# EVALUATION OF AMBIENT TOXICITY TESTS FOR DETECTING GROUNDWATER POLLUTION ENTERING STREAMS AND RIVERS: YEAR 1 PROGRESS REPORT

Michael J. Crossey
Joseph S. Meyer
Ann Boelter

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Department of Zoology and Physiology
College of Arts & Sciences
University of Wyoming

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Wyoming Water Research Center
University of Wyoming
Laramie, Wyoming

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## ABSTRACT


Groundwater pollution is an emerging environmental concern in the Rocky Mountain region. In the current two-year study, we are evaluating the utility of two sublethal toxicity tests for detecting migration of contaminated ground water into streams and rivers.

During Year 1, we tested groundwater or surface-water samples from five locations at each of two study sites: 1) the Laramie River as it flowed past a former railroad tie treating plant south of Laramie, Wyoming, from June 1985 to October 1985; and 2) Crow Creek as it flowed past an oil refinery in Cheyenne, Wyoming, from June 1985 to April 1986. Each water sample was tested for its effects on survival and reproduction of *Ceriodaphnia dubia* (an aquatic invertebrate) and survival and growth of fathead minnow (*Pimephales promelas*) larvae. Chemical analyses of water samples included routine water chemistry parameters, major inorganic ions, 11 trace elements, dissolved organic carbon, reverse-phase HPLC gradients, and GC-MS analyses of organics.

At the Laramie River, toxic ground water underlaid sediments adjacent to the tie treating plant. However, migration of ground water into the Laramie River did not adversely affect fathead minnows and *Ceriodaphnia*. Some water samples from Crow Creek were also toxic, due to industrial effluents and either contaminated ground water or storm sewer runoff following a flood.

Results of this study indicate that (1) ambient toxicity tests can be used in alkaline surface waters of the western U.S.; (2) they are sensitive enough to detect migration of contaminated ground water into surface waters; (3) they may be more sensitive in some cases than

routine, inexpensive chemical analyses for detecting the presence of contaminants; and (4) toxicity of contaminated ground water and an industrial discharge varied considerably during Year 1. In the summer of Year 2 we will collect surface-water and groundwater samples adjacent to the oil refinery on Crow Creek, in order to more accurately identify potential sources of groundwater toxicity found in Year 1 and correlate instream toxicity with stream flow rate.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF APPENDIX TABLES

# INTRODUCTION

Groundwater pollution is an emerging environmental problem in the Rocky Mountain region of the United States. Contamination of near-surface aquifers is an especially important concern because many potential pollutants are applied directly to the soil surface (e.g., herbicides, pesticides, solid and liquid wastes) or are buried at relatively shallow depths (e.g., landfills, hazardous chemical storage ponds, burial pits), where they can migrate into or be leached by ground water. Subsequently, contaminated water flowing through near-surface aquifers can enter surface waters and degrade water quality downstream. Chemical analyses of water from monitoring wells can sometimes be used to trace the transport of groundwater pollutants. However, identifying and quantifying all of the potential inorganic and organic pollutants can be time-consuming and expensive. And a major question still arises: Do contaminant concentrations identified in these analyses pose environmental hazards in receiving waters?

Therefore, it would be desirable to have sensitive biological tests to complement the chemical analyses that are routinely used to detect groundwater pollutants. The U.S. Environmental Protection Agency (EPA) recently developed relatively quick, sublethal toxicity tests using fish and invertebrates for monitoring the effects of industrial and municipal effluents that are discharged into surface waters (Mount and Norberg 1984, Norberg and Mount 1985). Those tests are designed to detect adverse effects on fish growth and invertebrate reproduction and to be more sensitive than traditional acute lethality tests. Because of this improved sensitivity, they have been used successfully (1) for testing instream (ambient) toxicity of effluents after they are discharged into receiving waters and (2) for more traditional serial-dilution testing of effluents before they enter receiving waters (e.g., Mount et al. 1984, Mount and Norberg 1985).

Unfortunately, groundwater contamination has not yet been addressed in the EPA ambient toxicity testing programs. Therefore, we are conducting a two-year study to evaluate the utility of the EPA fish and invertebrate toxicity tests to detect chemical pollution from groundwater and effluent sources along the Laramie River and Crow Creek in southeastern Wyoming. In this report, we (1) present results of our Year 1 investigations, (2) evaluate the toxicity test methods as they are currently being used by EPA and contract laboratories, (3) compare costs and sensitivity for detecting pollutants at our study sites among several levels of chemical analyses and toxicity tests, and (4) outline research to be conducted in Year 2 of this study.

# OBJECTIVES

The objectives of this two-year study are as follows.

1. Evaluate EPA ambient toxicity tests as monitors of effects of groundwater pollutants.
2. Compare the sensitivity of those biological tests to the sensitivity of chemical analyses for detecting the presence of groundwater contaminants.
3. Assess temporal variability of groundwater and surface-water contamination in two Wyoming streams.

By sampling surface waters adjacent to suspected groundwater contamination sources, we anticipated that the emergence of contaminated ground water into streams and rivers could be detected using biological tests. Then the near-surface ground water could be sampled to determine its toxicity, identify its chemical constituents, and ascertain whether it could have caused the observed instream toxicity. Using this sequential testing procedure, we hoped that a cost-effective approach could be developed to evaluate the potential environmental hazards of contaminated ground water entering streams and rivers.

# RELATED RESEARCH

Crossey and Bergman (1985) reported initial investigations of organic contaminant transport in ground water, surface water and sediments at the Union Pacific Tie Treatment Plant adjacent to the Laramie River in Laramie, Wyoming. Although toxicity tests were not conducted in that study, Crossey and Bergman (1985) demonstrated that (1) creosote oil underlaid Laramie River sediments and occasionally entered the Laramie River directly by way of oil seeps along the river bank, and (2) surficial sediments downstream from the tie treating plant were contaminated with chemical constituents identified in creosote oil.

Steadman (1986) reported preliminary studies of contamination along Crow Creek in Cheyenne, Wyoming. In that study, in situ biomonitoring and subsequent biochemical analyses of exposed fish at two sites adjacent to Frontier Oil Refinery property (formerly Husky Oil Refinery and Husky/RMT Properties, Inc.) demonstrated that (1) Crow Creek water downstream from the refinery's NPDES discharge was toxic to rainbow trout, and (2) groundwater or surface-water contaminants might be entering Crow Creek along the refinery's property upstream from the NPDES discharge pipe. Unfortunately, fathead minnow survival and growth and Ceriodaphnia survival and reproduction tests were not conducted in that study. Therefore, results of Steadman's (1986) biochemical analyses on rainbow trout cannot be interpreted directly with respect to the current study of ambient toxicity in Crow Creek.

