate from agricultural sources or biogeochemical processes in the canals and drains may be enriching drainwater with sulfates. Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is a common mineral associated with evaporative lakes, such as the historic Tule Lake. Soils in the study area derived from lacustrine deposits could potentially contribute sulfates to drainwater.

### Nutrients

#### Nitrogen

During diel water-quality monitoring in August 1991, nutrients were monitored about every 4 hours over a 24-hour period at nine sites. Single samples were also collected at sites 2, 3, and 5 during the same time period. The majority of the nitrogen was in the form of organic compounds (fig. 5), except at site 5 where nitrogen was about evenly divided between nitrate and organic forms. Organic nitrogen was also the dominant form of nitrogen measured in 1992 at the primary sampling sites and at additional Tule Lake sites that were monitored four times during the summer (fig. 6). The one exception, as in 1991, was site 5, located on the 101-C drain, where nitrate concentrations (1.3 mg/L) exceeded all other forms. Concentrations of dissolved organic nitrogen were generally highest in drains, Tule Lake, and the Lower Klamath Lake refuge (fig. 6).



Concentrations of dissolved inorganic nitrogen directly available for plant assimilation (nitrate plus ammonia) ranged from 0.07 to 1.37 mg/L in 1991 and from 0.035 to 3.65 mg/L in 1992. Mean concentrations at sites 1 and 2 above Tule Lake sump, in all return flows, and at sites in Tule Lake sump were at least 0.175 mg/L. Return flow sites had relatively high individual measurements of available nitrogen compared to upstream sites, indicating a source of additional nitrate and ammonia within the irrigated lands. The highest average available nitrogen (2.05 mg/L) was observed at site 5, with individual measurements of 3.54, 2.26, and 0.36 mg/L available nitrogen in July, August, and September, respectively. In contrast, water from Upper Klamath Lake (site 15) and sites downstream of Tule Lake sump (sites 11, 12, and 13) had much lower available nitrogen concentrations.

This may have been due to increased nitrogen utilization by primary producers that occurred in impounded waters, depleting concentrations in water and incorporating it in plant material.

Average nitrogen concentrations at many of the sites were at or above levels characteristic of eutrophic lakes and streams. The means for all measurements at all sites were 0.41 and 0.48 mg/L for 1991 and 1992, respectively, which fall within the range of most eutrophic systems. Mean total nitrogen levels in lakes classified as eutrophic have been reported to be about 0.2 mg/L (Rast, 1981).

Ammonia concentration was monitored at the primary sampling sites periodically throughout the 1991 and 1992 irrigation seasons, during the 1991 diel monitoring, and at selected sites in Tule Lake in 1992 (fig. 7). Ammonia was detected at all monitoring sites

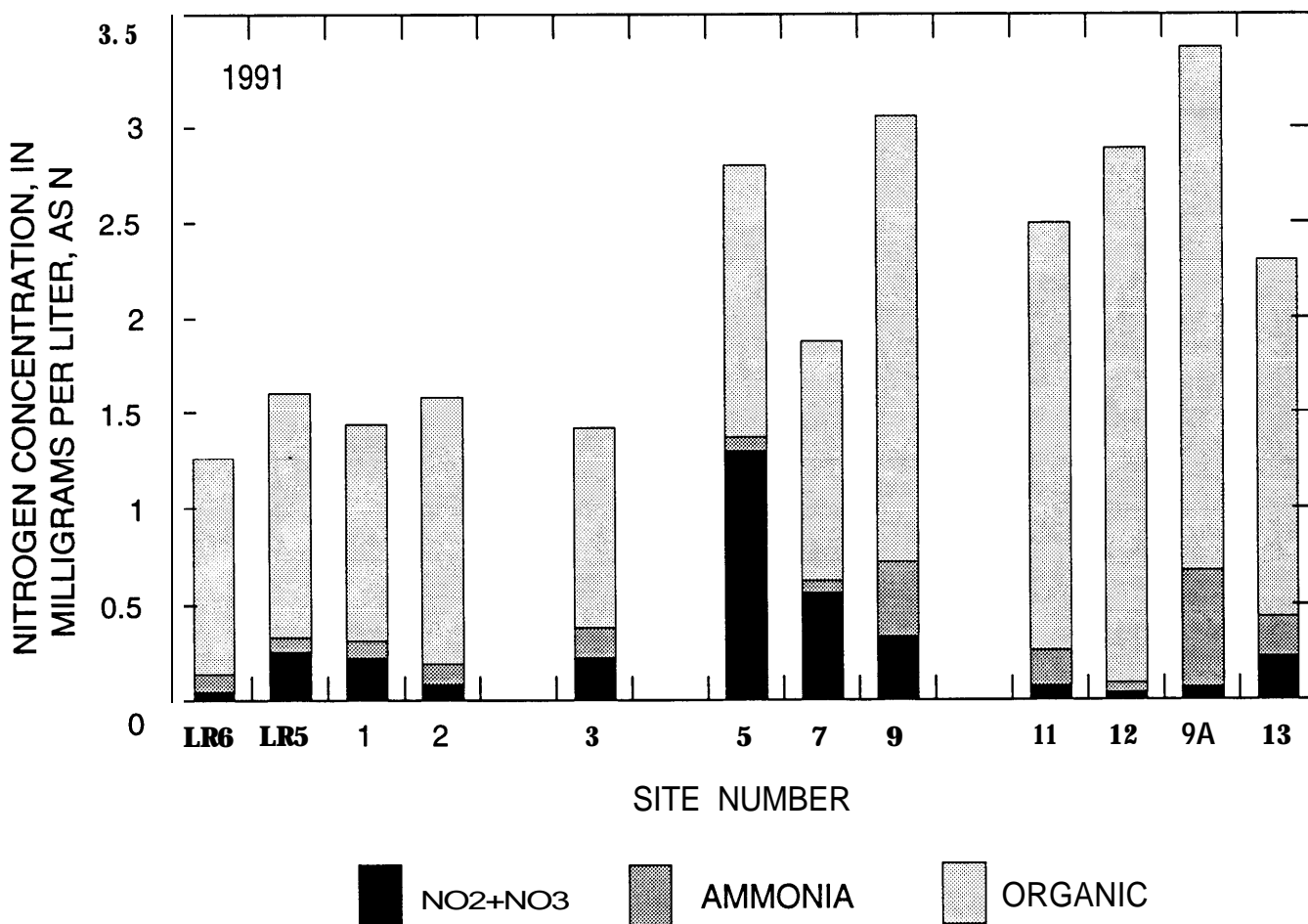


Figure 5. Mean total nitrogen concentrations in 1991, Klamath Basin.

in both years. High concentrations of ammonia measured in the study area appear to be related to high concentrations of dissolved organic nitrogen and environmental conditions conducive to ammonia production by microorganisms. There were no consistent differences between ammonia concentrations in irrigation drainwater and concentrations at upstream reference sites. Although ammonia concentrations were relatively high at site 9 in the 102 drain, concentrations at other drains (sites 5 and 7) were lower than some upstream reference sites (sites 1 and 2).

Ammonia concentrations at site 9 and site 10 nearby in Tule Lake were consistently high, and both sites had the highest concentrations of organic nitrogen measured at the primary sampling sites. Site 9a, located on the Lower Klamath NWR, was also relatively high when measured in 1991. This site was located on a management unit that had been flooded

for at least several years and had very little or no recirculation of water. Reductive deamination of organic nitrogen compounds by microbes in anaerobic sediments (Patrick, 1982) could contribute to the high ammonia concentrations observed at these locations.

Dissolved ammonia exists in both ionized and un-ionized forms. Un-ionized ammonia is significantly more toxic to fish than the ionized form; EPA criteria for the protection of aquatic organisms are based on the concentration of the un-ionized fraction of the total ammonia content (U.S. Environmental Protection Agency, 1985A, 1986b). The relative amounts of ionized ( $\text{NH}_4^+$ ) and un-ionized ( $\text{NH}_3$ ) ammonia in solution are a function of temperature, Ph, and salinity. As temperature and Ph increase, the fraction of ammonia in the un-ionized form also increases. Temperature and pH also affect the toxicity of ammonia independent of the effect these factors

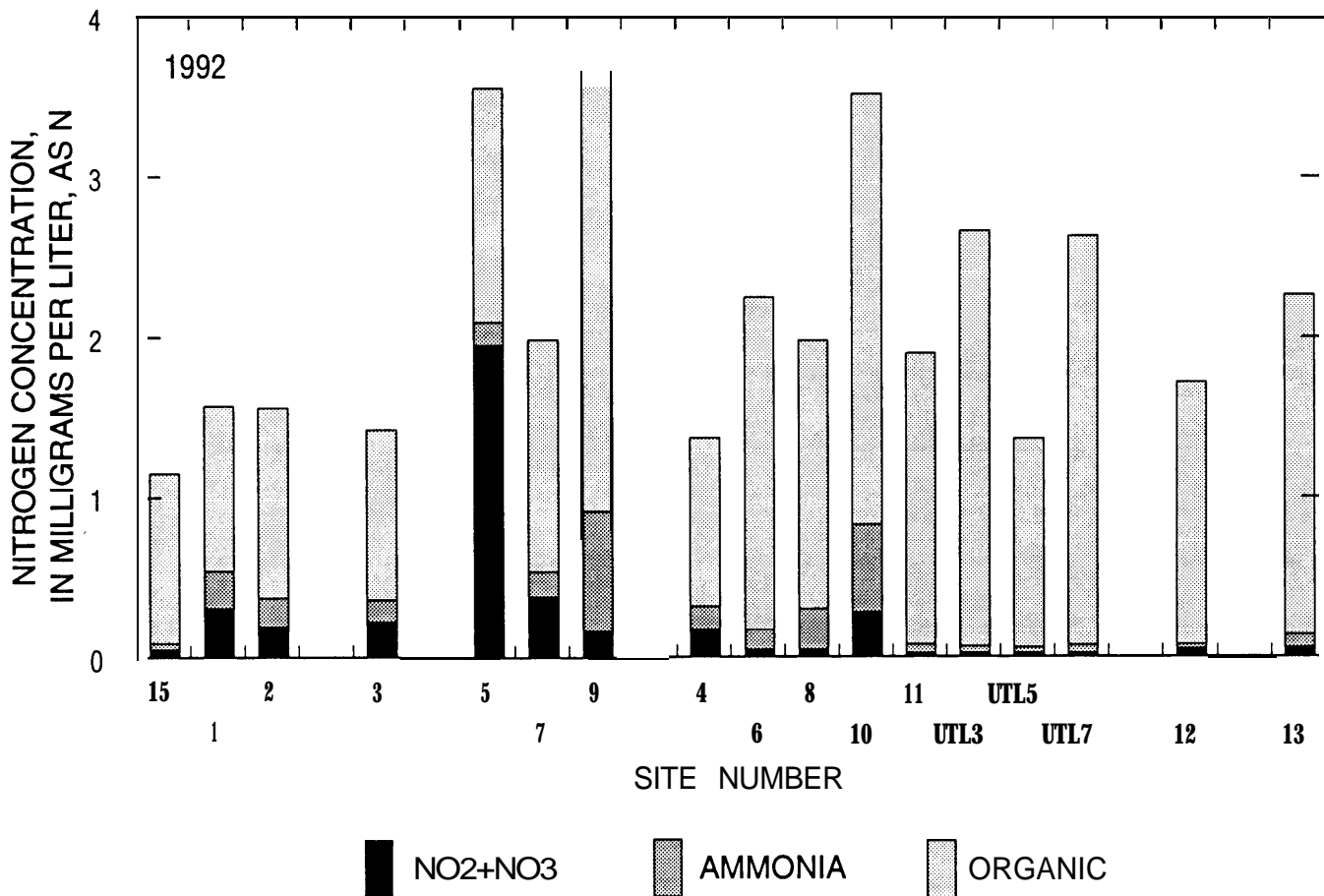


Figure 6. Mean total nitrogen concentrations in 1992, Klamath Basin.

have on ionization, and the toxic response of individual fish species is variable. The EPA criteria are based on empirical models that use toxicity data from a number of common fish species and are dependent on temperature, pH, and the presence or absence of coldwater fish species. Although not factors in EPA criteria, low dissolved-oxygen concentrations exacerbate ammo-

nia's toxicity, whereas long-term exposure to low concentrations of ammonia appear to decrease ammonia's toxic effects (U.S. Environmental Protection Agency, 1985a).

Table 6 lists the number of samples at each site with ammonia concentrations that exceeded the EPA 4-day ambient water-quality criteria for habitat without the presence of sensitive coldwater fish. Because most of the samples were collected at 1-week intervals, the values for ammonia concentration cannot be used to determine if EPA criteria were exceeded. However, the 4-day criteria provide a useful reference to assess toxic environmental conditions. Ammonia concentrations exceeded the 4-day criteria at 8 out of the 20 sites monitored. Sites with potentially toxic levels of ammonia were located all along the flow path, including water sources, agricultural drains, and receiving waters. The sites with the highest percentage of values above the criteria were sites 10 and 11 in Tule Lake sump. Sites with ammonia data for both 1991 and 1992 had similar concentrations in both years, except at site 13 where differences between years reflected differences in the source of irrigation water each year. Although ammonia was present at all sites, its toxicity was more a function of locally high pH and warm water temperature than of concentration. Site 15, for example, had the fourth lowest mean ammonia concentration, but the percentage of samples above criteria collected at that site (20 percent) was similar to site 9 (25 percent), which had the highest ammonia concentrations of all sites in 1992.

EPA 1-hour criteria, which represent acute toxic concentrations of ammonia, were exceeded at site LL46 (16 mg/L on the Tule Lake NWR leaselands. Ammonia concentrations at nearby sites were not nearly as high, and the single sample with a high concentration did not appear to represent widespread conditions in the area.

### Phosphorus

Dissolved total phosphorus concentrations (combined organic and inorganic phosphorus) ranged from 0.16 to 1.1 mg/L-P, (mg/L as phosphorus) with a mean value of 0.49 mg/L-P during the 1991 diel monitoring. Dissolved orthophosphate concentrations were only slightly lower at all sites, ranging from 0.1 to 1.0 mg/L-P, with a mean of 0.43 mg/L-P.

Most dissolved phosphorus appears to be in the form of orthophosphate and relatively little in organic

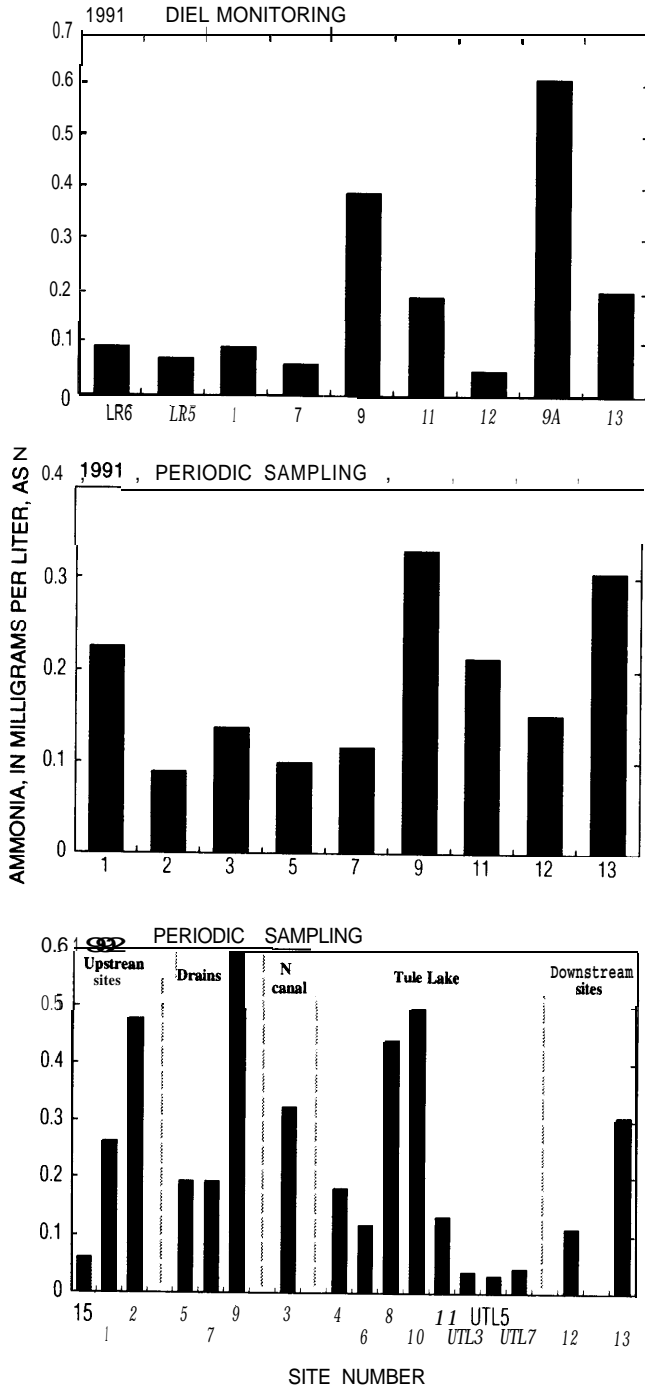


Figure 7. Mean ammonia concentrations in 1991 and 1992, Klamath Basin.

**Table 6.** Summary of water samples with ammonia concentrations greater than the 4-day criteria for protection of aquatic organisms without the presence of sensitive coldwater fish, Klamath Basin (U.S. Environmental Protection Agency, 1985a)

Site no. (fig. 1)	Number of samples analyzed		Number of values exceeding criteria		Percent of values exceeding criteria	
	1991	1992	1991	1992	1991	1992
LR-5	6		0		0	
LR-6	6		2		33	
	11	16	0	0	0	0
2	8	17	0	0	0	0
3	8	12	0	0	0	0
5	8	18	0	0	0	0
7	14	16	0	0	0	0
9	14	16	4	4	29	25
4		4		0		0
6		4		0		0
8		4		0		0
10		4		3		75
11	13	16		7	62	44
15		15		3		20
UTL-3		3		0		0
UTL-5		3		0		0
UTL-7		3		0		0
12	14	16	2	2	14	13
13	14	16	4	0	29	0
9A	7		7		100	

compounds. Dissolved phosphorus concentrations at sites 9 and 12 were significantly higher than at other sites (analysis of variance:  $p < 0.001$ ).