Fathead minnow and Ceriodaphnia ambient toxicity tests are rapidly becoming accepted by regulatory agencies as sensitive indicators of instream biological effects of industrial and municipal effluent discharges. But because these two toxicity tests are relatively new, they are continually being revised and tested in inter-laboratory comparisons. For example, we recently participated in a round-robin evaluation of the fathead minnow test that was coordinated by Dr. G. Michael DeGraeve of Battelle Columbus Laboratories in Columbus, Ohio. Dr. DeGraeve is currently investigating improved culture techniques for the Ceriodaphnia test and will coordinate a round-robin evaluation of that test protocol soon. Additionally, Dr. Donald Mount and Ms. Teresa Norberg-King of the U.S. EPA Environmental Research Lab in Duluth, Minnesota, continue to refine and evaluate fathead minnow and Ceriodaphnia test techniques at field research sites (Mount et al. 1984, Mount and Norberg 1985). We frequently communicate with these and other researchers around the United States regarding ambient toxicity tests. However, to our knowledge no one has yet used these tests to detect and evaluate the effects of contaminated ground water entering streams and rivers.

# METHODS

## Site Descriptions

Two surface waters in southeastern Wyoming were chosen for this study. Both the Laramie River and Crow Creek flow past industrial sites where groundwater flow patterns indicate discharge from the industrial property to the surface water. Because both sites have significant subsurface contamination, ground water is a potential pollution source for the adjacent stream or river.

Laramie River. The Union Pacific Tie Treatment Plant (UPTTP) is a U.S. EPA Superfund site located 1 km southwest of Laramie, Wyoming, adjacent to the Laramie River (Fig. 1). From the UPTTP site, the river flows northward through Laramie. Approximately 80 acres of the UPTTP property are heavily contaminated with creosote wastes emanating from a series of unlined waste ponds (CH2M/Hill 1985). The site is bordered on the north by Interstate 80 and on the west by the Laramie River and is underlain by contaminated alluvial sediments that extend from ground surface to bedrock, 5 to 10 m below ground surface. Ground water within the alluvial aquifer travels northwesterly across the site and discharges to the river along the west and northwest borders of the site. This alluvial aquifer is a major source of contaminants to the Laramie River (see CH2M/Hill 1984, 1985 for a complete geologic description).

In October 1983 an oily seep was discovered in the Laramie River adjacent to the UPTTP site, and free oil could be detected in the river up to 3 km downstream (Crossey and Bergman 1985). Subsequently, mini-piezometers were used to monitor and define the extent of the seep. In

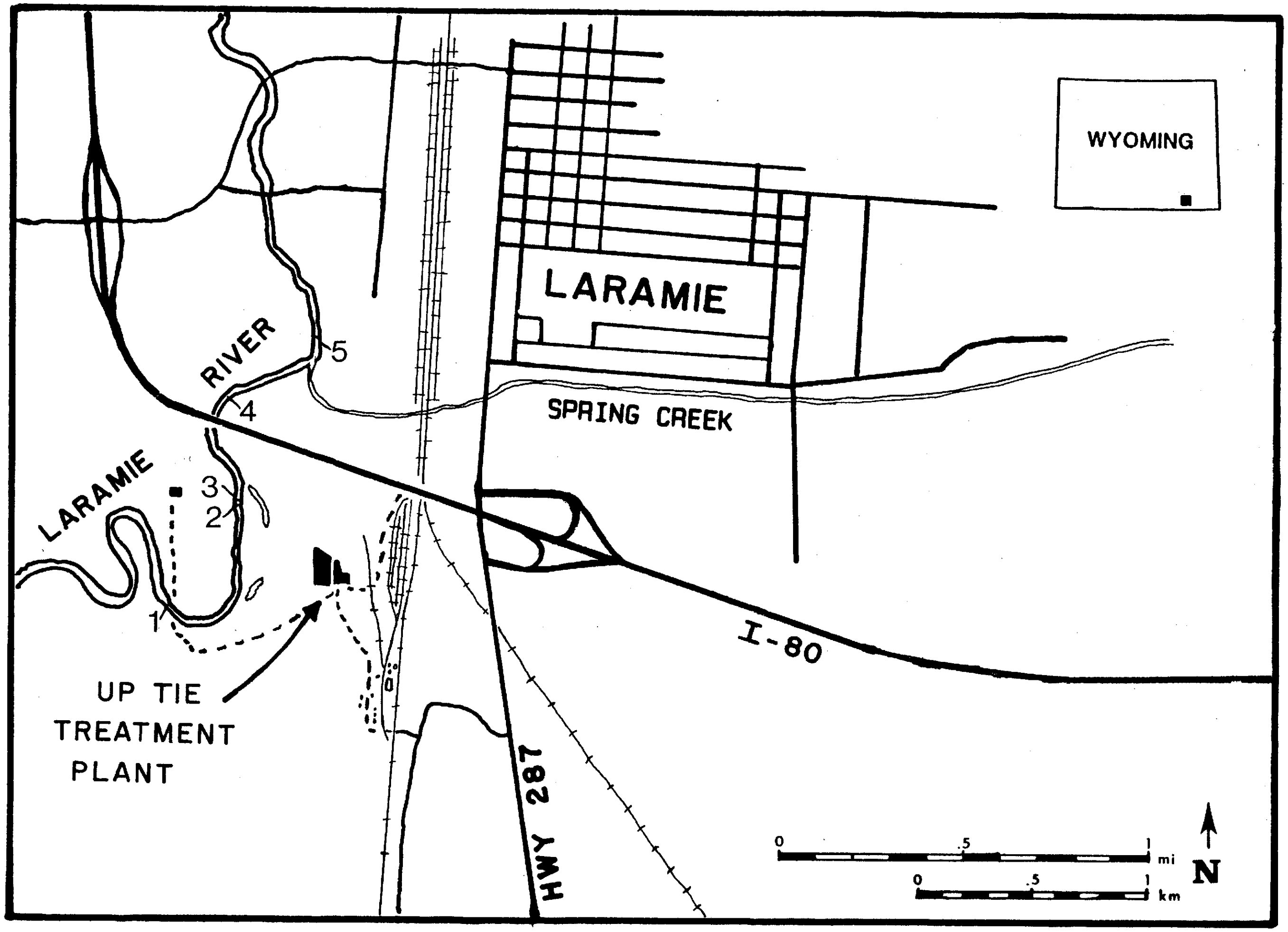


Figure 1. Location of the Laramie River study site, Laramie, Wyoming. Numbers denote sampling locations: 1 = Upstream control and Upstream piezometer (October sampling only), 2 = Above seep, 3 = Site piezometer, 4 = I-80, 5 = Spring Creek.