In 1992, mean dissolved phosphorus concentrations were lower than in 1991. Values ranged from less than the method reporting limit (less than 0.01) to 0.73 mg/L-P, with a mean of 0.24 mg/L-P. Mean total phosphorus levels at sites monitored in both 1991 and 1992 were 0.50 and 0.27 mg/L-P, respectively. Dissolved phosphorus concentrations in 1992 were very low in Upper Klamath Lake and increased to much higher levels downstream. Sites located in drains and downstream of drains tended to have the highest concentrations. Phosphorus concentrations within Tule Lake were highly variable. Locally dense mats of filamentous green algae were observed at times throughout the monitoring period in Tule Lake and may have assimilated a portion of the dissolved phosphate in some areas.

In 1992, nutrient data were collected periodically from the end of July to the beginning of September, and phosphorus levels appeared to decrease each month at all sites except site 13. The mean total phosphorus concentration for all sites was 0.32 mg/L-P in July, 0.26 mg/L-P in August, and 0.15 mg/L-P in September. The differences may be related to biogeochemical processes driven by changes in oxidation conditions or to enrichment from agricultural sources. Data available at this time are insufficient to clearly determine the cause of the observed trend.

The concentrations measured during this study are considerably higher than the concentrations found in most lakes considered eutrophic and are well into the range of hypereutrophic water bodies. About 95 percent of lakes classified as hypereutrophic in the Organization for Economic Cooperation and Development (OECD) eutrophication control studies had total phosphorus levels similar to or less than the Klamath studies mean 1991 value and about 70 percent had val-

ues at or below the 1992 mean (Rast, 1981). Phosphorus is common in igneous rocks (Hem, 1985), from which many of the soils in the predominantly volcanic basin are derived. The use of phosphate fertilizers in the study area is another potential source of phosphorus enrichment. Under oxidizing conditions, sediments tend to accumulate and store phosphorus compounds. In anoxic conditions, adsorbed orthophosphate is released to the water column where it is available for uptake by algae and other plants.

Nitrogen and phosphorus are assimilated and incorporated into typical aquatic algal and vascular plant tissue at a ratio of about 7: 1. Ratios lower than 7:1 indicate that an excess of phosphorus is available in the environment. The ratio of nitrogen and phosphorus in water samples collected during this study was below 7: 1 in 14 of the 17 sites sampled in 1992 (table 7), indicating that readily available phosphorus is abundant in the aquatic environment and is not limiting algal growth.

Site 15 at Upper Klamath Lake was the only site where phosphorus may have been limiting continued algal growth. Dense algal populations at site 15 may have taken up most available phosphorus, resulting in low concentrations in the water column.

#### Organic Carbon

Most of the organic carbon in water samples collected in 1992 was in the dissolved phase. Only a small fraction existed as particulate suspended material. Mean concentrations of dissolved organic carbon (DOC) are presented in figure 8. Mean concentrations from the study area are relatively high for most natural water bodies, which generally range from 0 to 30 mg/L (Wetzel, 1983). Drain sites 7, 9, and 13 were particularly high, with values ranging from 36 to 57 mg/L. Some individual measurements were more than 80 mg/L, values usually observed in sewage treatment plant effluent or drainage from peat marshes. DOC concentrations in Tule Lake were elevated midway between the upstream water sources and the drains.

These high concentrations of DOC represent an allochthonous (coming from outside the system) source of nutrients and chemical energy that could support increased microbial activity beyond the level that local primary production would allow. Increased

microbial activity affects water-quality conditions by consuming greater amounts of oxygen and contributing to the oxygen deficits common in the study area.

#### Pesticides

A total of 76 water samples were analyzed for 47 different pesticide residues (MacCoy, 1994). Eighteen samples were analyzed in 1991 and 58 in 1992. Fifty of the water samples had measurable concentrations of at least one pesticide. Sixteen different compounds (nine herbicides and seven insecticides) were detected and quantified in those samples (table 8). All pesticide concentrations were below acute toxicity values reported for aquatic organisms, listed in table 9.

Water collected from agricultural drains had a significantly higher frequency of pesticide detections when compared to sites upstream or downstream of Tule Lake than would have been expected by chance alone. A statistically significant frequency (57 percent) of all the herbicides detected in 1992 water samples occurred at return flow sites 3, 5, 7, or 9 (Chi square p value=0.0002). A significant frequency (65 percent) of all the insecticides detected in the 1992

**Table 7.** Ratios of mean available nitrogen ( $\text{NO}_3 + \text{NH}_4$ ) to mean dissolved-orthophosphorus concentrations in water samples collected in 1992, Klamath Basin

Site no. (fig. 1)	Nitrogen/phosphorus ratio
1	3.69
2	2.05
3	1.42
4	1.23
5	7.26
6	.42
7	1.57
8	.99
9	6.84
10	5.45
11	3.56
12	8.33
13	.46
15	16.77
UTL-3	6.04
UTL-5	.15
UTL-7	3.33

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4	<b>1.23</b>
5	<b>7.26</b>
6	.42
	1.57
8	.99
<b>9</b>	<b>6.84</b>
<b>10</b>	<b>5.45</b>
11	<b>3.56</b>
12	<b>8.33</b>
13	.46
15	<b>16.77</b>
UTL-3	<b>6.04</b>
UTL-5	.15
UTL-7	<b>3.33</b>

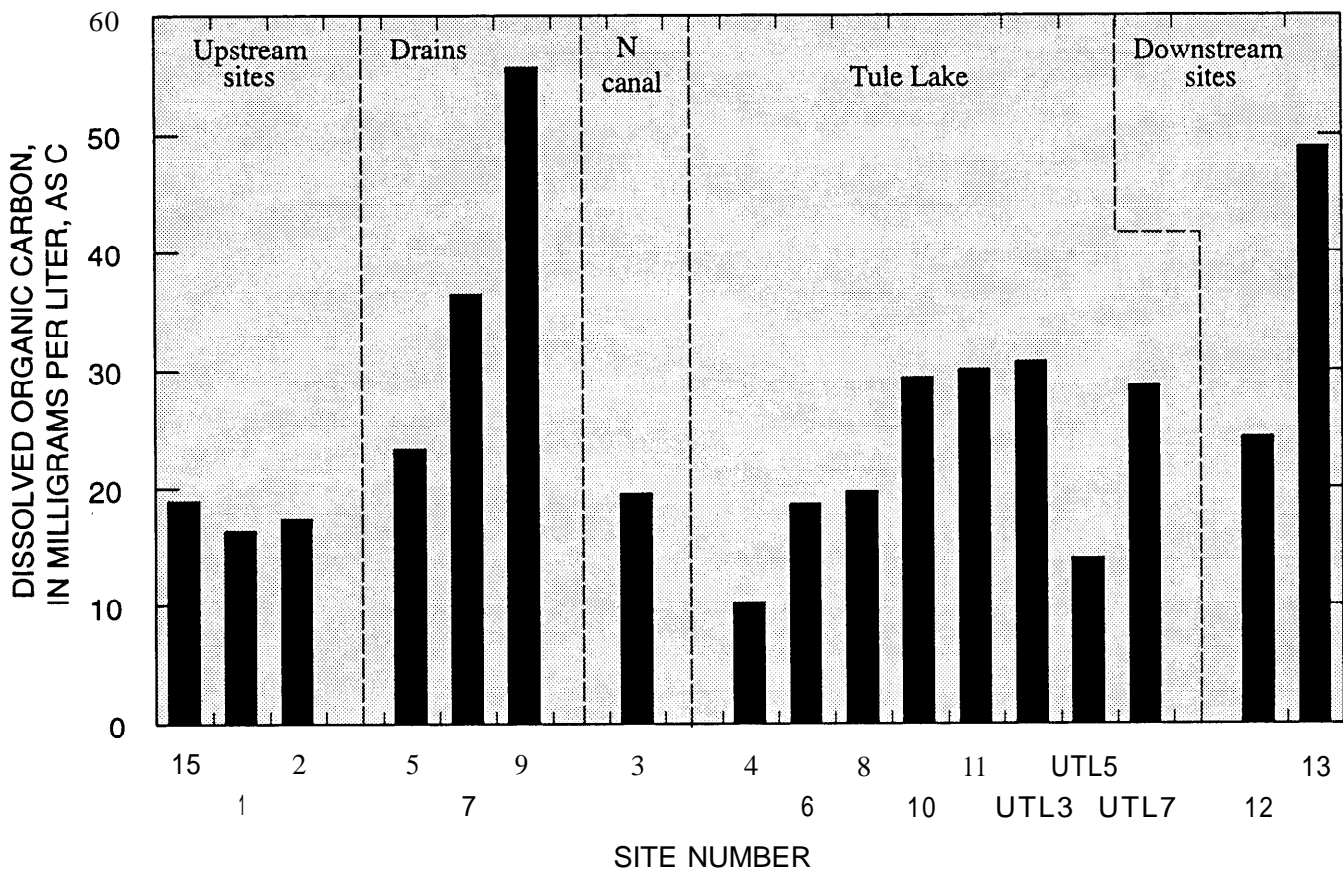
water samples occurred at the same sites (Chi square p value=0.02).

The most frequently detected compounds were the herbicides EPTC, metolachlor, metribuzin, pronamide, and simazine and the insecticide terbufos. All these compounds are highly soluble in water and readily transported in drainwater. EPTC is a thiocarbamate herbicide used on annual grassy weeds, perennial weeds, and some broadleaf weeds in potato and legume crops (Farm Chemical Handbook, 1991). It is considered to be slightly toxic to aquatic life. No standards or criteria have been reported for the protection of aquatic organisms or human health. EPTC was not used on crops in the study area in 1991 and was not detected in water samples. In 1992, it was applied from early May through mid-June and was detected at all sites in June and July but at no sites in August. The highest concentration reported was 0.32 pg/L at site 2, which is upstream of most agricultural inputs.

Metolachlor is an amide herbicide used for preemergent and preplant weed control (Farm Chemical Handbook, 1991) and is considered to be slightly to moderately toxic to aquatic life. No standards or criteria have been reported for protection of aquatic organisms or human health. Metolachlor was detected at five sites in 1991 and at seven sites in 1992. The highest concentration was 0.060 pg/L.

Metribuzin is a triazine herbicide used to control a large number of grass and broadleaf weeds infesting agricultural crops (Farm Chemical Handbook, 1991) and is considered nontoxic to aquatic life. No standards or criteria have been reported for protection of aquatic organisms. Metribuzin was detected at three sites in 1991 and at eight sites in 1992. The highest concentration was 0.430 μg/L.

Pronamide (Kerb) is an amine herbicide used on pre- or post-emergent grasses and certain broadleaf weeds (Farm Chemical Handbook, 1991) and is con-



**Figure 8.** Mean dissolved organic carbon during 1992 monitoring, Klamath Basin. Mean calculated from three measurements made at each site.

sidered moderately toxic. No standards or criteria have been reported for protection of aquatic organisms. Pronamide is categorized as a carcinogen whose use is highly restricted (U.S. Environmental Protection Agency, 1992a). Pronamide was detected at seven sites in 1992; the highest concentration was 0.011 µg/L.

Simazine is a triazine herbicide used to control annual grasses and broadleaf weeds (Farm Chemical Handbook, 1991) and is considered slightly to non-toxic. Simazine is considered a carcinogen, but not a primary pollutant by the EPA (U.S. Environmental Protection Agency, 1992a). The National Academy of Sciences criterion for freshwater aquatic organisms is 10 µg/L (National Academy of Sciences, 1973). Simazine was detected at five sites in 1991 and seven

sites in 1992. The highest concentration was 0.011 µg/L.

Terbufos is an organophosphorus insecticide and nematocide and is considered highly toxic to super toxic. Terbufos was detected at six sites in 1992, with the highest concentration 0.039 µg/L. There is no reported water-quality criterion for protection of aquatic organisms, and terbufos is not considered a human carcinogen or priority pollutant by the EPA.

Four other herbicides and six other insecticides also were detected during routine monitoring at primary sampling sites, but were neither frequent nor widespread (table 8). Ten of the 16 pesticides detected had no documented use on crops within the Tule Lake Irrigation District during the study. Nondocumented herbicides may have been used to control vegetation

**Table 8.** Summary of pesticide detections in water samples collected at primary sites in 1991 and 1992, Klamath Basin

[µg/L, microgram per liter]

Compound	Number of detections	Maximum concentration (µg/L)	Site no. (fig. 10)	Commonly used in study area
<b>Herbicide 1991</b>				
Cyanwine.....	1	0.021	2	No
Metolachlor .....	12	.029	2,3,7,9,11	No
Metribuzin .....	8	.430	2,3,7	Yes
Simazine .....	7	.010	2,3,7,9,11	No
<b>Insecticide 1991</b>				
Disulfoton .....	2	0.050	2,7	Yes
Ethoprop .....	1	.007	11	Yes
<b>Herbicide 1992</b>				
Atrazine .....	2	0.010	2,7	No.
Benfluralin .....	4	.005	2,7,9,12	No
EPTC .....	24	.320	All sites	Yes
Metolachlor .....	11	.060	1,2,3,5,7,11,15	No
Metribuzin .....	18	.088	1,2,3,5,7,9,11,13	Yes
Pronamide .....	7	.011	1,2,9,11,12,13,15	No
Simazine .....	<b>33</b>	.011	<b>1,2,3,5,7,9,11</b>	No
Trifluralin .....	4	.005	2,7,9,12	No
<b>Insecticide 1992</b>				
Chlorpyrifos .....	3	0.018	2,5,7	Yes
DDE.....	2	.002	7,12	No
Ethoprop .....	3	.004	5,7,9	Yes
Malathion .....	2	.013	2,3	No
Parathion. methyl .....	1	.025	7	Yes
Terbufos.....	9	.039	2,5,7,9,11, 12	No



**Table 9.** Acute toxicity of pesticides used and detected in the study area, Klamath Basin

[1&t--LC~==median lethal concentration; the concentration of compound in water to which test organisms are exposed and that is estimated to be lethal to 50 percent of the test organisms. EC<sub>50</sub>=median effective concentration; the concentration of compound in water to which test organisms are exposed and that is estimated to be effective in producing some sublethal response in 50 percent of the test organisms. µg/L, microgram per liter; mg/L milligram per liter. >, greater than reporting limit. Number in parenthesis indicate references]

Acute toxicity of pesticides used in the Klamath Basin				
Compound	Species	Common name	Test	Concentration (µg/L)
Acrolein .....	Castostomis commersoni ....	White sucker .....	96-hour LC <sub>50</sub>	14 (1)
	Daphnia magna.....	Water flea .....	48-hour LC <sub>50</sub>	57 (1)
	Gambusia affinis.....	Western mosquitofish.....	48-hour LC <sub>50</sub>	61 (1)
	Pimephales promelas.....	Fathead minnow .....	96-hour LC <sub>50</sub>	14 (1)
	Xenopus laevis.....	African clawed toad.....	96-hour LC <sub>50</sub>	4 (1)
Atrazine .....	Daphnia magna.....	Water flea.....	48-hour LC <sub>50</sub>	6,900 (3)
	Gammarus fasciatus.....	Scud .....	48-hour LC <sub>50</sub>	5,700 (3)
	Pimephales promelas .....	Fathead minnow .....	96-hour LC <sub>50</sub>	520 (3)
Benfluralin .....	Gammarus fasciatus.....	Scud Q Q Q Q Q	48-hour LC <sub>50</sub>	4,000 (4)
	Pimephales promelas .....	Fathead minnow .....	96-hour LC <sub>50</sub>	1,000 (2)
	Bufo b. japonicus.....	Toad .....	24-hour LC <sub>50</sub>	11,000 (1)
Chlorpyrifos .....	Daphnia magna.....	Water flea.....	6.6-hour EC <sub>50</sub>	1 (6)
	Gammarus fasciatus.....	Scud .....	24-hour LC <sub>50</sub>	0.76 (4)
	Pimephales promelas .....	Fathead minnow .....	96-hour LC <sub>50</sub>	.13 (6)
Cyanazine .....	Daphnia magna.....	Water flea.....	48-hour EC <sub>50</sub>	84,000 (5)
	Gammarus fasciatus.....	Scud .....	24-hour LC <sub>50</sub>	5,600 (4)
	Pimephales promelas .....	Fathead minnow .....	96-hour LC <sub>50</sub>	16,300 (4)
DDE .....	Daphnia magna.....	Water flea.....	48-hour EC <sub>50</sub>	4,700 (2)
	Gammarus fasciatus.....	Scud .....	24-hour LC <sub>50</sub>	4,200 (4)
	Pimephales promelas .....	Fathead minnow .....	96-hour LC <sub>50</sub>	12,400 (4)
	Pseudacris triseriata .....	W. chorus frog (tadpole) ....	96-hour LC <sub>50</sub>	800 (4)
Disulfoton .....	Daphnia magna.....	Water flea.....	24-hour LC <sub>50</sub>	.4-.9 (1)
	Gammarus fasciatus.....	Scud .....	24-hour LC <sub>50</sub>	.11 (4)
	Pimephales promelas .....	Fathead minnow .....	96-hour LC <sub>50</sub>	4.30 (4)
Dithiocarbamate ...	Daphnia magna.....	Water flea.....	48-hour LC <sub>50</sub>	970 (1)
	Physa acuta.....	Bladder snail .....	48-hour LC <sub>50</sub>	100,000 (1)
EPTC .....	Daphnia magna.....	Water flea.....	48-hour LC <sub>50</sub>	4,700 (1)
	Gammarus fasciatus.....	Scud .....	96-hour LC <sub>50</sub>	66,000 (4)
Malathion .....	Daphnia magna.....	Water flea.....	24-hour EC <sub>50</sub>	1 (4)
	GAMmarus f asciaTus.....	Scud .....	24-hour LC <sub>50</sub>	3.8(4)
	Pimephales promelas .....	Fathead minnow .....	96-hour LC <sub>50</sub>	8,650 (4)
	Pseudacris triseriata.....	W. chorus frog (tadpole) ....	96-hour LC <sub>50</sub>	200 (4)

**Table 9.** Acute toxicity of pesticides used and detected in the study area, Klamath Basin-Continued

Compound	Acute toxicity of pesticides used in the Klamath Basin			
	Species	Common name	Test	Concentration (µg/L)
Methyl parathion . .	Daphnia magna.. ..	Water flea .....	24-hour EC <sub>50</sub>	14 (4)
	Gammarus fasciatus.. ..	Scud .....	24-hour LC <sub>50</sub>	10 (4)
	Pimephales promelas .....	Fathead minnow .....	96-hour LC <sub>50</sub>	8,900 (4)
	Pseudacris triseriata .....	W. chorus frog (tadpole). ....	96-hour LC <sub>50</sub>	3,700 (4)
Metolachlor .....	Daphnia magna.. ..	Water flea.. ..	48-hour EC <sub>50</sub>	23,500 (4)
	Pimephales promelas .....	Fathead minnow .....	96-hour LC <sub>50</sub>	8,000 (4)
	Chironomus plumosus.. ..	Midge.. ..	48-hour EC <sub>50</sub>	3,800 (4)
Methamidophos.. ..	Hypophthalmichthys moliti..	Silver carp .....	48-hour LC <sub>50</sub>	158,500 (1)
Metribuzin .....	Daphnia magna.. ..	Water flea.. ..	48-hour EC <sub>50</sub>	100,000 (4)
Pronamide .....	..do .....	..do .....	48-hour LC <sub>50</sub>	>5,600 (7)
Simazine .....	..do .....	..do .....	48-hour LC <sub>50</sub>	> 10,000 (4)
Trifluralin.. ..	..do.. ..	..do .....	48-hour EC <sub>50</sub>	560 (4)
	Gammarus fasciatus.. ..	Scud .....	24-hour LC <sub>50</sub>	8,700 (4)
	Pimephales promelas .....	Fathead minnow .....	96-hour LC <sub>50</sub>	160 (4)
	Bufo b. japonicus.. ..	Fowler's toad (tadpole) .....	96-hour LC <sub>50</sub>	110 (4)
	Terbufos .....	Daphnia magna.. ..	Water flea.. ..	48-hour EC <sub>50</sub>
2,4-D.....	Gammarus fasciatus.. ..	Scud .....	96-hour LC <sub>50</sub>	.2(4)
	Pimephales promelas .....	Fathead minnow .....	96-hour LC <sub>50</sub>	390 (4)
	Chironomus plumosus.. ..	Midge.. ..	48-hour LC <sub>50</sub>	1.4 (4)
	Oncorhynchus mykiss .....	Rainbow trout .....	96-hour LC <sub>50</sub>	110,00 (4)
2,4-D.....	Pimephales promelas .....	Fathead minnow .....	96-hour LC <sub>50</sub>	180,000 (4)
	Daphnia magna.. ..	Water flea.. ..	48-hour EC <sub>50</sub>	1,200 mg/L (2)
	Gammarus fasciatus.. ..	Scud .....	96-hour LC <sub>50</sub>	2,400 (2)

- (1). U.S. Environmental Protection Agency, 1992, (AQUIRE). aquatic toxicity information retrieval data base: Duluth, Minnesota, Environmental Research Laboratory.
- (2). Johnson, W.W., and Finley, M.T., 1980, Handbook of acute toxicity of chemicals to fish and aquatic invertebrates: U.S. Fish and Wildlife Service Resource Publication 137.98 p.
- (3). Macek, K.J., Buxton. K.S., Sauter, S., Gniska, S., and Dean, J.W., 1976, Chronic toxicity of atrazine to selected aquatic invertebrates and fishes: U.S. Environmental Protection Agency, EPA 600/3-76-047, 58 p.
- (4). Mayer, F.L., and Eilersieck, M.R., 1986. Manual of acute toxicity--interpretation and data base for 410 chemicals and 66 species of freshwater animals: U.S. Fish and Wildlife Service Resource Publication 160, 506 p.
- (5). Nebeker, A.V., Cairns, M.A., Onjukka, S.T., and Titus, R.H., 1986, Effects of age on sensitivity of *Daphnia magna* to cadmium, copper, and cyanazine: Environmental Toxicology and Chemistry, v. 5, p. 527-530.
- (6). Odenkirchen. E.W., and Eisler, R., 1988, Chlorpyrifos hazards to fish, wildlife, and invertebrates--a synoptic review: U.S. Fish and Wildlife Service Biological Report 85( 1.13), 34 p.
- (7). Rohm and Haas Company, 1992, Material safety data sheet for Kerb 50-W A herbicide: Philadelphia, Pennsylvania, 10 p.

on roads and right-of-ways, or for other noncrop uses. Terbufos is not registered for use in California and was probably transported downstream from agricultural land in Oregon. Malathion was detected, and its occurrence at the monitoring sites also may result from its use in Oregon. DDT is no longer used in the United States, but one of its by-products, DDE, was detected at two sites. The source of DDE is most likely soil and sediment that accumulated DDT in the past when DDT was frequently applied to crops in the area.

Of the 32 pesticides known to be used in the study area (table 1), 9 were included in the analyses of routine samples. Two pesticides (methamidophos and acrolein) that were extensively used in the study area, but not included in the routine analyses, were the subject of special monitoring events described in other parts of this report. Most of the other documented pesticides not included in the analytical schedule were used in relatively small amounts, are not highly toxic, or are relatively volatile and not expected to be transported far from their point of application.

## TOXICITY OF IRRIGATION DRAINWATER AT PRIMARY SAMPLING SITES

### Microtox® Water Bioassays

Microtox® analyses were performed on 72 surface-water samples collected for the weekly static bioassays in 1991. High pH appeared to be responsible for toxicity measured in seven water samples. Only two water samples (sites 7 and 13 in August 1991) had a slight measurable toxicity that was not related to high pH. The causative agent for the observed toxicity in these two samples is not known. Although ammonia was detected at these two sites, Microtox® is not very sensitive to ammonia, and pesticide concentrations were near or below reporting limits.

### Duckweed (Lemna) Bioassays

A test was considered positive if growth was less than 80 percent of controls. Substantial growth stimulation was not observed in any of the duckweed tests, and 78 percent of the 1992 duckweed static tests were positive, indicating retarded growth relative to controls (Bennett, 1994). Mean organism survival at each site was compared to the mean survival in control

tests with a one-tailed t-test. Mean duckweed growth in water from all sites was less ( $p < 0.01$ ) than in mean control growth. Differences between site means were not statistically significant (analysis of variance,  $p = 0.3$ ).

### Static Aquatic Invertebrate Bioassays

No *Daphnia* static tests were positive for toxicity in 1991, and average *Daphnia* survival in drainwater from all sites was similar to average control survival. Eight percent of the *Hyalella* static tests were positive for toxicity in 1991, most occurring in the return flow sites during the week of July 3. During that week, a water sample from site 5 was submitted for pesticide analysis, but no residues were detected. The average *Hyalella* survival in drainwater from site 7 was lower ( $p < 0.05$ ) than control survival.

Again in 1992, no *Daphnia* static tests were positive for toxicity, and average *Daphnia* survival in test water was not different than average survival in control tests. *Daphnia* control tests were unacceptable during 2 weeks in 1992 (the weeks of August 5 and 19), but survival was good in the concurrent drainwater *Daphnia* tests. Fifteen percent of the static *Hyalella* bioassays were positive in 1992, occurring in water samples from throughout the water system and most from samples collected prior to mid-July.

### Static Fish Bioassays

Seven percent of the *Pimephales* static tests were positive for toxicity in 1991, all in return flows or sites downstream of Tule Lake sump (MacCoy, 1994), but with no apparent temporal pattern. During 1 week (August 7), the *Pimephales* control test failed to meet the criterion for an acceptable control test (survival 280 percent, U.S. Environmental Protection Agency, 1985b), but the data for the concurrent drainwater tests were used because they had good survival that week. The unacceptable control value was not included in calculating the mean *Pimephales* control survival. During 1991, the average *Pimephales* survival in drainwater samples from each site was not significantly different than average control survival, nor were there significant differences between upstream and drainwater sites.

Six percent of the *Pimephales* static tests were positive for toxicity in 1992 in water from throughout the drainwater system (MacCoy, 1994). Four *Pime-*

**phales** control tests during June 1992 were unsuccessful, due to the soft control water, but all the concurrent water tests had satisfactory survival.

### Static Frog Renewal Bioassays

In 1991, seven FETAX tests were done, but only three met the criterion (American Society for Testing and Materials, 1991) of  $\leq 15$  percent combined mortality and malformation in the control group. No individual *Xenopus* mortality tests were positive for toxicity in 1991. Malformation assessments could be made during 3 weeks in 1991. Twenty-seven percent of the *Xenopus* malformation tests were positive for toxicity (table 10), and all sites produced at least one positive malformation test. The most common malformations observed in the 1991 *Xenopus* embryos were optic ruptures and gut malformation or developmental delay (Boyer, 1993).

In 1992, FETAX tests were done during 8 weeks of the field season, and all control tests met the American Society for Testing and Materials (1991) criterion of  $\leq 15$  percent combined mortality and malformation. In 1992, the *Xenopus* tests were done in water samples at both field pH and pH adjusted to below 8.1 (as per ASTM protocol). However, *Xenopus* survival did not differ significantly between the pH-adjusted and non-pH-adjusted water samples (Boyer, 1993);

therefore, only results of tests done following the ASTM protocol are presented here. Due to an insufficient number of *Xenopus* embryos in 5 of the 8 weeks that *Xenopus* tests were done in 1992, not all sites could be tested each week. In that situation, return flow sites were given priority for testing. In 1992, 38 percent of the *Xenopus* mortality tests were positive for toxicity. Positive tests occurred throughout the summer in water from all tested sites except sites 3 and 12 (table 11). The average *Xenopus* survival in water samples from every site was lower ( $p < 0.01$ ) than average control survival. Eleven percent of the *Xenopus* malformation tests were positive for toxicity in 1992, and the average number of malformations was higher ( $p < 0.05$ ) than controls in water from sites 2, 7, 9, and 11 (table 11). Malformations frequently observed in 1992 were exophthalmus, axial curvature, microcephaly, cardiac edema, and severe body edema (Boyer, 1993).

Although mortality and malformations were significantly higher in water samples than in controls, the results of Kruskal-Wallis tests indicate no significant difference in toxicity between sites located on drains and sites upstream in the Lost River and Upper Klamath Lake for either year of monitoring ( $0.33 < p < 0.95$ ) for all tests.

Mortality or malformations (pigmentation changes or growth delay) were not observed in any of

**Table 10.** Results of *Xenopus* malformation bioassay, 1991, Klamath Basin

[Results are expressed as average percent malformation observed in replicate test beakers. Date indicates day of water collection and test initiation. Sites are shown in fig. 1. Positive test responses are in **bold**, indicating malformation exceeded that in the concurrent controls by greater than 20 percent. SD, standard deviation; SE, standard error]

Date	<i>Xenopus</i> static renewal bioassay results									Control
	Sites upstream of Tule Lake sump		Sites on return flows to Tule Lake sump				Sites downstream of Tule Lake sump			
	1	2	3	5	7	9	11	12	13	
7-10	<b>63</b>	<b>40</b>	<b>88</b>	85	18	<b>60</b>	<b>75</b>	<b>45</b>	10	5
7-17	<b>45</b>	13	<b>38</b>	<b>98</b>	<b>53</b>	3	<b>95</b>	25	<b>48</b>	5
8-14	<b>35</b>	13	13	<b>40</b>	<b>40</b>	13	18	18	8	0
Site mean .	147.7	<sup>1</sup> 22.0	<sup>1</sup> 46.3	<sup>1</sup> 74.3	37.0	25.3	<sup>1</sup> 62.7	<sup>2</sup> 29.3	22.0	3.3
SD . . . . .	14.2	15.6	38.2	30.4	17.7	30.4	40.0	14.1	22.5	2.9
SE . . . . .	8.2	9.0	22.1	17.6	10.2	17.6	23.1	8.1	13.0	1.7
Number of replicates . .	3	3	3	3	3	3	3	3	3	3

<sup>1</sup>Site mean difference from control mean,  $p < 0.05$ .

<sup>2</sup>Site mean difference from control mean,  $p < 0.01$ .

<sup>3</sup>Site mean difference from control mean,  $p < 0.005$ .

the larval bioassays done in 1992. The 7- and 14-day tests were done on water samples from sites 3, 5, 7, and 9.

### In Situ Aquatic Invertebrate and Fish Bioassays

During 1991, 43 and 46 percent of the *in situ* *Daphnia* and *Hyalella* tests were positive for mortal-

ity, respectively (tables 12 and 13). Average *Daphnia* survival at sites 1, 3, 5, 9, and 11 was lower ( $p < 0.05$ ) than the average survival of control organisms. Similarly, average *Hyalella* survival at sites 1, 5, 7, and 11 was lower ( $p < 0.05$ ) than average control survival.

Eighty-five percent of the 1991 *in situ* *Pimephales* tests were positive for mortality, and all sites

**Table 11.** Results of *Xenopus* mortality and malformation bioassays, 1992, Klamath Basin

[Results are expressed either as average percent survival or as malformation observed in duplicate test beakers. Sites are shown in fig. 1. Positive test responses are in **bold**, indicating mortality or malformation exceeded that in concurrent controls by greater than 20 percent. SD, standard deviation; SE, standard error]

Date	Xenopus static renewal bioassay results										
	Sites upstream of Tule Lake sump			Sites on return flows to Tule Lake sump				Sites downstream of Tule Lake sump			Control
	1	2	15	3	5	7	9	11	12	13	
Mortality results											
6-17			90	90	85	78	88	90			95
6-24			25	73	60	75	60	48	73		90
7-08	70	73	70	78	48	23	20	60	75	65	95
7-22	98	93	95	95	95	100	95	93	98	98	100
7-29				78	90	73	65	60			98
x-05				73	63	55	73	58			93
8-12	83	78	83	88	70	55	65	83			93
8-19				98	100	100	98	95			100
Mean.	83.7	81.3	72.6	84.1	76.4	69.9	70.5	73.4	82.0	81.5	95.5
SD . . .	14.0	10.4	28.2	9.9	18.7	25.5	25.0	18.8	13.9	23.3	3.6
SE . . . .	5.0	3.7	10.0	3.5	6.6	9.0	8.9	6.6	4.9	8.3	1.3
Num her.	3	3	5	8	8	8	8	8	3	2	8
Malformation results											
6-17			3	0	5	8	5	8			<b>0</b>
6-23			5	25	5	5	15	18	25		0
7-08	23	8	35	10	10	10	5	20	25	33	5
7-22	3	5	5	5	3	8	5	0	3	3	0
7-29				15	20	25	20	10			5
8-05				15	10	5	15	28			3
8-12	8	5	23	5	10	13	18	33			8
Mean.	11.3	6.0	14.2	10.7	9.0	10.6	11.9	16.7	17.7	18.0	3.0
SD . . .	10.4	1.7	14.2	8.4	5.7	6.9	6.6	11.6	12.7	21.2	3.2
SE . . .	3.9	.7	5.4	3.2	2.1	2.6	2.5	4.4	4.8	8.0	1.2
Num ber .	3	3	5	7	7	7	7	7	3	2	7

<sup>4</sup>Site mean significantly less than control mean,  $p < 0.05$ .

<sup>5</sup>Site mean significantly less than control mean,  $p < 0.01$ .

<sup>6</sup>Site mean significantly less than control mean,  $p < 0.005$ .

**Table 12.** Results of *Daphnia in situ* bioassays in 1991 and 1992, Klamath Basin

[Expressed as average percent survival observed in duplicate test chambers. Date indicates day of test initiation. Sites are shown in fig. 1. Reference value is survival in concurrent control test minus average 1991 travel mortality for *Daphnia* (20 percent). Positive test responses are in **bold**, indicating that drainwater mortality exceeded that of reference by >20 percent. SD, standard deviation; SE, standard error]

1991										
Date	Sites upstream of Tule Lake sump		Sites on return flows to Tule Lake sump				Sites downstream of Tule Lake sump			Reference value
	1	2	3	5	7	9	11	12	13	
6-05	75	80	70	<b>10</b>	85	65	85	85	65	80
6-12	30	70	85	<b>0</b>	65	35	75	70		80
6-19	0	60	45	65	35	70	65	90	65	80
6-26	80	50	55	45	70	55	55	65	85	80
7-03	40	0	<b>10</b>	5	80	75	40	75	70	80
7-10	65	55	60	35	80	95	70	80	100	80
7-17	80	90	90	80	95	95	90	90	95	70
7-24	25	30	50	5	25	30	45	75	<b>15</b>	75
7-31	70	65	5	25	90	95	80	80	<b>50</b>	75
8-07	0	80	35	0	0	5	50	0	<b>10</b>	80
8-14	90	65	0	40	60	65	85	85	85	80
8-21	30	85	30	30	<b>65</b>	<b>10</b>	50	45	90	80
8-28	45	100	<b>10</b>	55	<b>80</b>	60	70	100	80	80
Site mean ...	<sup>3</sup> 48.5	63.8	<sup>3</sup> 41.9	<sup>4</sup> 30.4	<b>63.8</b>	<sup>1</sup> 58.1	<sup>6</sup> 66.2	72.3	67.5	78.5
SD .....	30.5	26.6	30.1	26.1	<b>27.9</b>	30.4	16.7	25.6	29.3	3.2
SE.....	8.5	7.4	8.3	7.2	<b>7.7</b>	8.4	4.6	7.1	8.1	.9
Number.....	13	13	13	13	13	13	13	13	13	13

1992											
Date	Sites upstream of Tule Lake sump			Sites on return flows to Tule Lake sump				Sites downstream of Tule Lake sump			Reference value
	1	2	15	3	5	7	9	11	12	13	
6-10	100	90	80	95	90	85	90	85	95	90	100
6-17	65	35	30	100	85	60	40	55	100	100	95
6-24	40	65	45	90	90	80	90	75	95	80	100
7-01	70	85	90	75	65	70	55	100	85	95	90
7-08	20	55	25	40	40	50	0	20	25	25	85
7-15	55	55	40	100	80	45	90	100	65	45	100
7-22	100	<b>10</b>	40	40	40	60	100	100	80	35	100
7-29	55	40	85	45	60	20	55	90	70	95	80
8-05	30	0	30	60	80	80	100		95	100	80
8-12	85	0	75	50	40	95	30	90	85	95	95
8-19	80	90	85	0	45	45	75	80	65	65	100
8-26	70	90	100	85	80	85	95	65	85	75	95
Site mean ...	<sup>6</sup> 64.2	<sup>5</sup> 1.3	<sup>4</sup> 60.4	<sup>3</sup> 64.6	<sup>6</sup> 66.3	<sup>3</sup> 64.6	<sup>6</sup> 68.3	<sup>7</sup> 8.2	<sup>7</sup> 8.8	<sup>7</sup> 5.0	93.3
SD .....	25.6	34.6	27.7	31.0	20.5	21.9	32.2	24.2	20.7	26.6	7.8
SE.....	7.4	10.0	8.0	8.9	5.9	6.3	9.3	7.0	6.0	7.7	2.2
Number.....	12	12	12	12	12	12	12	11	12	12	12

<sup>6</sup>Site mean significantly less than control mean, p<0.05.