1984, an oil body was located 1 m below the surface of the river sediments at the same location (Crossey and Bergman 1985). It extended approximately 30 m along the river bank and halfway across the river channel and contained an estimated 4000 to 6000 L of creosote oil. As a result, the Laramie River was relocated approximately 50 m west of its former channel in September 1985, in order to control further contamination entering the river (Fig. 2). The former river channel was covered by several meters of fill and is no longer accessible for sampling. Additional remedial cleanup activities have been initiated at the UPTTP site by the Union Pacific Railroad.

Crow Creek. Frontier Oil Refinery is adjacent to Crow Creek, a small third-order stream that flows through Cheyenne, Wyoming (Fig. 3). Effluent from the refinery is regulated under an NPDES (National Pollution Discharge Elimination System) discharge permit and enters Crow Creek on the downstream (eastern) border of the refinery property. Although the refinery does not exceed those discharge permit limitations, Steadman (1986) reported adverse effects on rainbow trout placed in Crow Creek.

Since 1930, daily refinery operation, spills and leaking waste ponds have contaminated ground water beneath the property considerably. Abandoned waste ponds from the original refinery facility are buried at the southwest corner of the site. This complex of old ponds is designated the southwest surface impoundment (SWSI Site, Fig. 4) and is being decontaminated by the current operators of the refinery. Ground water flows northwest to southeast, traversing the site and discharging to Crow Creek (Bill Payne, Frontier Oil Refinery, personal

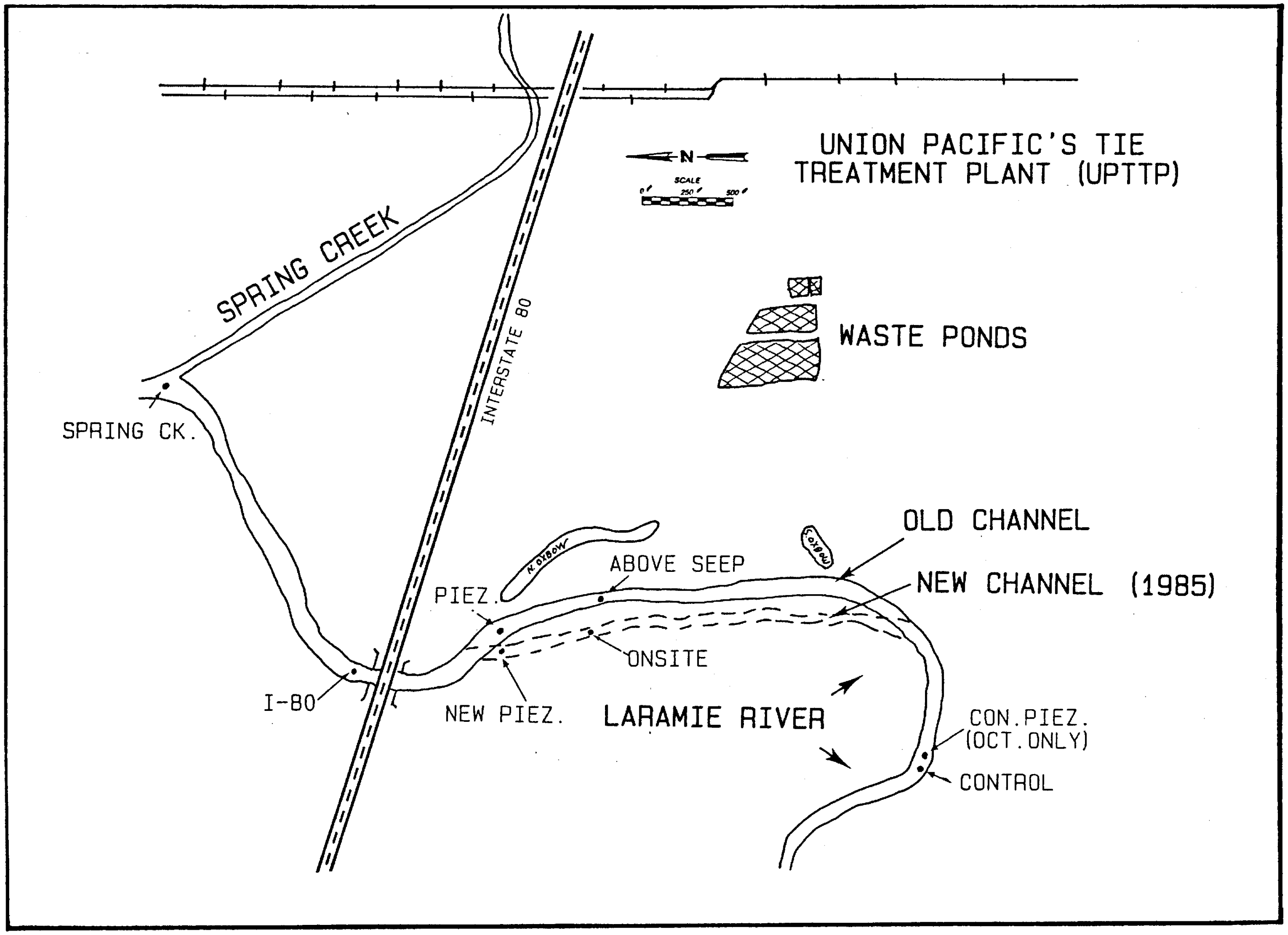


Figure 2. Laramie River sampling locations adjacent to the UPTTP. October samples were taken from the new channel; PIEZ. = interstitial water samples collected using a mini-piezometer.