<sup>4</sup>Site mean significantly less than control mean, p<0.001.

<sup>3</sup>Site mean significantly less than control mean, p<0.005.

had lower (at least  $p < 0.05$ ) average minnow survival than the control average (table 14). The control test during the week of August 7 had very low survival and was unacceptable, so none of the *in situ* tests that week were considered positive.

During 1992, 43 and 41 percent of the 1992 *in situ Daphnia* and *Hyalella* tests were positive for mortality, respectively (tables 12 and 13). Average *Daphnia* and *Hyalella* survival was lower ( $p < 0.05$ ) at all sites than the average survival of control organisms.

Eighty-three percent of the 1992 *Pimephales in situ* tests were positive for mortality, and all sites had lower ( $p < 0.005$ ) average minnow survival than the control average (table 14).

### **In Situ Duckling Bioassays**

In the 1991 duckling tests, weight gain, cold tolerance (expressed as loss in body heat), and brain AChE activity were compared between experimental groups using one-way analysis of variances with a null hypothesis of no effect among groups. If tests were significant ( $p < 0.05$ ), a Dunnett's test was performed to compare the control and test groups (Dunnett, 1955). Pearson correlation coefficient analyses were performed to examine the relation between body weight and bill and forearm lengths.

Duckling survival in the 1991 *in situ* tests was 100 percent during the 5 weeks that tests were done. The average weight gain during the 96-hour tests for each test group is presented by MacCoy (1994). Cages were not screened for tests done in June, so the ducklings may have supplemented their regulated diet with food material that entered cages at the monitoring sites. That uncontrolled factor in duckling growth precluded the use of the June tests to evaluate pesticide exposure. Cages were screened for the tests done in July and August to eliminate uncontrolled food sources. There were no consistent differences between reference sites and sites on drains in those tests. No significant differences in heat loss were found between groups in any of the cold-stress tests (MacCoy, 1994).

Results of the duckling brain AChE activity determinations were analyzed separately for birds subjected and birds not subjected to cold stress. In birds subjected to cold-stress tests, no significant differences in enzyme activity were found between control and test site birds during any of the tests. In birds not subjected to cold-stress tests, a significant ( $p = 0.016$ ) dif-

ference in activity between a test and a control group occurred only one time (site 5, test 1). The results of all bioassays indicate that the ducklings had no hazardous exposure to anti-cholinesterase insecticides.

### **CAUSES OF TOXICITY IN IRRIGATION DRAINWATER AT THE PRIMARY SAMPLING SITES**

The results of water-quality monitoring indicate that several water-quality factors could cause mortality of aquatic organisms. However, the predominant environmental hazard differed among locations along the irrigation water system (fig. 9). In 1992, high pH and ammonia concentrations were the primary environmental hazards upstream at site 15 in Upper Klamath Lake; low dissolved-oxygen concentration was the primary hazard at the other two sites upstream of Tule Lake (sites 1 and 2); both low dissolved oxygen and un-ionized ammonia were hazards in the return flows at sites 3, 5, 7, and 9; and high pH, low dissolved oxygen, and un-ionized ammonia were all hazards at the sites downstream of Tule Lake (sites 11, 12, and 13).

The percentage of tests showing toxicity at sites along the drainwater system in 1991 and 1992 is presented in figure 9. Malformations in *Xenopus* tests and mortality in *Hyalella* static tests occurred in water samples collected from upstream sites, irrigation drains, and sites downstream of Tule Lake sump. Toxicity was measured in *Pimephales* static tests of water samples collected only from return flows and sites downstream of Tule Lake sump.

The *in situ* tests positive for mortality in 1991 and 1992 are sorted by location in figure 9. In 1991, *Daphnia* and *Hyalella* experienced most positive tests (>43 percent of tests) at upstream and return flow sites, and *Pimephales* experienced most positive tests (>79 percent of tests) at return flow and downstream sites. All ducklings survived their *in situ* tests and are not included in the figure. In 1992, mortality of aquatic invertebrates and fish was high during *in situ* tests at all sites along the drainwater system.

The relation between 1992 *in situ* organism survival and average water quality during each test was examined by analysis of deviance, which is similar to analysis of variance. Analysis of deviance was calculated with the computer program Generalized Linear Model (GLIM), using a binomial error term and a logit

link function (Payne, 1985). This analysis was done using the data obtained by the continuous water-quality monitors transformed into standard normal **Z values**.

Mortality of *Daphnia* and *Hyalella* was related to pH measurements ( $p < 0.05$ ), and *Pimephales* mortality was related to dissolved-oxygen measurements

Table 13. Results of *Hyalella in situ* bioassays in 1991 and 1992, Klamath Basin

[Expressed as average percent survival observed in duplicate test chambers. Date indicates day of water collection and test initiation. Sites are shown in fig. 1. Reference value is survival in concurrent control test minus average 1991 travel mortality for *Hyalella* (15 percent). Positive test responses are in **bold**, indicating mortality in drainwater exceeded that in reference by greater than 20 percent. SD, standard deviation; SE, standard error]

Date	1991										
	Sites upstream of Tule Lake sump		Sites on return flows to Tule Lake sump				Sites downstream of Tule Lake sump			Reference value	
	1	2	3	5	7	9	11	12	13		
7-03			65	35	45	35				80	
7-10	30	80	20	25	35	30	35	100	90	85	
7-17	25	70	85	35	0	90	100	100	70	65	
7-24	40	45	10	90	25	70	45	45	35	75	
7-31	70	50	75	<b>15</b>	60	30	25	70	85	85	
8-14	70	100	100	85	90	95	75	90	30	85	
8-21	75	30	35	50	45		35	75	80	80	
8-28	100	80	95	85	100	95	100	85	95	85	
Site mean . . .	'58.6	65.0	60.6	'52.5	'80.0	63.6	'59.3	80.7	69.3	80.0	
SD . . . . .	27.5	24.3	34.7	30.0	32.9	31.1	31.9	19.5	26.4	7.1	
SE . . . . .	9.7	8.6	12.2	10.6	11.6	11.0	11.3	6.9	9.3	2.5	
Number . . . .	7	7	8	8	8	7	7	7	7	8	
Date	1992										
	Sites upstream of Tule Lake sump			Sites on return flows to Tule Lake sump				Sites downstream of Tule Lake sump			Reference value
	1	2	15	3	5	7	9	11	12	13	
6-10	70		0	100	70	100	100	90	95	80	95
6-17	95	35	5	85	80	100	95	65	95	90	100
6-24	<b>85</b>	85	60	100	100	100	100	90	100	100	100
7-01	85	95	75	100	70	90	85	85	70	55	100
7-08	100	75	75	75	60	65		30	60	100	100
7-15	55	65	40	85	60	85	60	90	90	45	100
7-22	100	60	30	80	100	100	80	95	60	90	100
7-29	75	65	40	45	80	65	65	65	80	80	100
8-05	65	90	50	95	90		80		75	60	100
8-12	80	0	50	60	70	<b>50</b>	80	85	50	65	100
8-19	60	95	55	40	60	85	90	85	70	85	100
8-26	90	100	100	85	95	80	100	90	85	100	0
Site mean . . . .	'80.0	'69.6	'48.3	'79.2	'77.9	'83.6	'85.0	'79.1	'77.5	'79.2	99.6
SD . . . . .	15.2	30.1	28.6	20.8	15.3	17.2	13.8	19.1	16.0	18.8	1.4
SE . . . . .	4.4	8.7	8.3	6.0	4.4	5.0	4.0	5.5	4.6	5.4	.4
Number . . . . .	12	11	12	12	12	11	11	11	12	12	12

<sup>1</sup>Site mean is significantly different from reference mean  $p < 0.05$ .  
 'Site mean is significantly different from reference mean,  $p < 0.005$ .



Table 14. Results of *Pimephales* in situ bioassays in 1991 and 1992, Klamath Basin

[Expressed as average percent survival observed in duplicate test chambers. Date indicates day of water collection and test initiation. Sites are shown in fig. 1. Reference value is survival in concurrent control test minus average travel mortality for *Pimephales* (25 percent). Positive test responses are in **bold**, indicating drainwater mortality exceeded that of reference by greater than 20 percent. SD, standard deviation; SE, standard error. Reference tests with unacceptably low survival are indicated by parentheses and were not included in calculation of reference average]

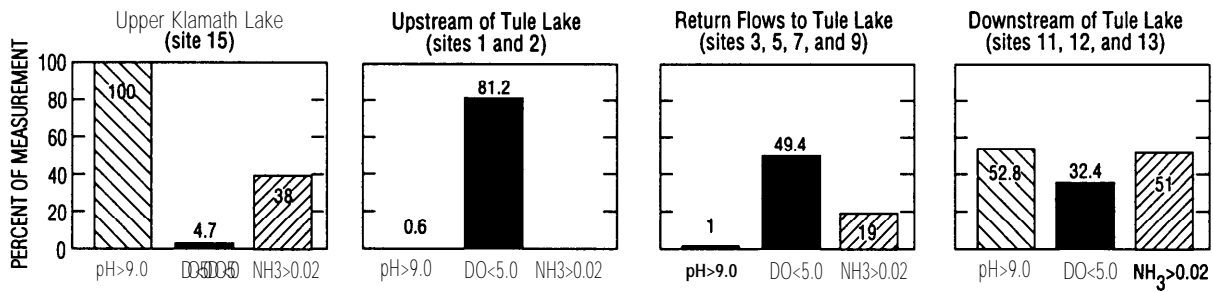
1991										
Date	Sites upstream of Tule Lake sump		Sites on return flows to Tule Lake sump				Sites downstream of Tule Lake sump			Reference value
	1	2	3	5	7	9	11	12	13	
6-05	30	35	35	0	35	15	25	15	10	75
6-12	25	<b>55</b>	30	<b>50</b>	20	25	20	65	<b>0</b>	70
6-19	25	30	50	20	0	5	50	90	<b>0</b>	75
6-26	35	0	10	5	40	0	40	50	35	70
7-03	50	15	40	0	20	10	50	25	10	75
7-10	60	40	25	0	60	25	20	45	5	75
7-17	40	30	35	30	20	15	40	25	5	75
7-24	10	10	10	5	20	0	25	15	0	75
7-31	0	0	5	0	20	0	20	20	20	75
8-07	0	15	35	10	0	0	5	0	0	(5)
8-14	15	5	0	15	0	0	5	0	0	70
8-21	10	5	5	5	5	0	50	55	0	75
8-28	25	15	20	5	40	5	10	85	0	70
Site mean ...	25.0	19.6	23.1	11.2	121.5	7.7	27.7	37.7	6.5	73.3
SD .....	18.3	17.0	15.9	14.7	18.3	9.5	16.7	29.9	10.5	2.6
SE. ....	5.1	4.7	4.4	4.1	5.0	2.6	4.6	8.3	2.9	.7
Number. ....	13	13	13	13	13	13	13	13	13	12

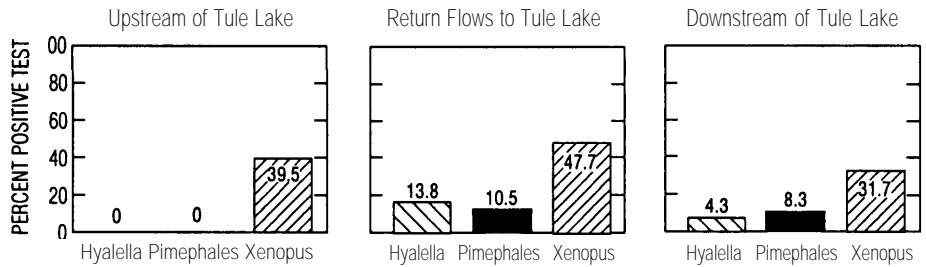
1992											
Date	Sites upstream of Tule Lake sump			Sites on return flows to Tule Lake sump				Sites downstream of Tule Lake sump			Reference value
	1	2	15	3	5	7	9	11	12	13	
6-17	25	0	5	45	50	80	35	60	60	45	90
6-24	0	0	65	50	65	40	40	40	60	40	100
7-01	65	75	35	85	50	35	0	85	80	15	100
7-08	60	5	65	60	25	50	10	30	65	55	100
7-15	45	0	80	60	20	60	60	40	45	0	90
7-22	25	0	80	90	30	60	0	55	35	45	70
7-29	0	20	30	75	75	60	0	65	35	65	80
8-05	30	0	0	0	40	20	50		30	0	75
8-12	60	0	70	25	40	45	50	70	50	0	75
x-19	65	40	90	0	20	30	10	55	0	0	90
8-26	0	35	50	20	30	35	20	60	5	10	70
Site mean ...	34.1	15.9	51.8	46.4	40.5	46.8	25.0	56.0	42.3	25.0	85.5
SD .....	26.5	24.7	30.6	31.7	18.1	17.2	22.7	16.1	24.6	25.2	11.9
SE. ....	8.0	7.4	9.2	9.6	5.5	5.2	6.8	4.8	7.4	7.6	3.6
Number. ....	11	11	11	11	11	11	11	10	11	11	11

\*Site mean is significantly different than reference mean, p<0.05.

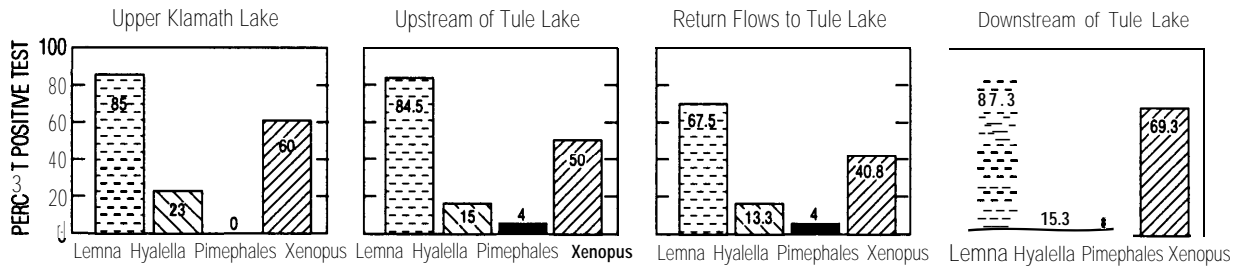
\*Site mean is significantly different than reference mean, p<0.005.



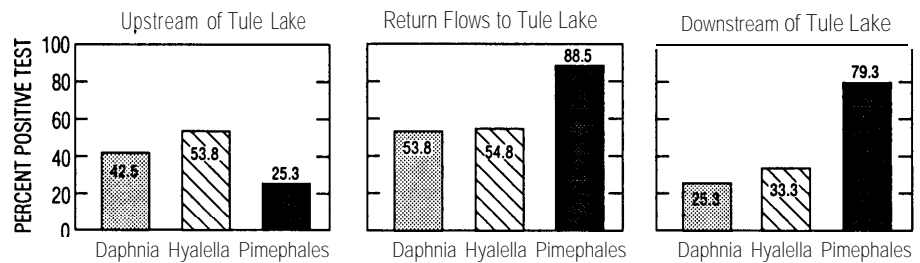
### Water Quality Extremes 1992



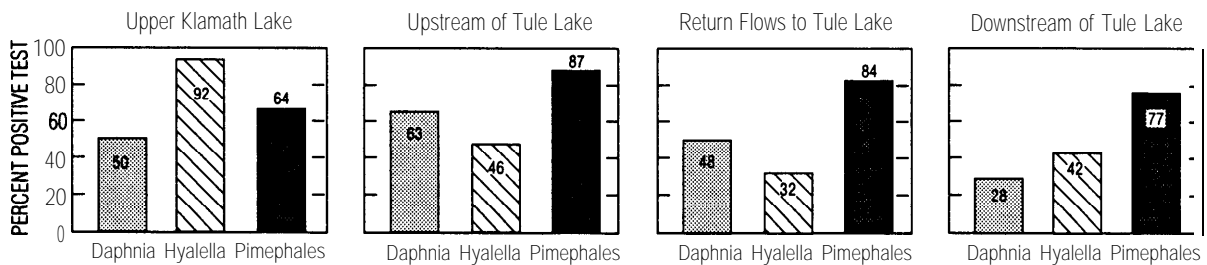
### Static Bioassays 1991



### Static Bioassays 1992



### In Situ Bioassays 1991



### In Situ Bioassays 1992

Figure 9. Water-quality extremes in 1992, and static and *in situ* bioassays in 1991 and 1992, Klamath Basin.

( $p < 0.10$ ). *Daphnia* mortality was also related to the frequency of pH measurements above 9.0 ( $p < 0.05$ ).

In *situ Pimephales* mortality was further examined by analysis of deviance using the frequency of pH and dissolved-oxygen measurements that exceeded the criteria for protection of warm-water juvenile fishes (U.S. Environmental Protection Agency, 1986b). In this analysis, *Pimephales* mortality was related in the following manner to low dissolved oxygen and high pH:

- dissolved oxygen  $< 5.0$  mg/L (not significant)
- dissolved oxygen  $< 4.0$  mg/L ( $p < 0.05$ )
- dissolved oxygen  $< 3.0$  mg/L ( $p < 0.01$ )
- dissolved oxygen  $< 5.0$  and pH  $> 9.0$  ( $p < 0.05$ )
- dissolved oxygen  $< 4.0$  and pH  $> 9.0$  ( $p < 0.01$ )
- dissolved oxygen  $< 3.0$  and pH  $> 9.0$  ( $p < 0.01$ )

Toxicity and mortality patterns from bioassay tests in 1991 and 1992 indicate that water in the study area may be consistently hazardous to certain organisms (table 15). In both years, no *Daphnia* static tests were positive for toxicity, and 6 to 7 percent of *Pimephales* static tests were positive. *Hyalella* exhibited more frequent toxicity, 8 and 17 percent of static tests. *Xenopus* exhibited frequent toxicity (expressed as both mortality and developmental malformations) in the static bioassays, with 27 percent of the 1991 tests positive for malformations and 49 percent of the 1992 tests positive for toxicity or malformations.

The *Xenopus* tests were the only static bioassay done as a renewal test, with the test water replaced daily with a fresh amount of original sample. This may have been an important difference in exposure to volatile water contaminants, such as ammonia. In comparative tests with *Lemna* (Wang, 1991b), un-ionized ammonia did not inhibit duckweed growth below a concentration of 9.0 mg/L using static methods, whereas duckweed growth was inhibited 20 percent at un-ionized ammonia concentrations of 3.0 mg/L under renewal test procedures. Therefore, static renewal procedures should be employed in bioassay tests when volatile contaminants are suspected, and water samples should be stored in a manner to preserve them.