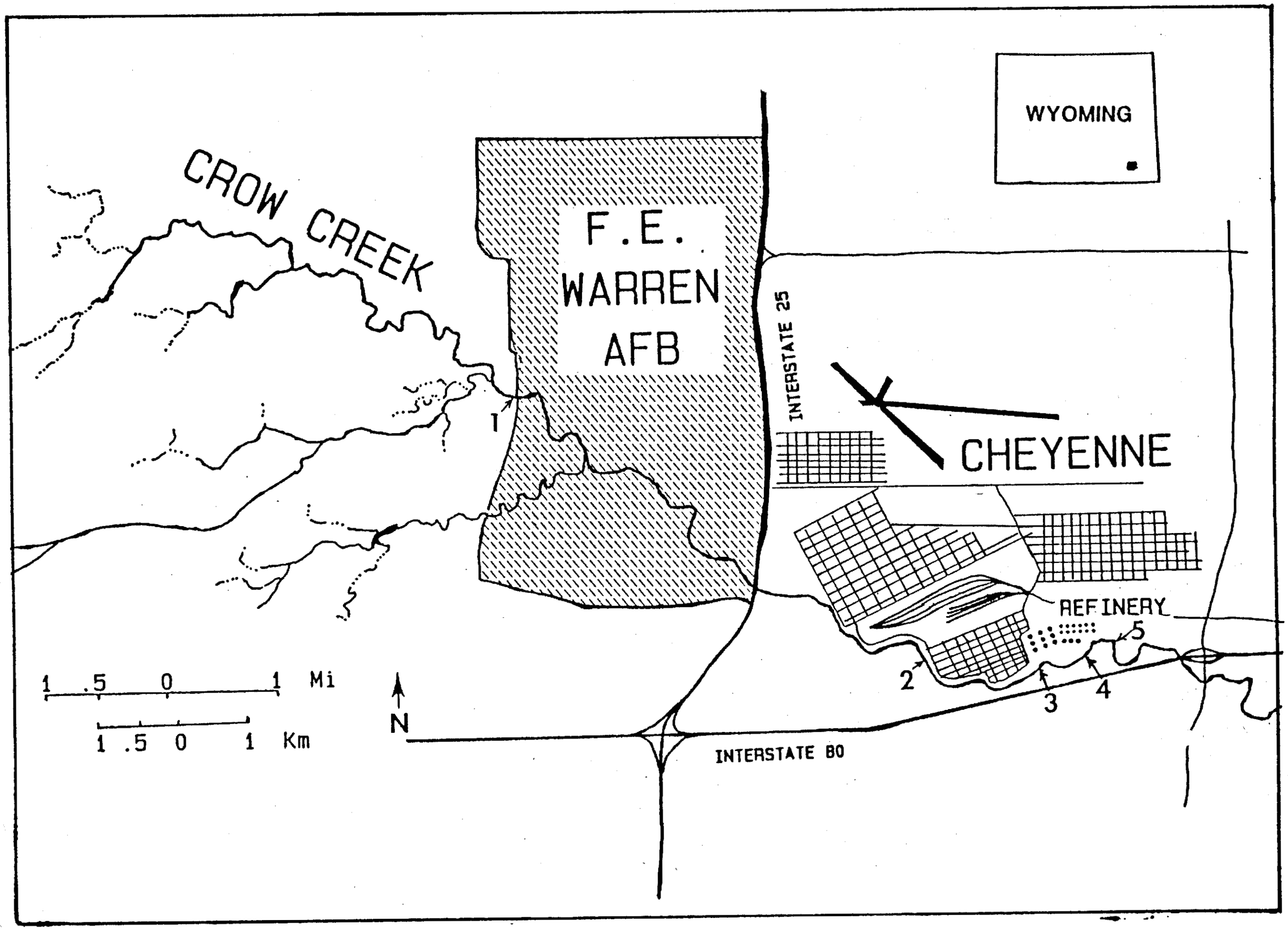


Figure 3. Location of the Crow Creek study site, Cheyenne, Wyoming. Numbers denote sampling locations: 1 = Upstream control, 2 = Optimist Park, 3 = Morrie Avenue, 4 = Refinery, and 5 = NPDES.

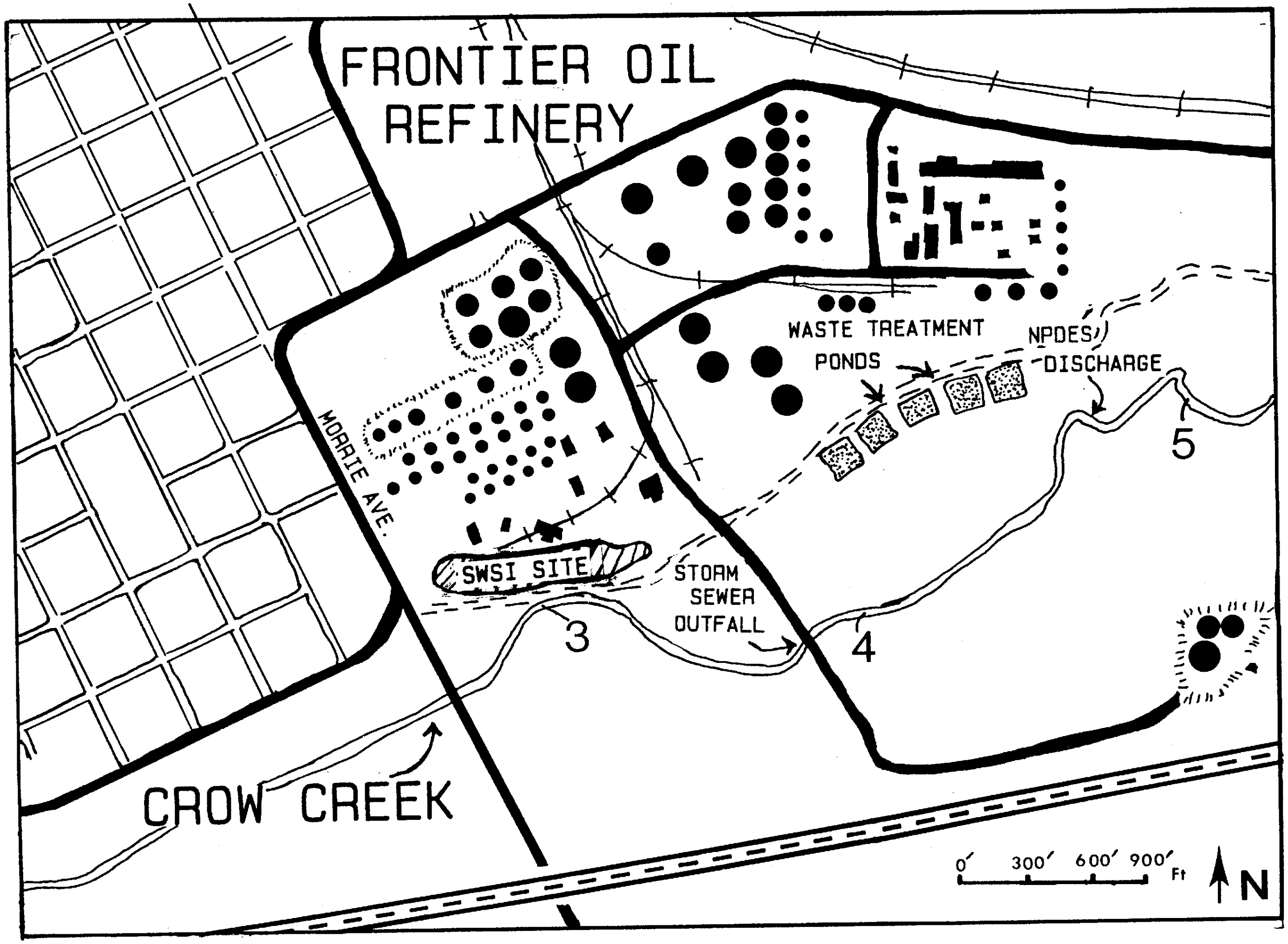


Figure 4. Crow Creek sampling locations adjacent to Frontier Oil Refinery. Numbers denote sampling locations: 3 = Morrie Avenue, 4 = Refinery, 5 = NPDES. The Morrie Avenue site lies immediately adjacent to the buried waste ponds (SWSI site).

communication). Hence, in addition to the regulated effluent, Crow Creek may also be contaminated by ground water upstream from the NPDES discharge.

On August 1, 1985, torrential hail and rain storms centered over downtown Cheyenne caused a major flood in Crow Creek. Peak stream flows during the flood were 65 $m^3/s$ (2300 cfs) at the Interstate 25 bridge, approximately 5.8 km upstream from the oil refinery's NPDES discharge; 234 $m^3/s$ (8260 cfs) at the Morrie Avenue bridge, approximately 0.9 km upstream from the NPDES discharge; and 211 $m^3/s$ (7470 cfs) at the Interstate 80 bridge, approximately 1.2 km downstream from the NPDES discharge (Druse et al. 1986). For comparison, the flow rate of Crow Creek at Optimist Park on July 23, one week before the flood, was 0.10 $m^3/s$ (3.6 cfs) and on August 7, one week after the flood, was 0.17 $m^3/s$ (5.9 cfs; U.S. Geological Survey, Cheyenne, Wyoming, unpublished file data). Flood waters covered low-lying ground on the refinery property and abutted waste treatment ponds and the SWSI Site. Hence, groundwater flow probably increased considerably through the areas of heaviest surface and subsurface contamination at the refinery during and immediately after the flood.

Sample Collection, Preservation and Storage

Water samples from the Laramie River site were collected on June 14, July 18, August 9, and October 3, 1985. June, July and August samples were taken from the original river channel, whereas October samples adjacent to the UPTTP site were taken from corresponding locations in the new river channel (Figs. 1 and 2). On each sampling date, four river water samples and either one (in June, July and August) or two (in

October) interstitial water samples were collected. The river water samples were (1) an upstream control approximately 0.5 km above the UPTTP site; (2) river water flowing directly over the location of the oil body that lay beneath the river sediments (or at a corresponding location in the new river channel in October); (3) approximately 0.5 km downstream from the oil body, at the Interstate 80 bridge; and (4) approximately 1.3 km downstream from the oil body, below the confluence of the Laramie River and Spring Creek, a small stream that flows through Laramie. Interstitial water was withdrawn from sediments using Teflon mini-piezometers (Lee and Cherry 1978) inserted 1 m below the riverbed, from which water was siphoned by a hand-powered vacuum pump. In June, July and August, the piezometer was placed approximately 30 m downstream from the river-water sampling location that was directly over the oil body (sample 2 described above), in order to avoid sampling creosote oil in the sediments. The two interstitial waters sampled in October were withdrawn from river sediments at (1) the upstream control location, and (2) in the new channel at the same location as the river water sample.

At Crow Creek, water samples were collected on June 13, July 17, August 20, October 24, and December 12, 1985 and February 24 and April 29, 1986. On each sampling date, five surface-water samples were collected at the following locations: 1) an upstream control above the Round Top Road bridge west of F.E. Warren Air Force Base; 2) at Optimist Park, approximately 8.1 km downstream from the control and immediately downstream from the Union Pacific Railroad yards; 3) 50 m below the Morrie Avenue bridge and adjacent to the upstream end of the SWSI site on the refinery property, approximately 10.1 km downstream from the control; 4) below the county road bridge midway along the refinery property, approximately 10.6 km downstream from the control; and 5) 50 m below the refinery's NPDES discharge pipe at the downstream end of the refinery property, approximately 11.0 km downstream from the control (Figs. 3 and 4).

At each surface-water and groundwater sampling location, a 19-L grab sample was collected in a polyethylene jug, stored in a cooler, and returned to the University of Wyoming Red Buttes Environmental Biology Lab south of Laramie in < 2 h. Samples were refrigerated at $4^{o}C$ for subsequent toxicity tests. A 1-L aliquot was drawn from each sample for chemical analyses. Subsamples for cation and trace element analyses were filtered (0.45 µm cellulose acetate filter) and acidified with redistilled $HNO_3$ (1 ml/L). Subsamples for anion analyses, dissolved organic carbon, and high performance liquid chromatography were filtered (0.45 µm cellulose acetate filter) and refrigerated at $4^{o}C$.

### Toxicity Tests

*Test Organisms*. Stock cultures of fathead minnows (*Pimephales promelas*) and *Ceriodaphnia dubia* (an aquatic invertebrate) were originally obtained from the U.S. EPA Environmental Research Lab in Duluth, Minnesota, and have been cultured at the Red Buttes Environmental Biology Lab for several years. Neonates from those stock cultures were used for all toxicity tests conducted in this study.

Fathead minnow adults are maintained in our laboratory at $25^{o}C$ in brood tanks that contain plastic spawning tiles. Brood tanks are checked daily for newly fertilized eggs, which adhere to the undersides of tiles. One day prior to beginning a test, tiles to which unhatched eggs are attached are placed in a basin containing clean culture water. The following day, fathead minnow fry that have hatched (and thus are < 24 h old) are removed from the basin and used to begin a toxicity test.

Ceriodaphnia are cultured at 25°C in our laboratory in glass dishes. These brood cultures are transferred to fresh water three times per week. Four h before a test is started, adult Ceriodaphnia in a brood culture are transferred to clean water and the remaining young are discarded. Offspring born to the transferred adults within the next 4 h are removed from the culture dish and used to begin the toxicity test.

Ambient Toxicity Tests. To test instream toxicity, we adopted two short-term, sublethal tests that were recently developed by the U.S. EPA for assessing effects of industrial and municipal effluents. The 7-d survival and growth test using fathead minnows and the 7-d survival and reproduction test using Ceriodaphnia dubia were first described by Mount and Norberg (1984) and Norberg and Mount (1985). Standardized protocols for these tests have been published more recently by Horning and Weber (1985).