*Lemna* bioassays were done only in 1992, but it was the species that exhibited the most frequent static toxicity, with 78 percent of tests positive for reduced growth (table 15). Because the *Lemna* test results indicate growth inhibition rather than acute mortality, the high rate of positive tests could be due to growth-limiting conditions in the test water rather than an acute toxicity hazard. The causes of growth limitation in the tests remain unknown. Although many water samples contained low concentrations of herbicides, restrictive growth conditions also were measured in samples from sites where no herbicides were detected.

The static test results indicate that at times water in the study area was hazardous to diverse types of

**Table 15.** Toxicity and mortality patterns from bioassay tests in 1991 and 1992, Klamath Basin

[--, no data]

	<i>Daphnia</i>	<i>Hyalella</i>	<i>Pimephales</i>	<i>Xenopus (FETAX)</i>	<i>Lemna</i>	<i>Anus</i>
<b>1991 (in percent)</b>						
Static tests						
with toxicity . . . . .	0	8	7	0 mortality/ 27 malformations . . . . .	--	--
<i>In situ</i> tests						
with mortality . . . . .	33	35	85	--	--	0
<b>1992 (in percent)</b>						
Static tests						
with toxicity . . . . .	0	17	6	38 mortality/ 11 malformations . . . . .	78	--
<i>In situ</i> tests						
with mortality . . . . .	43	41	83	--	--	--

aquatic organisms, particularly early-life stages of a vascular plant, an amphipod, and an amphibian. Because the static tests were aerated and conducted under laboratory conditions, dissolved-oxygen and temperature extremes were not a factor for organisms during these tests. Rather, the results indicate that one or more toxicants probably caused the reduced growth, malformation, and mortality in the static tests. Concentrations of ammonia were high enough to be toxic to the most sensitive species and, as noted previously, may have been related to the higher toxicity response observed in *Xenopus*, the only species tested with a static renewal procedure. On the basis of available pesticide toxicity data, the measured pesticide residues were not high enough to be toxic.

All invertebrate and fish species tested in *situ* (*Daphnia*, *Hyaella*, and *Pimephales*) exhibited a high frequency of mortality (at least 41 percent of tests), but *Pimephales* was most sensitive to the *in situ* test conditions, with toxicity measured in at least 83 percent of its tests in both years. The *in situ* results indicate that water in the study area is frequently hazardous to early-life stages of aquatic invertebrates and fish. There was much more mortality in animals tested *in situ*, indicating that environmental conditions (high pH, fluctuating dissolved oxygen, ammonia) presented additional hazards beyond those present in the static laboratory tests. Because *in situ* test responses reflect effects of both water contaminants and ambient water-quality factors over the duration of the test, the results indicate that overall water-quality conditions throughout the Klamath irrigation system reduce the survival of all *in situ* test organisms.

Mallard ducklings exposed to drainwater in a limited number of *in situ* tests had good survival with no indication of exposure to anti-cholinesterase compounds. These results indicate that oral and dermal exposure to drainwater, on the occasions tested, was not acutely hazardous to ducklings.

## PESTICIDE DRIFT AND WATER QUALITY IN TULE LAKE NATIONAL WILDLIFE REFUGE WATERWAYS

### Pesticide Drift

Aerial applications of pesticides present the risk of off-target chemical drift. Drift is made up of pesticide droplets that are deposited downwind from the target area, plus the vapor that remains airborne for an

extended period of time. Although the amount of drift that occurs following an aerial application is highly dependent upon local topography and weather conditions, pesticide drift can be a common phenomenon in agroecosystems.

Methamidophos is a systemic anti-cholinesterase organophosphorus insecticide used on fresh market and seed potato crops and is widely used in the study area. Methamidophos was detected on the sampler at the edge of the field in only 3 of the 12 applications monitored, but in all those applications, methamidophos was also detected on the over-water samplers (table 16). Windspeed and direction at all sites prior to those three sprays was less than 2.0 mi/h toward the waterway being monitored (Moore, 1993). The methamidophos formulation used in these spray events contained 40-percent active ingredient (a.i.), applied at a rate of 1 lb a.i. per acre, yielding a target application concentration of 4,483  $\mu\text{g}/\text{m}^2$ . Therefore, the over-water deposits were approximately 19 to 23 percent of the target rate (table 16). This amount of off-target pesticide drift is fairly typical of the amount reported by Tome and others, (1991). No chemical measurements of the actual amount of methamidophos in the water were obtained. However, potential methamidophos water concentrations were extrapolated from the over-water deposition measurements. In a simplified scenario where all the methamidophos deposited on the water mixes completely with the water below it, the highest concentration of methamidophos would have been approximately 3.12  $\mu\text{g}/\text{L}$  at site 226 (table 16). That methamidophos exposure would have been below both the mallard  $\text{LD}_{50}$  of 8.5 mg/kg (Smith, 1987), and *Daphnia*  $\text{LC}_{50}$  of 26  $\mu\text{g}/\text{L}$  (Mobay Chemical Corp., written commun., 1992). Therefore, the potential for aquatic toxicity to these species from methamidophos was low in the application events monitored in this study.

Based upon monitoring a small number of aerial applications, over-water drift of methamidophos occurred in 25 percent of the applications and in all three applications in which the pesticide was documented to have been applied to the edge of the field, as is done in routine applications in the study area. In all three cases, the wind conditions were good for applications, but the field edges were only 25 ft from the waterway. It was unfortunate that more routine spray events were not monitored because it is impossible to determine from this small study if over-water drift was

**Table 16.** Methamidophos residues on deposition samplers and estimated potential water concentrations, 1992, Klamath Basin

[SD, standard deviation; ft, feet;  $\mu\text{g}/\text{m}^2$ , microgram per square meter;  $\mu\text{g}/\text{L}$ , microgram per liter.

Methamidophos spray drift results								
Site no. (fig. 10)	Spray date	Field no.	Site distance and direction from field (ft)	Water depth (ft)	Deposit on field sampler ( $\mu\text{g}/\text{m}^2$ )	Over-water deposit mean $\pm$ SD @g/m <sup>2</sup> )	Over-water deposit as percent of target rate	Estimated water concentration @g/L)
224	8-10	8307	25 West	3.3	935	832 $\pm$ 293	18.6	0.832
226	8-02	8351	25 South	1.0	935	1,039 $\pm$ 147	23.2	3.12
227	8-02	8352	25 South	2.3	1,247	1,039 $\pm$ 74	23.2	1.48

less likely from fields farther from waterways, which would have suggested sufficient buffer strip margins for the leaselands.

#### Water Quality

Drains had significantly higher ( $p \leq 0.05$ ) specific conductance and ammonia concentrations than delivery canals. Mean conductance in canals and drains was 500 and 950 nS/cm, respectively. The mean ammonia concentration in canals was 0.07 mg/L (SD=0.06, n=24) and in drains 1.16 mg/L (SD=3.30, n=22). Sites were visited in late afternoon or early evening, limiting information about water quality to that time of day.

Several drain sites apparently had conditions particularly conducive to ammonia production. Site 206 (fig. 10) (on drain 102-F) had an ammonia concentration of 1.4 mg/L and average (n=3) measurements of 3 percent *Daphnia* survival, 1.0-ft water depth, 1,770  $\mu\text{S}/\text{cm}$  specific conductance, 23°C temperature, 0.8 mg/L dissolved oxygen, and 7.4 pH. Site 226 (on drain 101 -B-2) had an ammonia concentration of 2.1 mg/L and average (n=2) measurements of 5 percent *Daphnia* survival, 1.3-ft water depth, 1,080  $\mu\text{S}/\text{cm}$  specific conductance, 21.5°C temperature, 0.5 mg/L dissolved oxygen, and 6.9 pH. The highest measured ammonia concentration was 16 mg/L at site 46. Conductance was 1,650  $\mu\text{S}/\text{cm}$ , water temperature was 26°C, and dissolved oxygen was 6.0 mg/L. No *Daphnia* mortality data were available.

Fifty-two and 51 percent of the *Daphnia in situ* tests adjacent to small grain and potato fields, respectively, were positive for mortality. The average *Daphnia* survival in all waterways on the Tule Lake NWR leaseland was lower ( $p < 0.05$ ) than in reference tests (91.3f3.5 SD, n=8), with average survival in field drains (48.6 percent) lower ( $p < 0.05$ ) than in delivery canals (63.9 percent) (table 17). The mean ammonia concentration in drains (1.16 mg/L) was above the *Daphnia* LC., value of 0.66 mg/L NH<sub>3</sub>-N reported by Alabaster and Lloyd (1982), indicating that ammonia toxicity probably influenced *Daphnia* survival at most drain sites.

Twelve sites were monitored during methamidophos application events, with four sites monitored on both pre- and post-spray days (table 18). Nine of the *Daphnia* tests were positive for mortality. However, at four sites where pre- and post-spray survival could be compared, none of the post-spray survival rates were lower than pre-spray rates, indicating the methamidophos application was not the factor influencing *Daphnia* survival. As described previously, total ammonia concentrations toxic to *Daphnia* were approached in most drain sites and exceeded at site 226, suggesting that poor water quality caused low *Daphnia* survival.

Poor water quality was a problem in virtually all the Tule Lake NWR waterways during July and August 1992, producing widespread *Daphnia* toxicity throughout the waterways around Tule Lake sump. In

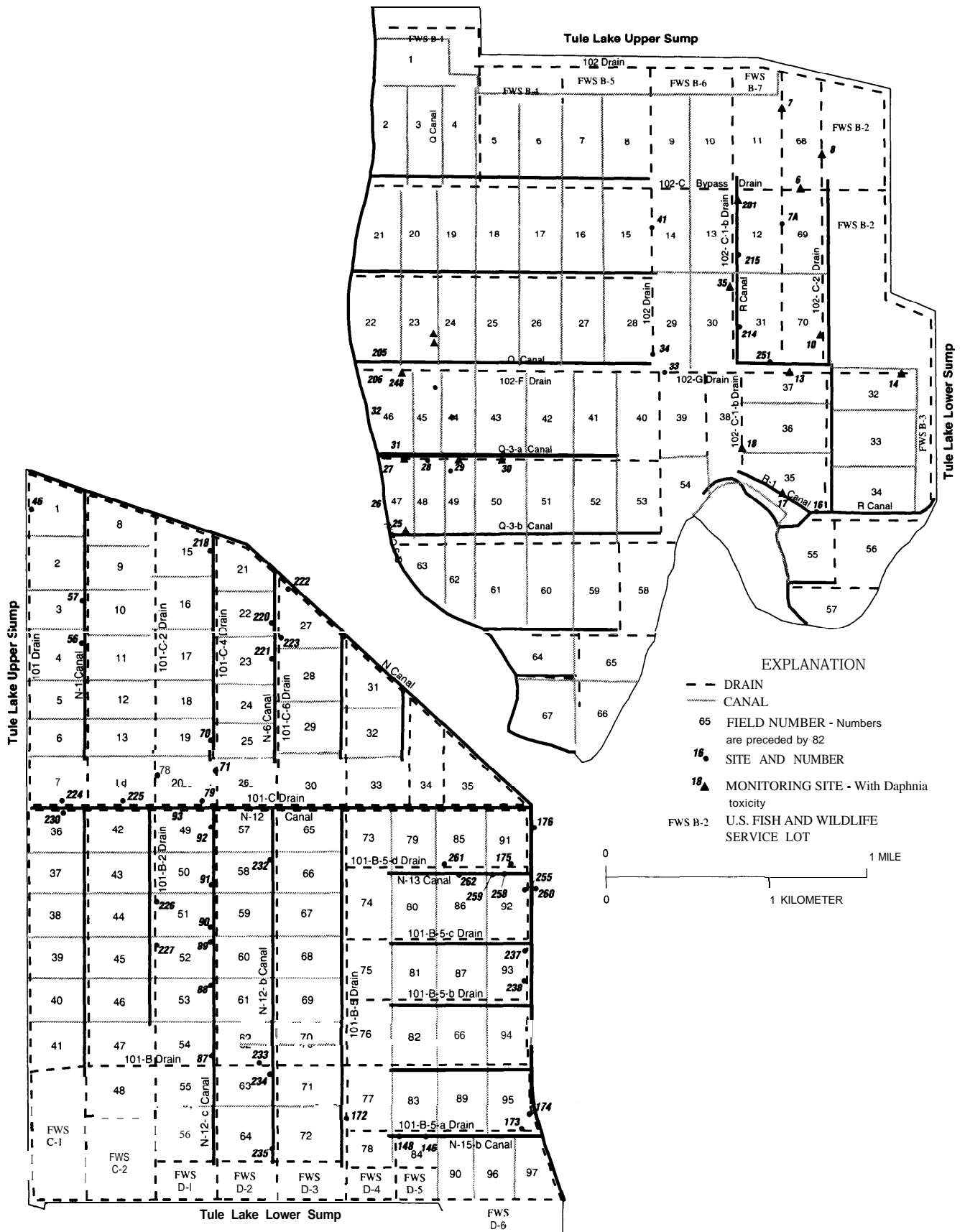


Figure 10. Tule Lake National Wildlife Refuge leaselands.

the smaller water volumes present in the tributary drains, water quality becomes especially severe, resulting in very poor, and sometimes hazardous,

aquatic habitat for invertebrates throughout the refuge. The high pH conditions in the waterways may accelerate hydrolysis of organophosphorus and carbamate

**Table 17.** Water quality and *Daphnia* survival in Tule Lake National Wildlife Refuge canals and drains during July and August 1992, Klamath Basin

Measurement	Canals			Drains		
	Mean	Standard deviation	Number	Mean	Standard deviation	Number
Water temperature (°C) .....	24.6	1.1	48	23.2	1.1	41
Specific conductivity (microsiemens per liter).....	550	24	49	<sup>1</sup> 1,040	234	43
Dissolved oxygen (microsiemens per liter) .....	10	.4	49	8.3	1.3	40
pH .....	8.7	.1	49	8.1	.2	41
Total ammonia (microsiemens per liter) .....	.07	.06	24	1.16	3.30	22
<i>Daphnia</i> survival .....	63.9	10.4	49	48.6	.14	42

<sup>1</sup>Difference between means of canals and drains are significantly different, p<0.05.

**Table 18.** Methamidophos application biomonitoring results, Klamath Basin, 1992

[Entries in **bold** indicate that *Daphnia* mortality was less than 20 percent in concurrent reference tests. Field number prefixes S and E indicate leaseland fields either south or east of Tule Lake upper sump, respectively. ft, feet. --, no data]

Methamidophos application biomonitoring results							
Sile no. (fig. 10)	Date	Field no.	Distance to field (ft)	Application (Yes/No)	Methamidophos detected on deposition samplers (Yes/No)	<i>Daphnia</i> survival (percent)	Duckling survival (percent)
201	8-01	s12	75	Y	N	55	100
214	8-01	s31	60	Y	N	75	--
215	8-01	s12	60	Y	N	60	100
222	8-07	E27	20	N	Prespray	35	--
222	8-08	E27	20	Y	N	40	100
223	8-07	E27	70	N	Prespray	95	--
223	8-08	E07	70	Y	N	100	100
224	9-10	E07	25	Y	Y	45	100
225	8-10	E14	25	Y	N	55	--
226	8-01	E51	25	N	Prespray	0	--
226	8-01	E51	25	Y	N	<b>10</b>	100
227	8-01	E52	25	N	Prespray	70	--
227	8-02	E52	25	Y	Y	100	100
237	7-24	E93	50	Y	N	20	--
238	7-24	E93	50	Y	N	35	--
<b>251</b>	8-01	s31	50	Y	N	90	100

insecticides, shortening the duration of hazard and making chemical detection difficult.

Mallard duckling *in situ* tests in the waterways during eight of the spray events were not affected by methamidophos. They had 100-percent survival and normal brain AChE activity. Ducklings drank and swam in the water for 8 to 10 hours post-spray, but did not have exposure to wild food in the waterway. Therefore, the ducklings were not exposed to chemicals deposited on or incorporated into foods in the waterways, another route of exposure for wild waterfowl.

## TRANSPORT AND TOXICITY OF ACROLEIN

Sampling times, locations (fig. 2), and results of the acrolein monitoring study are given in table 19. A well-defined front of acrolein in water was not detected, but 35 of the 52 field tests were positive for acrolein. Thirteen of the duplicate samples were sent to the NWQL for analysis. Twelve of those samples were positive in the field test, but laboratory results were above reporting limits for only three of these samples. A value of 4.5 mg/L was measured in a sample collected just upstream of site A2, 0.4 mi downstream of the application point, and 2.5 hours after the application was begun. The other confirmed detections occurred on July 15, 48 hours after the application was made. One of those was 0.0024 mg/L at the point of application and the other was 0.027 mg/L at the farthest (3.0 mi) downstream site (fig. 2). The EPA aquatic life criteria indicate that acute and chronic toxicity may occur at concentrations as low as 0.068 and 0.021 mg/L, respectively (U.S. Environmental Protection Agency, 1986b). Sensitivity to acrolein is variable, and some organisms may not be protected by the general criteria. Although acrolein is a volatile compound and is lost from aquatic environments rather rapidly, it can be toxic in water for several days. In laboratory studies, acrolein persisted in a large tank for up to 150 hours (Bowmer and Higgins, 1976). The compound's EPA pesticide-use label requires that acrolein-treated water be withheld from fish-bearing water for 6 days post-application.

Results of the bioassays done during the acrolein monitoring study are presented in table 20.

The bioassay test at site A2 at 0 and 2 hours post-application were compromised due to vandalism. Other more isolated sites were not bothered. No substantial invertebrate toxicity was observed, although the 0- and 2-hour assessments could not be made at the site closest to the injection point. Toxicity to minnows was observed (mortality greater than 20 percent of reference) at site A2 24 hours post-treatment, at site A4 24 hours post-treatment, and at sites A6 and A7 24 hours post-treatment. The minnow survival patterns suggest acrolein caused a pulse of toxicity that moved down the canal. The low survivability at site A7 in the 24 hour post-treatment bioassay and the presence of acrolein at a concentration above the chronic criterion suggest that toxic levels of acrolein existed at the site a substantial time after an acrolein application was made. The water sample in which acrolein was detected at site A7 was collected at the end of the 24-hour bioassay and represents the minimum concentration that could have occurred during the bioassay. Because other acrolein applications were being made in the same general area during the monitoring effort, there is some chance that the acrolein presence in the N canal was related to applications made after the monitored application or in another drain.

Water can be released from the N canal to Tule Lake at a point just below site A7. The canal's gates were closed during the period of monitoring, although water leaked through the gates into the lake (approximately 15 ft<sup>3</sup>/s). Dilution of canal water leaking into the lake may rapidly lower the concentration below current criteria.

## CONTAMINANTS AND TOXICITY IN BOTTOM SEDIMENT

### PESTICIDES IN BOTTOM SEDIMENT

In 1990, 25 bottom-sediment samples were analyzed for organochlorine compounds. Fifteen of these were collected in Tule Lake sump. Chlordane was detected in 84 percent of the samples (less than 1.0-6.0 pg/kg), DDD in 100 percent (0.2-4.4 µg/kg), DDE in 100 percent (0.3-4.5 µg/kg), and DDT in 20 percent (0.2-0.5 µg/kg). The maximum concentra-



**Table 19.** Field and laboratory analyses of acrolein concentrations in water samples collected July 13-15, 1992, Klamath Basin

All concentrations are in milligram per liter. See figure 2 for site locations. <, actual value is less than value shown. Numbers in parentheses are laboratory values]

Site no. Miles downstream	A1			A2			A3	A4	A5	A6	A7
	0.0	0.15	0.4	0.6	1.0	1.1	1.6	2.0	2.2	2.4	3.0
Date	Time										
7-13	0950										
	0										
	0.05										
	(<0.02)										
	1005										
	0										
	1020										
	.02										
	.1										
	1035										
	(<0.02)										
	1050										
	.01										
	1105										
	0										
	1120										
	.4										
	(<0.02)										
	1135										
	.1										
	1150										
	0										
	1205										
	.05										
	0.2	0.01									
	1220										
	.2										
	1235										
			4.5								
	1250										
	0										
	1305										
	0.5										
	(<0.02)										
	1320										
	1335										
	.01										
	1350										
	0										
	1405										
	0										
	(<0.02)										
	1420										
	0.1										
	0										
	1435										
	.01										
	1450										
	.05										
	1505										
	1520										
	0										
	1535										
	1550										
	0										
	1605										
	.74		.12								
	(<0.02)										
	1620										
	.45										
	(<0.02)										
	1635										
	.08										
	0.55										
	1650										
	1705										
	.42										
	1720										
	1735										
	.05										
	1750										
	1805										
	0										
	1820										
	1835										
	0										
	1850										
	0										
7-14	0900 to										
	.25						<.05	.13	.05	.06	.25
	1100										
	(<0.02)										
7-15	0830 to										
	.6						.15		1.5	0	.1
	0930										
	(0.0024)										
	(<0.02)										
	(0.027)										

**Table 20.** Percent survival of *Daphnia* and fathead minnows before and after application of acrolein, Klamath Basin

[Time is in hours from application. Sites are shown in figure 2. NA, not available]

<i>Daphnia</i>				
Time	Site A2	Site A4	Site A6	Site A7
-24	80	90	95	95
0	NA	80	70	95
2	NA	95	100	95
24	75	65	100	100
Fathead minnows				
-24	65	60	85	85
0	NA	70	80	85
2	NA	10	60	90
24	10	10	55	25

tions of chlordane, DDD, and DDE were detected in the N canal at the north side of Tule Lake NWR. These concentrations are similar to those found in bottom sediment during the 1989 reconnaissance study (Sorenson and Schwarzbach, 1991) and are less than those commonly found in soil and sediment (California Department of Food and Agriculture, 1985; Eisler, 1990).

In 1992, chlorophenoxy acid herbicides were analyzed in 17 sediment samples and organophosphorus and carbamate pesticides in 2 sediment samples. Concentrations of these herbicides and insecticides were below the reporting limit of 10 pg/kg.

### ARSENIC AND MERCURY IN BOTTOM SEDIMENT

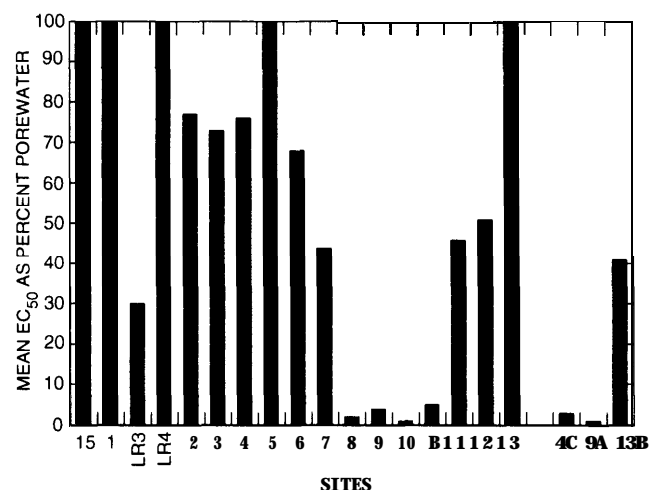
Arsenic and mercury were analyzed in 11 bottom sediment samples in 1992. Arsenic was detected in all of the samples, with a geometric mean of 8.8 ug/g dry weight (range, 2.53-25.66 ug/g). The highest arsenic concentrations, with a mean of 20.2 ug/g dry weight (range, 15.8-25.7 ug/g), were from Units 4C, 9A, and 13B at Lower Klamath Lake. This is in the same general area of the refuge where elevated levels of arsenic (15 ug/g) were detected in 1989 (Sorenson and Schwarzbach, 1991). Mercury was detected in 10 of the 11 samples, with a geometric mean of 0.053 ug/g (range, 0.026-0.167 ug/g). Mean mercury sediment concentrations at Lower Klamath Lake sites (0.073 ug/g) were twice as high as mean concentrations at Tule Lake sites (0.036 ug/g). Arsenic and mercury concentrations are within or just

above the 95th percentile baseline range (1.2-22 ug/g for arsenic and 0.0085-0.25 ug/g for mercury) measured in soils of the western United States (Shacklette and Boerngen, 1984) and within reference ranges in bottom sediment (Eisler, 1987, 1988). Sorenson and Schwarzbach (1991) discussed the significance of the locally elevated arsenic and mercury concentrations and attributed them to natural sources related to the volcanic geology of the basin.

### MICROTOX® BIOASSAY OF SEDIMENT POREWATER

The results of Microtox® sediment porewater bioassays are summarized in figure 11. Sites 8,9,10, B, 4C, and 9A had the greatest toxicity in 1992, with mean EC<sub>50</sub>'s of less than 5 percent. Sites LR3, 7, 11, and 13B had mean EC<sub>50</sub>'s of less than 50 percent.

Toxicity at these sites can be attributed to a combination of several natural and anthropogenic effects. MicrotoxB is not very sensitive to ammonia even at concentrations as high as 40 mg/L (Ankley and others, 1990), but it is sensitive to natural sulfur compounds, which can be significant sources of toxicity (Jacobs and others, 1992). Sites 4C, 9A, and 13B were subjected to concentrated waterfowl populations in 1992 because of drought conditions. As Units 4C and 9A dried, waterfowl were concentrated in the confined borrow areas along the dikes where the sediment samples were collected. The sediment was anaerobic and very malodorous. These conditions can produce



**Figure 11.** Mean MicrotoxB EC<sub>50</sub> of sediment porewater in 1992, Klamath Basin.

high levels of sulfides and other toxicants in sediment. Although water was supplied to Unit 13B and porewater toxicity there was less than the toxicity at sites 4C and 9A, the mean  $EC_{50}$  was still less than 50 percent. Sediment at site 13B was also strongly malodorous and high in organic detrital matter.

## TRACE ELEMENTS AND PESTICIDES IN BIOTA

### TRACE ELEMENTS

#### Blue-Green Algae

Arsenic, boron, mercury, and selenium concentrations in the blue-green algae, *Aphanizomenon flos-aquae*, generally increased at downstream sampling sites with site 1 (J canal at Anderson Rose Dam) having the lowest concentrations, site 3 (N canal) having intermediate concentrations, and site 13 (Klamath Straits drain) having the highest concentrations of all four trace elements. At all three sampling locations, concentrations of arsenic, boron, mercury, and selenium in the blue-green algae were below dietary thresholds for waterfowl.

Algae is one of the best mediums for monitoring concentrations of arsenic (Jenkins, 1981). Arsenic was detected in blue-green algae collected at all three sites in the Klamath Basin (dry weight concentrations ranged from 1.6 mg/kg at site 1 to 2.7 mg/kg at site 13). All concentrations were below the concentration of 30 mg/kg that Camardese and others (1990) found in vegetation associated with agricultural drainwater that altered the growth, development, and physiology of ducklings.

Mercury concentrations were greater than the reporting limit only at site 3 (0.038 mg/kg dry weight) and site 13 (0.07 mg/kg dry weight). Heinz (1979) found that mallards fed a diet of 0.5 mg/kg mercury (as methylmercury dicyandiamide, dry weight) exhibited abnormal egg-laying behavior and experienced impaired reproduction.

Boron concentrations were 12 mg/kg dry weight at sites 1 and 3, but increased to 13 mg/kg dry weight at site 13. Concentrations at all these sampling sites were below the 1,000 mg/kg boron concentration (as boric acid, dry weight) that significantly lowered mallard hatching success rates and 21-day-old duckling

survival rates (Patuxent Wildlife Research Center, 1987).

Concentrations of selenium ranged from below the reporting limit at site 3 to 1.4 mg/kg dry weight at site 13. The selenium concentration at site 1 was at the reporting limit (0.3 mg/kg dry weight). Heinz and others (1987) found that mallards fed a diet supplemented with 8-16 mg/kg selenium (as selenomethionine, dry weight) produced significantly more abnormal embryos than controls and significantly lowered duckling survival.

#### Aquatic Invertebrates

Backswimmers and water boatmen were collected near site 12 in the Lower Klamath refuge and analyzed for selenium, arsenic, and mercury (MacCoy, 1994). All concentrations were below levels of concern (Eisler, 1987; Lemly and Smith, 1987).

#### Fish

Mercury was detected in fish at all sites sampled in the Klamath Basin in 1992. Fathead minnows (juveniles) were collected at the Lower Klamath NWR in the Klamath Straits drain near site 12. Tui chub were collected in the Lost River below Clear Lake dam, in the Lost River below Anderson Rose dam, in the N canal near site 3, in the 101-B drain near site 7, and in the channel to pump D near site 11.

The geometric mean mercury concentration for 20 tui chub fish samples collected from all five sampling sites in the Klamath Basin was 0.049 mg/kg wet weight. This value was less than the 85th percentile of 0.17 mg/kg wet weight for the 1984-85 National Contaminant Biomonitoring Program (Schmitt and Brumbaugh, 1990). The geometric mean concentration was 0.080 mg/kg wet weight for the 6 tui chub adults and 0.039 mg/kg wet weight for the 14 tui chub juveniles.

#### Avian Eggs

Arsenic concentrations were below reporting levels in the 11 American avocet eggs collected at Lower Klamath NWR in 1991, in the 10 American coot eggs collected at Lower Klamath NWR in 1991, and in the 9 western grebe eggs collected at Lower Klamath NWR and the Tule Lake upper sump in 1991.

Selenium was analyzed only in American avocet eggs collected from Lower Klamath NWR in 1991. Selenium was detected in all but 1 of the 11

eggs collected. The maximum selenium concentration was 2.85 mg/kg dry weight and the mean concentration was 1.40 mg/kg dry weight. Dry weights were calculated from wet weights and percent moisture values provided by the laboratory doing the analysis. Selenium concentrations in avocet eggs were not toxicologically significant. Skorupa and others (1991) have suggested a "3/20" guideline for dry weight selenium concentrations in eggs. Under these guidelines, eggs with selenium concentrations less than 3 µg/kg are not at risk, those greater than 20 µg/kg are at great risk, and those between 3 and 20 µg/kg require a case-by-case analysis of reproductive performance.

No eggs contained the levels of mercury (0.5 mg/kg) that Fimreite (1971) identified as the lowest observable effect level in avian eggs. Western grebes were the only avian species in which eggs were collected from both the Lower Klamath NWR (6 eggs) and the Tule Lake upper sump (19 eggs). Mercury concentrations in Lower Klamath eggs ranged from 0.065 to 0.123 mg/kg wet weight; Tule Lake concentrations ranged from 0.043 to 0.139 mg/kg wet weight. A t-test of the geometric mean concentrations of mercury showed no significant differences in Lower Klamath NWR and Tule Lake western grebe eggs ( $p=0.178$ ,  $d.f.=23$ ).

Mercury residues in eggs from all six avian species were less than the 0.790 to 2.000 mg/kg wet weight concentrations that are linked to impaired reproduction in various bird species (Fimreite, 1971; Spann and others, 1972; National Academy of Sciences, 1978; Heinz, 1979; and Eisler, 1987).

## ORGANOCHLORINE COMPOUNDS

### Fish and Invertebrates

Organochlorine compound concentrations were measured in fish and invertebrates to assess potential exposure through diet to avian species. The dominant fish in aquatic community surveys throughout the lower basin were tui chub, fathead minnows, and juvenile cyprinids. These fish represented the predominant prey species available to fish-eating birds foraging in canals, wetland units, and in Tule Lake.

Thirteen composite samples of tui chubs and one composite of fathead minnows were analyzed for organochlorine compounds. Minnows were the only species collected from the Klamath Straits drain.

Adult chubs were observed and collected only in the Lost River below Clear Lake dam and below Anderson Rose dam. Adults were separated from juveniles in composite samples. Most fish composites analyzed for organochlorine compounds, however, were composed of juvenile fish. DDE was the only organochlorine residue detected and only in adult tui chub in the Lost River below Anderson Rose dam (0.01 mg/kg wet weight).

Invertebrates sampled for organochlorine analysis included one composite of leeches and two composites of chironomid larvae from sediment in mid-Tule Lake (upper sump) in 1991. Concentrations of all organochlorine compounds, including DDE, were below the 0.01 mg/kg reporting limit.

### Avian Eggs

Avian eggs were collected for organochlorine analysis from eared grebes ( $n=4$ ) mallard ( $n=1$ ), western grebes ( $n=17$ ), and white-faced ibis ( $n=21$ ). Eggs were collected from fail-to-hatch nests of white-faced ibis nesting at Lower Klamath NWR in 1990 ( $n=5$ ), 1991 ( $n=6$ ), and 1992 ( $n=10$ ). The intended collection of eggs from western grebes at both Lower Klamath and Tule Lake was possible only in 1991 and then only from three nests at Lower Klamath. Western grebes did not nest at Lower Klamath in 1992 because the "permanent water" wetland unit utilized by grebes in previous years was drained due to drought conditions and reduced refuge water supply. The frequency of detection and mean concentrations of organochlorine compounds are summarized in table 2.1.

DDE was the only organochlorine compound found in all avian eggs analyzed. Concentrations of p,p' DDE were greater in ibis than in grebe eggs in all sampling years and were high enough to affect eggshell thickness in ibis. One third of all ibis eggs from the Klamath Basin had DDE concentrations greater than 8 mg/kg.

A high proportion of western grebe and ibis eggs had detectable concentrations of trans-nonachlor. Trans-nonachlor is a persistent degradation product of the cyclodiene pesticide chlordane, as well as a component of the technical chlordane product. Chlordane, a pesticide used to control wood-destroying insects, is one of the few organochlorines still in use; although it is not used in Klamath agriculture, it may have been used in upstream log storage facilities on the Klamath River and in residential treatments for termites. Trans-

**Table 21.** Percent frequency of detection and geometric mean concentrations of organochlorine compounds in eggs of white-faced ibis (21 eggs), western grebes (17 eggs), and eared grebes (4 eggs), Klamath Basin

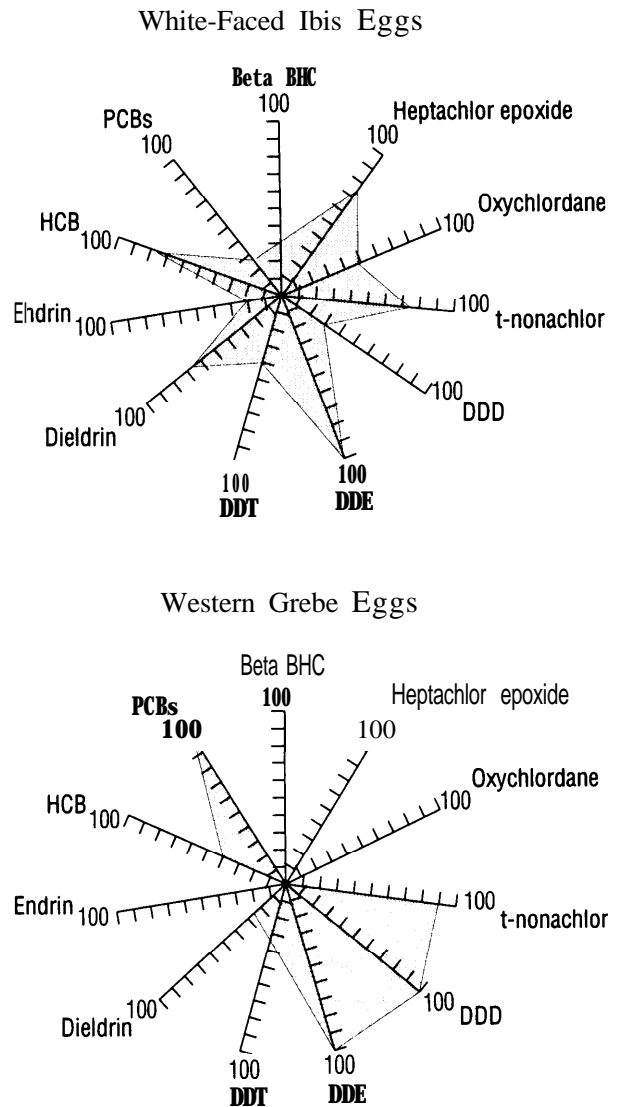
[>, actual value is greater than value shown]

Sample type	BHC beta	Dieldrin	Endrin	HCB	Hept- epoxide	oxy- chlordane	p,p' DDD	p,p' DDE	p,p' DDT	PCBs	T- nonachlor
<b>Percent frequency of detection</b>											
White-faced ibis.....	29	67	19	76	67	48	33	100	38	24	88
Western grebe .....	0	24	0	41	6	6	100	100	35	100	76
Eared grebe.....	0	0	0	0	0	0	0	100	0	0	0
<b>Geometric mean concentrations, in milligram per kilogram wet weight</b>											
White-faced ibis.....	0.003	0.026	0.002	0.047	0.014	0.01	0.005	2.13	0.119	0.004	0.021
Western grebe .....	.001	.002	.001	.003	.001	.001	.173	.780	.004	.670	.023
Eared grebe.....	>.01	>.01	>.01	>.01	>.01	>.01	>.01	.13	>.01	>.01	>.01

nonachlor occurred in nearly all eggs of both species, with a geometric mean of about 0.02 mg/kg in both ibis and grebes. Exposure to trans-nonachlor is not unique to the Klamath Basin and could just as easily occur at wintering locales.