In ambient toxicity tests, water samples are not serially diluted as is done in traditional toxicity tests. Instead, the water sample is tested as collected, and upstream water serves as an "ambient control" for the sample of interest. Additionally, laboratory water is used as a "laboratory control" in case no test organisms survive in any instream sample. However, statistical comparisons of downstream water samples are made only to the upstream control, since the objective of the ambient test is to determine if the influx of a pollutant source changes the response of the test organisms relative to upstream water.

Temperature for all 7-d fathead minnow and *Ceriodaphnia* tests was maintained at 25°C using recirculating water baths, and tests were run under a 16-h light/8-h darkness photoperiod.

We conducted fathead minnow tests using 1-L glass beakers that contained 500 ml of test water. Either two or four replicate beakers were tested for each water sample and the laboratory control. We began the study using two replicates per sample, as was the practice at several other laboratories at that time (Horning and Weber 1985 recommend a minimum of two replicates per sample). However, we expanded to four replicates per sample after August 1985 when we discovered that our ability to resolve significant differences between treatments and the upstream control was low and that variances often were not equal using only two replicates.

To begin a test, ten neonate fathead minnow larvae were placed in each beaker. Beakers were covered with watch glasses to decrease sample evaporation, and the fish were fed 0.1 ml (approximately 700-1000 shrimp) of a concentrated suspension of newly hatched brine shrimp (*Artemia salina*) three times per day. The number of live larvae in each beaker was recorded every 24 h, and dead larvae were removed at that time. Additionally, all but approximately 75 ml of the exposure solution was siphoned daily out of each beaker to remove feces and uneaten brine shrimp. Then, 500 ml of fresh exposure water warmed to 25°C was gently poured into the beakers. At the end of Day 7, all surviving fathead minnows in each beaker were placed as a group into a small aluminum weighing boat and oven dried at 100°C. Dry weight of each group of fish (biomass in each replicate beaker) was determined on a Sauter electronic micro-balance. Finally, endpoints of survival and growth (average dry weight per fish) in downstream waters were compared to the upstream control as described below in Statistical Analyses.

We conducted *Ceriodaphnia* tests using 30-ml plastic cups that contained 15 ml of test water. Ten replicate beakers were tested for each water sample and the laboratory control. To begin a test, one neonate *Ceriodaphnia* was placed in each beaker. Beakers were covered with watch glasses to decrease sample evaporation, and a yeast/algae suspension (50 #l containing approximately $10^6$ algal cells and 200 #g of yeast) was added to each beaker once a day as food for the *Ceriodaphnia*. Survival and reproduction were monitored every 24 h, and on Days 3 and 5, live adults were transferred to beakers containing fresh exposure water. *Ceriodaphnia* usually begin reproducing by Day 4 of a test and have at least three broods by the end of Day 7. Tests were terminated on Day 7, and endpoints of survival and reproduction (average number of offspring/female) in downstream waters were compared to the upstream control as described below in Statistical Analyses.

The reproduction endpoint in *Ceriodaphnia* tests can be computed two ways (Hamilton 1986). MOA (mean overall) reproduction is the traditional measure of average number of offspring produced per female, and is calculated by dividing the total number of offspring produced in a test by the number of females that started the test. If a female dies before reproducing, her offspring total is recorded as zero. Standard errors of the estimate of total reproduction are computed by the usual method for estimating a mean value (Hamilton 1986). MIM (mean ignoring mortality) reproduction calculations isolate reproductive effects of a toxicant from survival effects. To estimate the MIM value, the mean number of offspring produced per live adult is computed for each day of the test. Then those means are summed over all seven days of the test to compute average total reproduction. An adult death is treated mathematically as though it occurred halfway through that 24-h period. Standard errors of the estimate of total reproduction are computed using a Bootstrap technique (Hamilton 1986), which requires high-speed computer calculations.

The MOA statistic integrates both survival and reproduction into an estimate that is more interpretable as a population-level response to a toxicant, whereas the MIM statistic subtracts out the effects of differential survival and is more interpretable as an organism-level, physiological/reproductive response to a toxicant. Both measures were computed in this study and the results are compared in this report. To compute these statistics, we used BSVAR, a computer program available from Dr. John Rodgers at the U.S. EPA Environmental Research Lab in Duluth, Minnesota.

Acute Toxicity Tests. Acute toxicity tests using fathead minnows and *Ceriodaphnia dubia* were performed for Laramie River interstitial water collected in June 1985 and for Crow Creek water collected below the oil refinery NPDES discharge in June and July 1985. All tests followed ASTM (1980) standard practices and were conducted at 25°C under a 16-h light/8-h darkness photoperiod. Fathead minnows were tested for 96 h in 80 ml of test solution contained in a 150-ml glass beaker, whereas *Ceriodaphnia* were tested for 48 h in 15 ml of test solution contained in a 30-ml plastic cup. Exposure concentrations were 10, 18, 32, 56 and 100% of the full-strength water sample; in addition, a laboratory control was tested. All exposure concentrations < 100% were diluted with laboratory control water (Table 1).

Acute toxicity test procedures for both species were similar. To begin a test, 10 neonate fathead minnows or Ceriodaphnia were placed in each of three replicate beakers for each exposure level and the control. Beakers were covered with watch glasses to decrease sample evaporation, and no food was added during the test. Every 24 h, survival of test animals was observed, dead animals were removed from the beakers, and live animals were transferred to fresh exposure solutions. At the end of each test, percentage survival at each exposure level was computed. LC50 (median lethal concentration) values were then calculated using the trimmed Spearman-Karber method (Hamilton et al. 1977) and expressed as percent of full-strength ground water or stream water. [Note that as LC50 values decrease, toxicity of the water increases.]

## Chemical Analyses

Routine chemical parameters, including temperature, pH, conductivity, alkalinity, hardness and total ammonia, were analyzed at the Red Buttes Environmental Biology Lab by standard methods (APHA 1980). Methods for these measurements were (1) pH using a Corning Model 10 pH meter, (2) conductivity using a Extech Model 440 conductivity meter, (3) alkalinity and hardness by titration, and (4) total ammonia using an Orion Ionalyzer Model 407A equipped with a selective-ion ammonia probe. Free ammonia ($NH_3$) was computed from temperature, pH and total ammonia values using equilibrium calculations described by Emerson et al. (1975).