### Sources of Organochlorine Pesticide Contamination in Avian Eggs

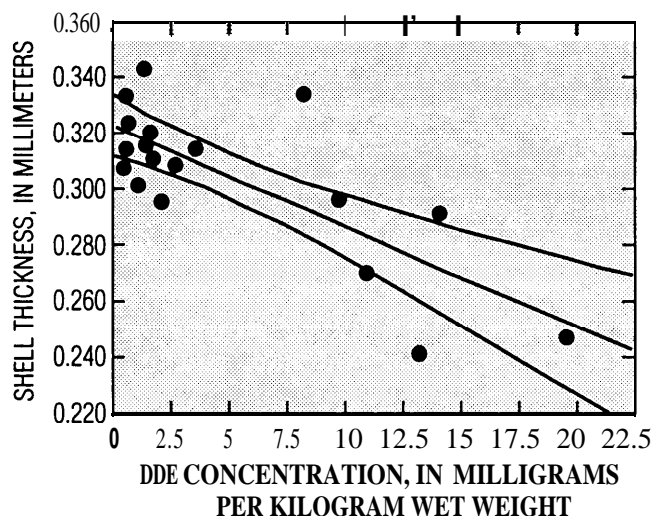
Radial plots of the detection frequency of different organochlorine compounds illustrate how ibis and grebe eggs differ in their organochlorine profiles (fig. 12). DDD and PCB were detected in all grebe eggs, yet ibis had few eggs with detectable levels of DDD or PCB. Ibis, however, had a highly heterogeneous organochlorine profile, with 11 different compounds detected. The more homogeneous organochlorine profile of the western grebe indicates a different source of organochlorine exposure. While nesting in the Lower Klamath Basin, western grebes feed on fish in the sumps and canals. Ibis feed on earthworms in flooded pastures and benthic invertebrates in the exposed mudflats and shallow water of the refuge. Winter migratory locales also differ greatly, with ibis moving as far south as the coast of Mexico and western grebes wintering offshore or in San Francisco Bay (the most likely source of elevated PCB exposures). The higher levels of DDD in grebes may reflect their specialized piscivorous diet. DDD is produced through reductive dechlorination of DDT, which can occur both in anaerobic sediment and by metabolic action of fish gut microflora (C.J. Schmitt, National Contaminant Biomonitoring Program, written commun., 1989).



**Figure 12.** Percent frequency of detection of selected organochlorine compounds in white-faced ibis and western grebe eggs collected between 1990 and 1992, Klamath Basin.

## Eggshell Thickness Measurements

In this study, eggshell thinning was found in white-faced ibis eggs at Lower Klamath NWR (fig. 13). Ibis are very sensitive to the eggshell thinning effects of DDE and experienced severe eggshell thinning during the 1970's in the western United States. Rare since that period, ibis have since become more abundant throughout the west, re-establishing colonies on many refuges. Some portion of their population appears, however, to have a persistent problem with organochlorine exposure. The most severe white-faced ibis eggshell thinning effect was observed in 1991, coincident with the higher DDE concentrations



**Figure 13.** Regression plot of white-faced ibis eggshell thickness and DDE concentrations in eggs collected at the Lower Klamath National Wildlife Refuge in 1991 and 1992. Regression  $r^2=0.6$ .

in that year (table 22). The DDE content of ibis eggs was negatively correlated with eggshell thickness ( $R^2+0.604$ ,  $p<0.0001$ ). Mean eggshell thickness of ibis eggs, however, was not as reduced as the eggs at Colusa NWR in 1989 (Dileanis and others, 1992) or Carson Lake in the mid- 1980's (Henny and Herron, 1989); mean eggshell thickness in both of those studies was 13 percent lower than pre-DDT era values. Henny and Herron (1989) estimated that DDE was affecting about 20 percent of ibis production at Carson Lake.

The avocet, coot, eared grebe, mallard, and western grebe eggshells collected for this study did not appear to be affected by eggshell thinning (table 22). All western grebe eggshell-thickness values for eggshells collected at Lower Klamath NWR and Tule Lake were within the range reported for the pre-1947 values (mean= $0.385\pm0.030$  mm) for northern California and Oregon except one eggshell (mean= $0.354$  mm) collected in the Tule Lake upper sump in 1992 (Boellstorf and others, 1985).

## Free-Living Waterfowl Cholinesterase Evaluation

Most waterbirds collected as carcasses or moribund during 1991 and 1992 had brain AChE values that were similar to those reported for normal specimens of that species by Hill (1988). In 1991, 5 of the 13 mallards were below the normal AChE range (9-15). In 1992, 8 ducks were collected on Lower Klamath NWR and 19 ducks were collected at Tule Lake NWR; all AChE values were within the normal range of healthy wild birds.

**Table 22.** Eggshell thickness of avian eggs collected at Lower Klamath and Tule Lake National Wildlife Refuges, 1990-92

Species	Location	Year	Number of eggs	Eggshell thickness (millimeter)	
				Mean	Standard error
American avocet.....	Lower Klamath.....	199 1	8	0.248	0.011
American coot.....	Lower Klamath.....	1991	10	.325	.019
Eared grebe.....	Tule Lake.....	1992	4	.296	.008
Mallard.....	Lower Klamath.....	1990	10	.339	.021
Western grebe.....	Lower Klamath.....	199 1	7	.424	.037
Western grebe.....	Tule Lake.....	199 1	10	.467	.034
Western grebe.....	Tule Lake.....	1992	9	.405	.027
White-faced ibis.....	Lower Klamath.....	1990	5	.318	.017
White-faced ibis.....	Lower Klamath.....	199 1	10	.296	.026
White-faced ibis.....	Lower Klamath.....	1992	10	.308	.017

# EFFECT OF IRRIGATION DRAINWATER ON COMPOSITION OF AQUATIC COMMUNITIES

## BENTHIC MACROINVERTEBRATES

The taxa of organisms identified in the 1990 and 1991 benthic macroinvertebrate surveys are presented by MacCoy (1994). Overall, 35 benthic invertebrate taxa (groups identified to the family level) were observed over the 2-year sampling period. There was not a significant difference between sites in the number of taxa identified at the primary sampling sites in 1991. Twenty-nine taxa were identified at these sites: 26 taxa in the upstream sites (sites 1 and 2), 24 taxa in the return flow sites (sites 3, 5, 7, and 9), and 23 taxa in the downstream sites (sites 11, 12, and 13).

Oligochaeta and Chironomidae were the common dominant taxa at the primary sampling sites in June, July, and August 1991; at the Upper Tule Lake sites in July 1990; and at the Tule Lake, Clear Lake, Lost River, and Lower Klamath sites in August 1990. Oligochaeta constituted 38.7 to 79.1 percent of the taxa, and Chironomidae constituted 6.7 to 28.0 percent of the taxa at these locations. Members of these taxa are tolerant of low dissolved-oxygen concentrations, and oligochaetes are often the most common organisms in the benthic communities of eutrophic streams and lakes (Jonasson, 1969; Brinkhurst, 1974).

## WATER-COLUMN INVERTEBRATES

Twenty-two different taxa of aquatic invertebrates were identified in water-column invertebrate surveys. Taxa that comprised at least 5 percent of a collection are included in graphs of the survey results in figure 14. These figures show both the total organism count and relative taxa composition of each collection. Site 2, on the Lost River above Tule Lake sump, had the greatest taxa richness, with 19 different taxa. Most of the other sites had at least 12 different taxa, but site 15 had only 6 taxa, with most collections dominated by either daphnids or copepods. Return flow sites 5 and 9 had very low average total organism counts (<20 organisms) on three collection occasions. In addition, site 5 was unusual in that daphnids were

very rare and never comprised >5 percent of any collection. Total organism count and relative composition of water-column invertebrates was dynamic at all sites. However, at sites 12, 13, and 15, copepods became dominant in late summer samples (60 to 100 percent of all organisms), whereas at sites 12 and 15, daphnids dominated early summer samples (daphnids were never observed to be numerous at site 13).

Acute toxicity measured in *Daphnia* bioassays (table 23) was not significantly higher in drains than it was in upstream reference sites. No clear relationship was evident between the water-column invertebrate surveys and survival of *Daphnia* in the weekly *in situ* bioassay tests at the monitoring sites. Although average *Daphnia* survival was only 51.3 to 78.8 percent, there were no significant differences in survival among the sites. Two sites had lower ( $p < 0.05$ ) numbers of daphnids, the return flow site 5 (mean=1.5, SD=1.0) and the downstream site 13 (mean=3.7, SD 8.5), but those sites did not have significantly different *in situ Daphnia* survival or a higher number of positive *in situ* bioassay tests. *In situ* tests measure acute toxicity and may not reflect other factors that can affect *Daphnia* populations.

## FISH COMMUNITIES AND FISH HEALTH SURVEYS

During 1991 and 1992, tui chub, fathead minnows, or juvenile cyprinids were the dominant fish at all survey locations (fig. 15). The average Index of Biological Integrity (IBI) calculated for each site ranked all sites as poor or very poor aquatic habitat (table 24), including the Lost River upstream site that had been selected to serve as a reference site.

Eight species of fish were identified in the surveys. Native fishes collected in the surveys included an individual juvenile sculpin (from the upper Lost River site), an individual juvenile sucker (from the lower Lost River site), tui chub, blue chub, and large scale chub, which is probably a hybrid of tui and blue chub (Peter B. Moyle, University of California-Davis, oral commun., 1992). Non-native species collected included fathead minnow, yellow perch, and Sacramento perch. Because very small juvenile cyprinids could not be identified to species and could have been

either chub or fathead minnows, they were not included in the IBI calculations. External anomalies occurred on 5 to 37 percent of individual fish at all locations and frequently included fin erosion, external parasites, lesions, tumors, and spinal deformations (Littleton, 1993). The proportion of abnormalities observed in each fish collection is presented in table 25. A larger number of abnormalities was observed in fish collected farthest downstream in the drainwater system, but this trend was not statistically significant.

## FROG POPULATIONS

Two species of frogs were heard during the frog call surveys in 1991 and 1992, the native Pacific chorus frogs (*Pseudacris regilla*, formerly *Hyla regilla*) and the introduced bullfrog (*Rana catesbeiana*). In general, low numbers of calls were heard, and no frogs were heard at many stations in either year (Boyer, 1993). Pacific chorus frogs were heard calling throughout the duration of the 8-week survey, but bullfrogs were only heard during late June and July after

**Table 23.** Comparison of 1992 *Daphnia* survival during *in situ* bioassays, Klamath Basin

[Sites are listed in their general order along drainage system. Within a column, mean values followed by the letter A do not differ significantly (p greater than 0.05). Positive bioassays were those in which mortality exceeded that in reference tests by more than 20 percent]

Site no. (fig. 1)	<i>In Situ Daphnia</i> survival			Frequency of positive <i>in situ</i> bioassays	Number of Daphnids in water-column surveys		
	Mean (percent)	Standard deviation	Number of tests		Mean	Standard deviation	Number of surveys
15	60.4 A	27.7	12	50	33.1 A	45.4	6
1	64.2 A	25.6	12	58	22.8 A	21.6	6
2	51.3 A	34.6	12	67	44.7 A	32.4	6
3	64.6 A	31.0	12	50	57.3 A	28.8	6
5	66.3 A	20.5	12	50	1.5 B	1.0	6
7	64.6 A	21.9	12	50	14.8 A	14.8	6
9	68.3 A	32.2	12	42	14.2 A	21.4	6
11	78.2 A	24.2	11	27	14.7 A	24.0	6
12	78.8 A	20.7	12	25	24.2 A	33.9	6
13	75.0 A	26.6	12	33	3.7 B	8.5	6

**Table 24.** Summary of fish Index of Biological Integrity (IBI) scores and aquatic habitat ratings from surveys during 1991 and 1992, Klamath Basin

[--, no data]

Survey locations	IBI scores				Aquatic habitat rating
	October 1991	June 1992	September 1992	Average score	
Upper Lost River.....	--	17	--	17	Poor.
Lower Lost River .....	13	17	13	14.3	Very poor.
Site 3 drain .....	--	17	9	13	Poor.
Site 7 drain .....	--	11	9	10	Very poor.
Site 11 Tule Lake.....	--	13	13	13	Poor.
Site 12 drain .....	--	7	9	8	Very poor.



water temperatures were higher than 22°C, the reported minimum temperature for calling by that species (Duellman and Treub, 1986).

The shoreline around Tule Lake was divided into transects (Boyer, 1993); within each transect, vegetation and water depth varied. The average number of calling frogs heard in each transect around Tule Lake, as well as the number of calls heard on the Indian Tom Lake and Lower Klamath transect routes, are presented in figure 16. The presence of calling frogs on Tule Lake seemed influenced by type of shoreline vegetation. Areas that had more variety of terrestrial and emergent vegetation, such as transects T1 and T4, had calling frogs. Parts of transects T1 and T4 had thin-stemmed emergent plants, and Pacific chorus frogs were present in those areas. Transects T1 and T4 also had water depths of up to 7 ft dominated by cattail (*Typha* spp.) with dense, thick stems, habitat favored by bullfrogs. However, few bullfrogs were heard calling in those areas. Historical records indicate that bullfrogs had been hunted in those areas during the 1960's. Finally, it was noted that, although similar habitats also occurred in greater abundance along the Lower Klamath transect routes, fewer calling frogs were heard there than at Tule Lake.

## CHANGES IN AQUATIC COMMUNITIES

Aquatic communities in the Klamath Basin have undergone important compositional shifts since the early 1900's (fig. 17). The algae community of Upper Klamath Lake has shifted from a diatom to a blue-green algae dominated community and, in the last 30 years, to nearly a monoculture of *Aphanizomenon flos-aquae*. Historically, the region had many endemic mollusks, but it now supports a reduced mollusk fauna comprised mostly of Pulmonate snails and other pollution-tolerant taxa. The benthic macroinvertebrate community is now dominated by chironomids and oligochaetes, both of which are tolerant to poor water-quality conditions. The fish community has become simplified and dominated by short-lived, tolerant species. Native trout and sucker fishes have become rare or endangered, while fathead minnows are becoming common. Although initial changes occurred when the Klamath Reclamation Project reduced the basin's wetland habitat and created agricultural land, more recent aquatic community shifts are related to increased organic pollution, eutrophication, and poor water quality.

**Table 25.** Percentage of samples with abnormalities in each of the fish health index characteristics for each date and sampling site, 1991 and 1992, Klamath Basin

[Data for a healthy population of brook trout are included as a reference (Goede and Barton, 1990). ND, No proportional data given]

Date	Location (site nos.)	Parasites	Extremities	Eyes	Gills	Mesenteric Fat	Spleen	Hind gut	Kidney	Liver	Number
10-91	Lost River (LR3) .....	36	39	4	18	46	7	11	32	32	28
10-91	Tule Lake and drains (3,7,11) .....	32	47	21	11	32	11	16	16	5	19
10-91	Lower Klamath ( 12) . .	60	5	0	15	85	10	5	0	20	20
6-92	Lost River (LR3) .....	38	26	1	19	41	23	11	12	13	94
6-92	Tule Lake and drains (3,7,11) .....	41	33	0	11	19	10	2	5	11	125
6-92	Lower Klamath (12) . .	8	26	2	8	14	30	2	8	21	66
9-92	Lost River (LR3) .....	18	11	0	0	33	14	2	0	6	100
9-92	Tule Lake and drains (3,7,11) .....	9	61	3	0	6	6	3	3	0	33
9-92	Lower Klamath ( 12) . .	17	34	0	0	20	3	0	0	0	35
	Reference fish .....	ND	ND	0	5	ND	0	0	0	0	20



Figure 14. Water-column invertebrate surveys at primary sites in 1992, Klamath Basin.

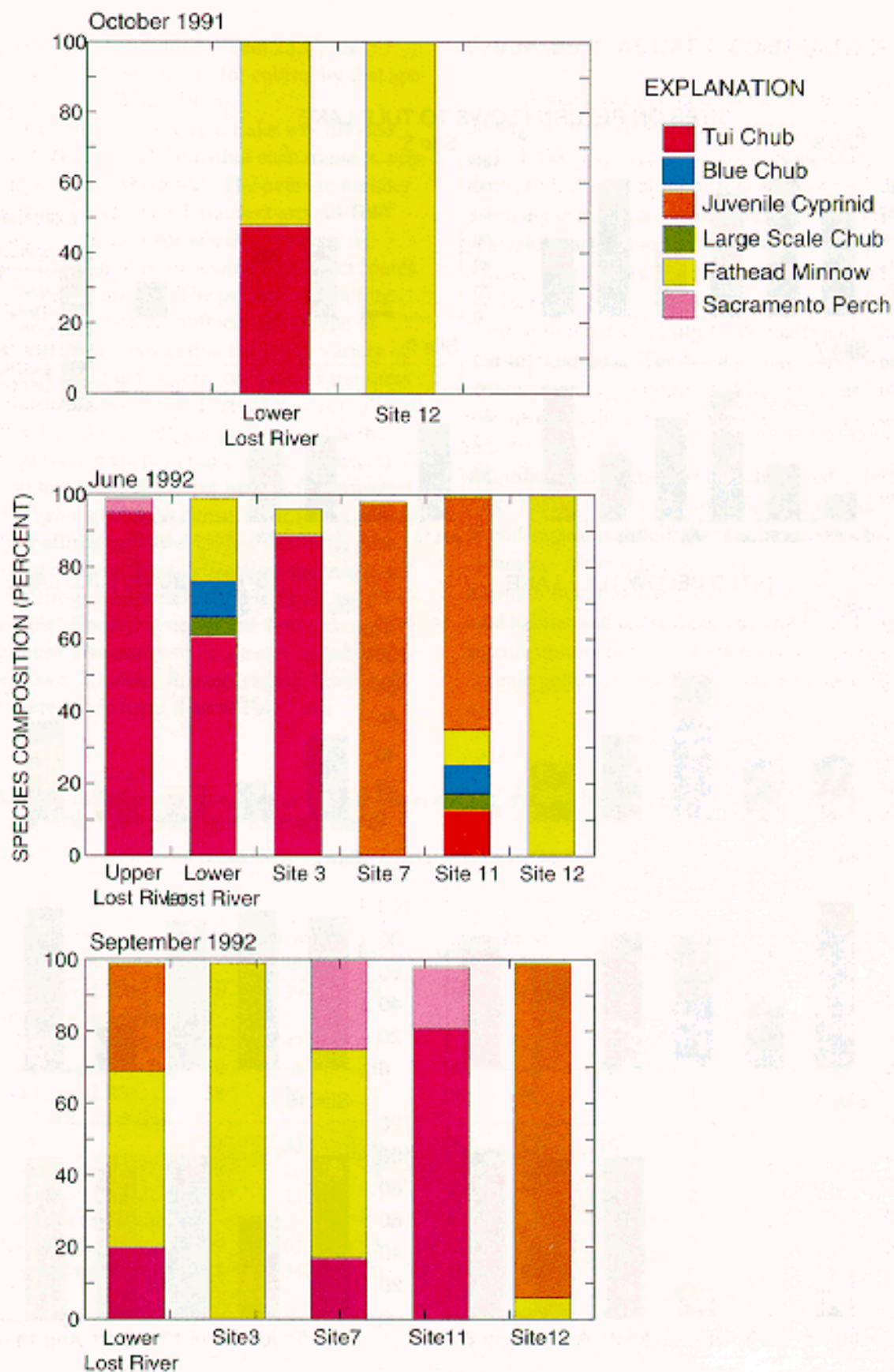


Figure 15. Species composition in fish surveys in 1991 and 1992, Klamath Basin.

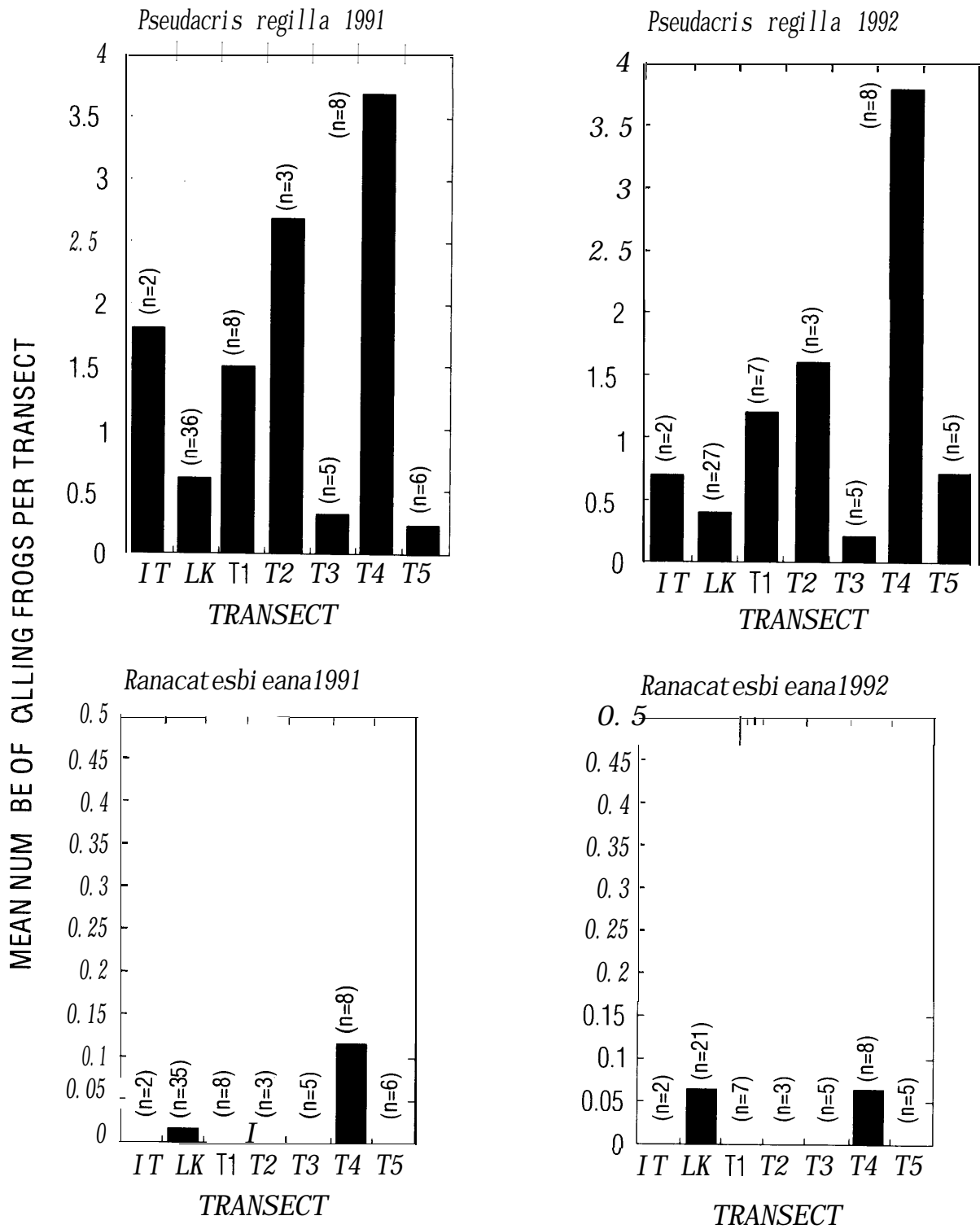


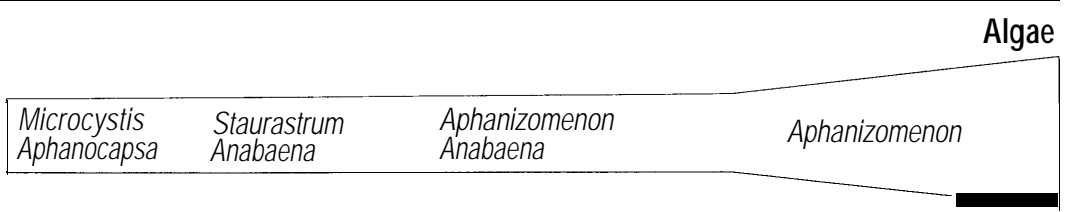
Figure 16. Mean number of calling frogs at individual transects in 1991 and 1992, Klamath Basin.

						<b>Amphibians</b>
Tiger salamander						
Pacific chorus frog						
Yellow-legged frog						
Spotted frog						Spotted frog
Western toad						Threatened
Bullfrog						

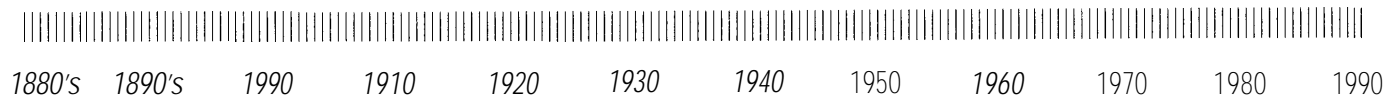
						<b>Fishes</b>
Lost River sucker	Tui chub					
Short nose sucker	Blue chub					
Klamath Lake sculpin	Rain bow trout					
Klamath <i>specied</i> dace	Slender sculpin	Yellow perch	Blue chub	Fathead minnow	Sucker	
Pit-Klamath lamprey	Marbien sculpin		Tui chub		Endangered	
Klamath largescale sucker	Pacific lamprey					

						<b>Molluscs</b>
<i>P. ultramontanum</i>						
<i>P. archimedis</i>	<i>Amnicola n. sp.</i>	Physidae		Lymnaeidae	Andonta	
<i>H. nemberryl</i>		Planorbidae			Gonidea	

						<b>Aquatic Invertebrates</b>
Copepods	Chironomids		Chironomids	Cladocera	Oligochaetes	Leeches



						<b>Wetland Acres</b>
350,000+ acres of natural wetlands						
	Klamath Project					
		Tule Lake dried and cultivated				
			< 75,000 acres of wetlands remain			



**Figure 17.** Historical changes in aquatic communities in the study area (based on available records). Not to scale.

## SUMMARY AND CONCLUSIONS

The effect of irrigation drainage on the water quality and wildlife in the Klamath Basin in California and Oregon was evaluated using several different approaches. From 1990 to 1992, water-quality characteristics and chemical contaminants were monitored at sites upstream and downstream of irrigated farmland. Laboratory and *in situ* bioassays using a variety of test organisms were done to evaluate the toxicity of water, and estimates were made of the size of aquatic invertebrate and fish populations, species diversity, and fish health.

Water-quality characteristics indicative of highly eutrophic systems were documented during the summer months of 1991 and 1992. Dissolved-oxygen concentrations varied over a wide range each day in response to oxygen production by photosynthesizing plants and algae during daylight hours and oxygen consumption by respiring organisms during the night. The median dissolved-oxygen concentrations measured during periodic visits to the primary sampling sites were below the minimum aquatic habitat criterion (5 mg/L) at more than half the sampling sites in 1991 and 1992. In 1992, during periods of continuous water-quality measurements at the primary sampling sites, dissolved oxygen was below criterion from 4 to 83 percent of the time. Dissolved oxygen tended to be low in all parts of the study area: upstream of, within, and downstream of agricultural drains.

Photosynthesis by dense aquatic plant and algal populations causes large diurnal variation in pH by altering the carbonate equilibrium in the poorly buffered water of the study area. During periods of continuous monitoring in 1992, pH measurements were frequently above 9 at sites upstream and downstream of irrigated land.

Nitrogen and phosphorus concentrations were generally at or above threshold levels characteristic of eutrophic lakes and streams. The highest average concentrations of total soluble nitrogen at the primary sampling sites were measured in the drainwater return flows that enter Tule Lake and in the Lower Klamath NWR. At most sites, the largest percent of dissolved nitrogen was organically bound, with much smaller fractions of the total nitrogen load in the form of nitrate, nitrite, and ammonia.

Concentrations of dissolved nitrate and ammonia, forms that are important plant nutrients, were highest in drains entering Tule Lake and in the Lower

Klamath NWR. Concentrations in the Upper Klamath and Tule Lake tended to be low, most likely due to uptake by aquatic plants. Fish are particularly sensitive to ammonia, and concentrations potentially toxic to fish existed throughout the study area.

Concentrations of ammonia in samples from small drains on the Tule Lake refuge leaseland were higher than those measured in the larger drains at the primary sampling sites. The mean concentration in leaseland drains (1.2 mg/L) was significantly higher ( $p=0.05$ ) than the mean concentration in canals delivering water to the leaseland fields (0.07 mg/L) and higher than concentrations reported to be lethal to *Daphnia magna* ( $LC_{50}$ , 0.7 mg/L). Dissolved oxygen and *Daphnia* survivability measured during *in situ* bioassays were correspondingly lower in the leaseland drains than in water delivery canals.

Water samples collected from Tule Lake had less soluble nitrogen than water from drains, except in the vicinity of the 102 drain. Excess nutrients entering Tule Lake are probably removed from solution and incorporated into the algal biomass. Phosphorus is another major plant nutrient that is abundant in the study area waterways. Nitrogen:phosphorus ratios above 7, which might limit continued plant growth, were observed in only 3 of the 17 sites where nutrients were measured in 1992.

Dissolved-organic-carbon concentrations were high at all primary sampling sites and could support large microbial populations. Consumption of oxygen during microbial respiration may exacerbate critically low dissolved-oxygen concentrations in the waterways.

Nutrients leaching from croplands have been documented for many agricultural areas, and excess fertilizer may contribute to the total nutrient load. Another probable nutrient source is the large quantity of organic material entrained in the flows diverted from Upper Klamath Lake for irrigation. During the summer, dense populations of the blue-green algae *Aphanizomenon* grow in Upper Klamath Lake. Water diverted to agricultural lands through the "A" canal contains large amounts of the algae, which can be observed throughout the upper canals of the water delivery system. The highest concentrations of dissolved organic carbon and organic nitrogen were measured in the drains and in waterways downstream of the drains. These concentrations could result when algal cells disintegrate and decompose on their way downstream. Evaporation of water in irrigated fields

and drains may also concentrate nutrients in the drainwater.

Pesticides were frequently detected in water samples collected at the primary sampling sites during the two summers of monitoring. Many of these pesticides were compounds that are soluble in water. The most frequently detected pesticides were simazine, metribuzin, eptam, metolachlor, and terbufos. All the insecticides detected (chlorpyrifos, disulfoton, DDE, ethoprop, malathion, methyl parathion, and terbufos) are considered moderately to super toxic to aquatic organisms, most with *Daphnia* LC<sub>50</sub>'s of <10 mg/L. All pesticide concentrations in the drainwater samples were substantially below acute toxicity values reported for aquatic organisms.

Aerial applications of pesticides to crops grown on Tule Lake NWR leaseland resulted in pesticide drift into refuge waterways. Aerial drift was monitored by use of deposition samplers at the edges of fields and in the middle of the adjacent waterways. Pesticide drift depends on many factors, including wind and the distance between waterways and fields. The distance from treated fields to waterways ranged from 7 to 130 ft.

During the period when methamidophos was being applied to potato fields, 12 attempts were made to monitor pesticide drift. Study personnel were unable to obtain the information needed to identify specific fields prior to pesticide application and, therefore, relied on a general knowledge of pesticide use and chance in selecting monitoring sites. Methamidophos was detected on the deposition sampler at the edge of a field in 3 of the 12 attempts, providing evidence that an application had been made to those fields and that the application provided full-field coverage. In all three of the known applications, methamidophos was also detected on duplicate samplers in the adjacent waterway. The deposits of methamidophos over the water were about 19 to 23 percent of the target application rate of methamidophos for potatoes. This amount of off-target pesticide drift is fairly typical of the amount reported in the literature. The estimated water concentrations of methamidophos from the monitored drift events ranged from 0.8 to 3.1 µg/L, levels that were nonhazardous to aquatic invertebrates and fishes. There were no insecticide-related mortalities during *in situ Daphnia* bioassays, and mallard ducklings penned at the sites had normal levels of brain cholinesterase. All documented instances of pesticide drift were during calm wind conditions (<2.0

mi/h). but from fields very close to the waterways (about 25 ft from field edge to waterway, in all cases).

The herbicide acrolein has been used extensively in the study area to manage aquatic plant growth in irrigation canals and drains. Although acrolein is not used directly on wildlife refuges, there is potential for it to be transported to refuge water. A single application on farmland adjacent to the Tule Lake NWR was monitored over a period of 3 days to evaluate the fate and toxicity of acrolein and the potential for the pesticide to be transported to refuge water. Acrolein is toxic to fish at the concentrations observed in treated waterways. Fathead minnow 24-hour survival at the N canal adjoining Tule Lake, 3.0 mi downstream of the application point, declined from 85 percent to 25 percent during the monitoring period.

Water samples collected at the primary monitoring sites caused static laboratory bioassay toxicity in up to 78 percent of *Lemna minor* tests, in up to 49 percent of *Xenopus Laevis* tests, in 17 percent and 8 percent of *Hyalella azteca* and *Pimephales promelas* tests, respectively, and 0 percent in *Daphnia magna* tests. *In situ* exposure caused mortality in more than 83 percent of *Pimephales* tests and in more than 41 percent of *Daphnia* and *Hyalella* tests. Both static and *in situ* bioassay tests indicated water throughout the study area presented a hazard to early life stages of diverse types of aquatic organisms. Duckweed and frogs were the species most affected under conditions of the static laboratory toxicity tests, whereas *Daphnia*, *Hyalella*, and fathead minnows were affected by ambient environmental conditions in the *in situ* tests, with fathead minnows being the most severely affected species.

Embryos of African clawed frogs (*Xenopus*) exposed to water samples in 1991 exhibited up to 98-percent malformation. In 1991, mortality varied significantly ( $p < 0.05$ ) among sites and test weeks, although no significant interaction was detected between sites and test weeks. Average *Xenopus* survival at two sites was significantly lower ( $p < 0.05$ ) than average control survival.

In 1992, thirty-eight percent of the *Xenopus* mortality tests were positive for toxicity, most occurring throughout the summer in water from return flows and sites downstream of Tule Lake sump. The average *Xenopus* survival in water samples from every site was significantly lower ( $p < 0.01$ ) than average control survival. Eleven percent of the *Xenopus* malformation

tests were positive for toxicity in 1992, and the average number of malformations was higher ( $p < 0.05$ ) than controls in water from four sites. The agent(s) that produced malformations is unknown.

Results of mallard duckling tests at the primary sampling sites in 1991 indicate that ducklings had no hazardous exposure to anti-cholinesterase insecticides.

Although water from the study area resulted in measurable toxicity to a variety of organisms, the degree of toxicity between sites upstream or downstream of agricultural land was not statistically different in any of the bioassays. High pH, low dissolved oxygen, and ammonia appear to be responsible for hazardous conditions.

Organochlorine pesticide concentrations in 25 bottom-sediment samples collected in 1990 were below baseline levels commonly found in soils and sediment. Seventeen bottom-sediment samples were analyzed for chlorophenoxy acid herbicides, and two samples were analyzed for organophosphorus and carbamate insecticides in 1992. No pesticides were detected in any of these samples. Sediment toxicity, measured with Microtox® bioassays, was detected at sites upstream and downstream of agricultural drains. Toxicity was highest in some of the agricultural drains and in the Lower Klamath NWR.

Tissue residues of the trace elements selenium, mercury, and arsenic revealed no bioaccumulation problems. Selenium is at background concentrations in biota and water. Arsenic and mercury concentrations did not exhibit the locally elevated levels found in the 1988 reconnaissance study, perhaps due to changes in water management at Lower Klamath that allowed flushing of some units. Concentrations of p,p' DDE in white-faced ibis were correlated with an observed mean 11-percent eggshell thinning in 1991. Concentrations of other organochlorine compounds also were high in some ibis eggs in 1991. However, ibis populations appear to be increasing, and some ibis eggs were relatively low in DDE concentration. DDE concentrations in eggs of western grebes were not as high as in the eggs of ibis.

Concentrations and types of organochlorine compounds detected in grebe and ibis eggs were highly variable and indicated different sources of organochlorine exposure in these species. The heterogeneity of ibis organochlorine contamination indicates a diversity of exposures in individual ibis. Concentrations of DDE in ibis were extraordinarily high when compared to concentrations in other birds, inverte-

brates, and fish. Both observations support the conclusion that ibis are exposed to organochlorine compounds outside the basin.

Fish and aquatic invertebrate populations inhabiting all sampled areas were representative of pollution-tolerant species assemblages. The aquatic communities that were monitored retained little of their historic ecological structure. Extensive hydrologic modifications and hypereutrophic conditions in Klamath Basin waterways have degraded the quality of aquatic habitat and altered biological communities.

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