Major inorganic cations ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$ and $Sr^{2+}$) were analyzed by the University of Wyoming Plant Sciences Department, using a Perkin-

Table 1. Quality of dilution water used for fathead minnow (*Pimephales promelas*) and *Ceriodaphnia dubia* acute toxicity tests in June and July 1985.

| Parameter | Filtered fathead minnow tank water[a] | 50% raceway/ 50% deionized water |
|---|---|---|
| pH (units) | 8.3<br>(7.8 - 8.5) | 8.4 |
| Conductivity (μS/cm at 25°C) | 498<br>(487 - 514) | 255 |
| Alkalinity (mg/L as $CaCO_3$) | 197<br>(178 - 208) | 164 |
| Hardness (mg/L as $CaCO_3$) | 254<br>(238 - 265) | 230 |

[a]Values expressed as means for five acute toxicity tests; ranges of values presented in parentheses.

Elmer Model 5500 inductively coupled argon plasma spectrophotometer (ICP). Major inorganic anions ($Cl^-$, $NO_3^-$, $F^-$ and $SO_4^{2-}$) were analyzed at the Red Buttes Environmental Biology Lab using a Dionex 2110i ion chromatograph equipped with an electrical conductivity detector. The carrier eluant was a 0.0025 N $Na_2CO_3$/0.0027 N $NaHCO_3$ buffer. We computed $NH_4^+$ concentrations by subtracting free ammonia from total ammonia, and we computed $HCO_3^-$ and $CO_3^{2-}$concentrations from temperature, pH and alkalinity values using equilibrium calculations described by Drever (1982).

Eleven inorganic trace elements (Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Se and Zn) were also analyzed by the UW Plant Sciences Department using ICP. Because ICP methods have relatively high detection limits (10-100 #g/L), we additionally analyzed Cd, Cr, Cu and Zn using a Perkin-Elmer Model 2380 atomic absorption spectrophotometer (AA) at the Red Buttes Environmental Biology Lab. AA analyses are considerably more expensive and time-consuming than ICP analyses, but they allowed us to obtain detection limits of 0.1 #g/L for Cd and Zn and 1.0 #g/L for Cr and Cu. We expected that concentrations of these four elements might be high in some samples and that they might contribute to instream toxicity.

Organic analyses were performed at three levels of resolution. Dissolved organic carbon (DOC) concentrations were determined using an Oceanography International organic carbon analyzer equipped with an infrared $CO_2$ detector, located in the UW Geology Department. Reverse-phase high performance liquid chromatography (HPLC) gradients of water samples were run on a Waters Model 402 HPLC equipped with ultraviolet and fluorescence detectors, located at the Red Buttes Environmental Biology Lab. HPLC samples (50 #l) were injected onto a #$C_{18}$ Radial Pak column and eluted over a 30-min run, using a linear gradient from 100% $H_2O$ to 100% $CH_3CN$ at 2.0 ml/min. Blank gradients (no injection) and a standard mixture containing several aromatic hydrocarbons were also run for comparison with the test samples. Finally, the Laramie River interstitial water collected in June 1985 was analyzed using gas chromatography/mass spectrometry (GC/MS) by Rocky Mountain Analytical Lab in Denver, Colorado. Because of the high cost of GC/MS scans compared to DOC and HPLC analyses, only the Laramie River interstitial water collected in June 1985 was analyzed by this method.

Statistical Analyses

Survival. Because only 10 *Ceriodaphnia* (10 replicate beakers x 1 animal/beaker) were tested per sample, their 7-d survival in Laramie River and Crow Creek waters was analyzed using Fisher's Exact Test (Sokal and Rohlf 1981). We also used Fisher's Exact Test to analyze 7-d survival in fathead minnow tests in which only 20 animals (2 replicate beakers x 10 animals/beaker) were tested (all Laramie River samples and June, July and August 1985 Crow Creek samples). Survival at a downstream site was judged to be significantly less than survival in the upstream control when the one-tailed probability associated with that comparison was $< 0.013$. Four non-independent comparisons between downstream sites and the upstream control were made for each sampling date; hence, the Kimball inequality guarantees an overall significance level of $\alpha \leq 0.05$ for the family of survival comparisons when $\alpha_i = 0.013$ (Neter et al. 1985).

For fathead minnow tests in which 40 animals (4 replicate beakers x 10 animals/beaker) were tested (October and December 1985 and February and April 1986 Crow Creek sampling dates), we compared 7-d survival using MINNOW, a statistical package for analyzing fathead minnow survival and growth tests that was programmed for IBM personal computers by Dr. Jeffrey Giddings of Oak Ridge National Laboratory (ORNL). Briefly, that program computes an analysis of variance (ANOVA) on arcsine-square-root-transformed percent survival data and then tests for decreased survival in downstream waters relative to the upstream control, using Dunnett's one-tailed critical values at the $\alpha = 0.05$ level (Dunnett 1955, Dunnett 1964). Dunnett's is a post hoc multiple comparison procedure designed for comparisons of a control with several treatments, in which a specified overall significance level is to be maintained for a family of non-independent comparisons.

Reproduction. Total numbers of offspring produced by *Ceriodaphnia* (using MOA and MIM calculations) were analyzed by ANOVA computed on untransformed data. We then tested for decreased reproduction in downstream waters relative to the upstream control using Dunnett's one-tailed critical values at the $\alpha = 0.05$ level. If all *Ceriodaphnia* females died in water from a given sampling location, that location was not included in the post hoc comparison of MIM total reproduction.

Growth. Seven-day fathead minnow weights were analyzed using the ORNL computer program, MINNOW. It computes an ANOVA on untransformed weights and then tests for decreased growth in downstream waters relative to the upstream control, using Dunnett's one-tailed critical values at the $\alpha = 0.05$ level. If all fathead minnow larvae died in water from a given sampling location, that location was not included in the post hoc comparison of growth.

Homogeneity of Variances. Homogeneity of variances in ANOVA was tested using Hartley's F-max test (Milliken and Johnson 1984). Although ANOVA is relatively robust to non-homogeneity of variances, Milliken and Johnson (1984) suggest using paired *t* tests instead of ANOVA when the null hypothesis of homogeneous variances can be rejected at the 0.01 level. We did not use ANOVA when (a) variances were significantly non-homogeneous ($P < 0.01$) in *Ceriodaphnia* reproduction tests (MOA reproduction: June, July and October 1985 Laramie River samples and June, July, October and December 1985 and February 1986 Crow Creek samples; MIM reproduction: July 1985 Laramie River samples and December 1985 Crow Creek samples), or (b) when $\max_i\{\widehat{var_i}\}/\min_i\{\widehat{var_i}\} > 100$ in fathead minnow tests using only 2 replicate beakers per sample (June, July and August 1985 Laramie River samples and July 1985 Crow Creek samples). In those cases, we used the following statistic to compare a downstream site to the upstream control:

$$t^* = \frac{\bar{x}_t - \bar{x}_c}{\sqrt{[\widehat{s.e.}(\bar{x}_t)]^2 + [\widehat{s.e.}(\bar{x}_c)]^2}} ,$$

where $\bar{x}_t$ = mean value for downstream site, $\bar{x}_c$ = mean value for upstream control, $\widehat{s.e.}(\bar{x}_t)$ = standard error of the estimate of $x_t$, and $\widehat{s.e.}(\bar{x}_c)$ = standard error of the estimate of $x_c$. Reproduction or growth at a downstream site was judged to be significantly less than reproduction or growth in the upstream control when $\underline{t}^*$ was greater than Dunnett's one-tailed critical value at $\alpha = 0.05$.

## RESULTS

### Laramie River

Toxicity Tests. All fathead minnow larvae and *Ceriodaphnia* tested in the interstitial water in June 1985 died in < 24 h (Figs. 5 and 7 and Appendix Table A-1). That interstitial water was collected from a mini-piezometer inserted 1 m deep in river sediments adjacent to the UPTTP, 30 m downstream from the creosote oil body. Fathead minnow survival and growth and *Ceriodaphnia* survival and reproduction at all other sampling locations in June 1985 were not significantly lower than in the upstream control (Figs. 5, 6, 7 and 8 and Appendix Table A-1), although there was a trend toward decreased fathead minnow survival in river water collected directly over the oil body and downstream at the I-80 bridge. Acute lethality tests conducted on the interstitial water in June 1985 showed the 96-h LC50 (median lethal concentration) for fathead minnows was 20% of full-strength interstitial water and the 48-h LC50 for *Ceriodaphnia* was 18% of full-strength interstitial water.

In July 1985, fathead minnow growth in interstitial water was significantly lower than in the upstream control; and in August 1985, fathead minnow survival and growth in interstitial water were also significantly lower than in the upstream control (Figs. 5 and 6 and Appendix Table A-1). *Ceriodaphnia* survival and reproduction were not adversely affected at any sampling location in July and August 1985 (Figs. 7 and 8 and Appendix Table A-1).

After the Laramie River was rechanneled in September 1985, fathead minnow survival and growth and *Ceriodaphnia* survival and reproduction were not adversely affected in interstitial and river waters collected

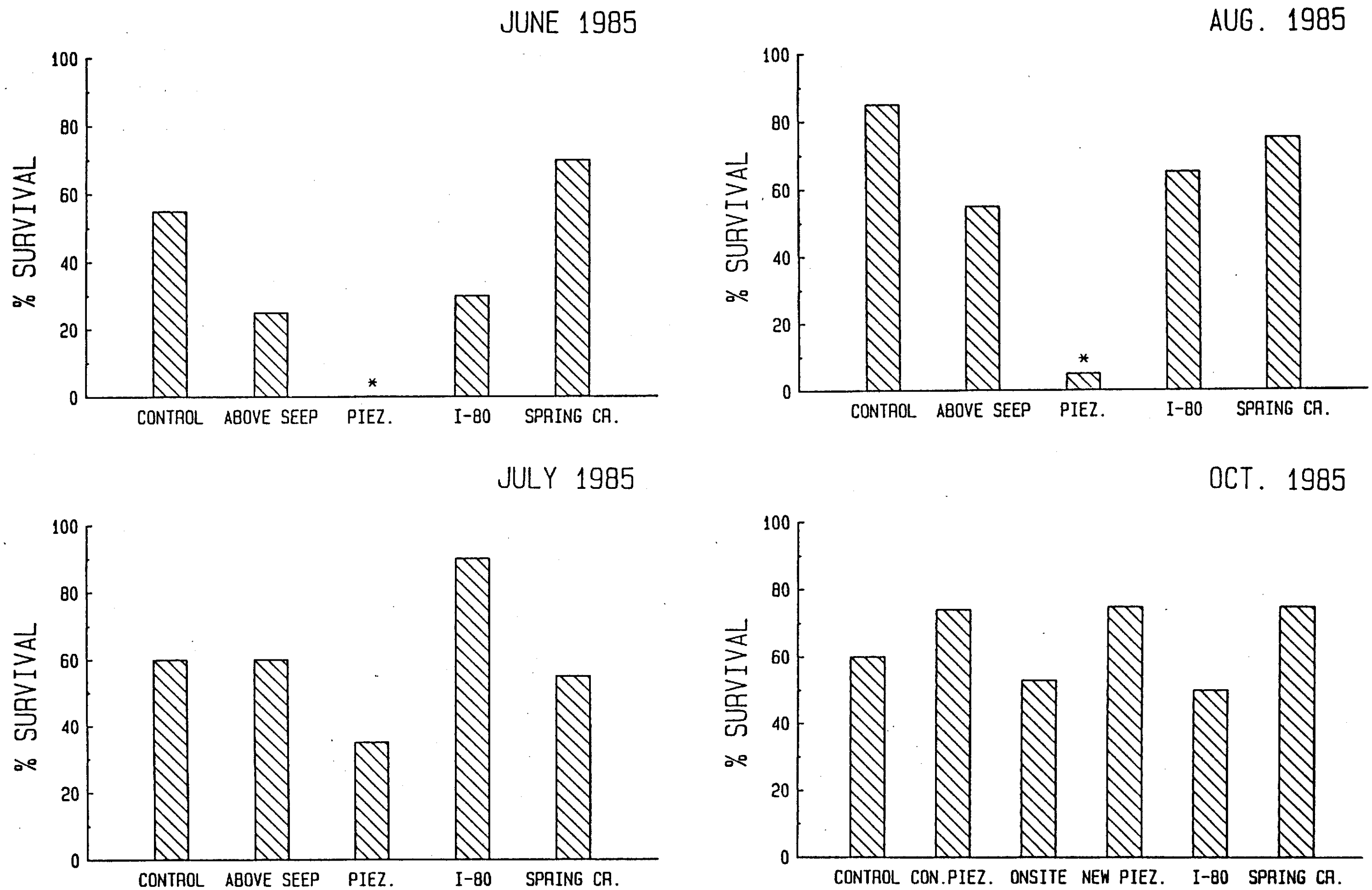


Figure 5. Fathead minnow (Pimephales promelas) survival in Laramie River water and interstitial water (PIEZ.) from June to October 1985. * = significantly lower survival than upstream control ($P < 0.05$).

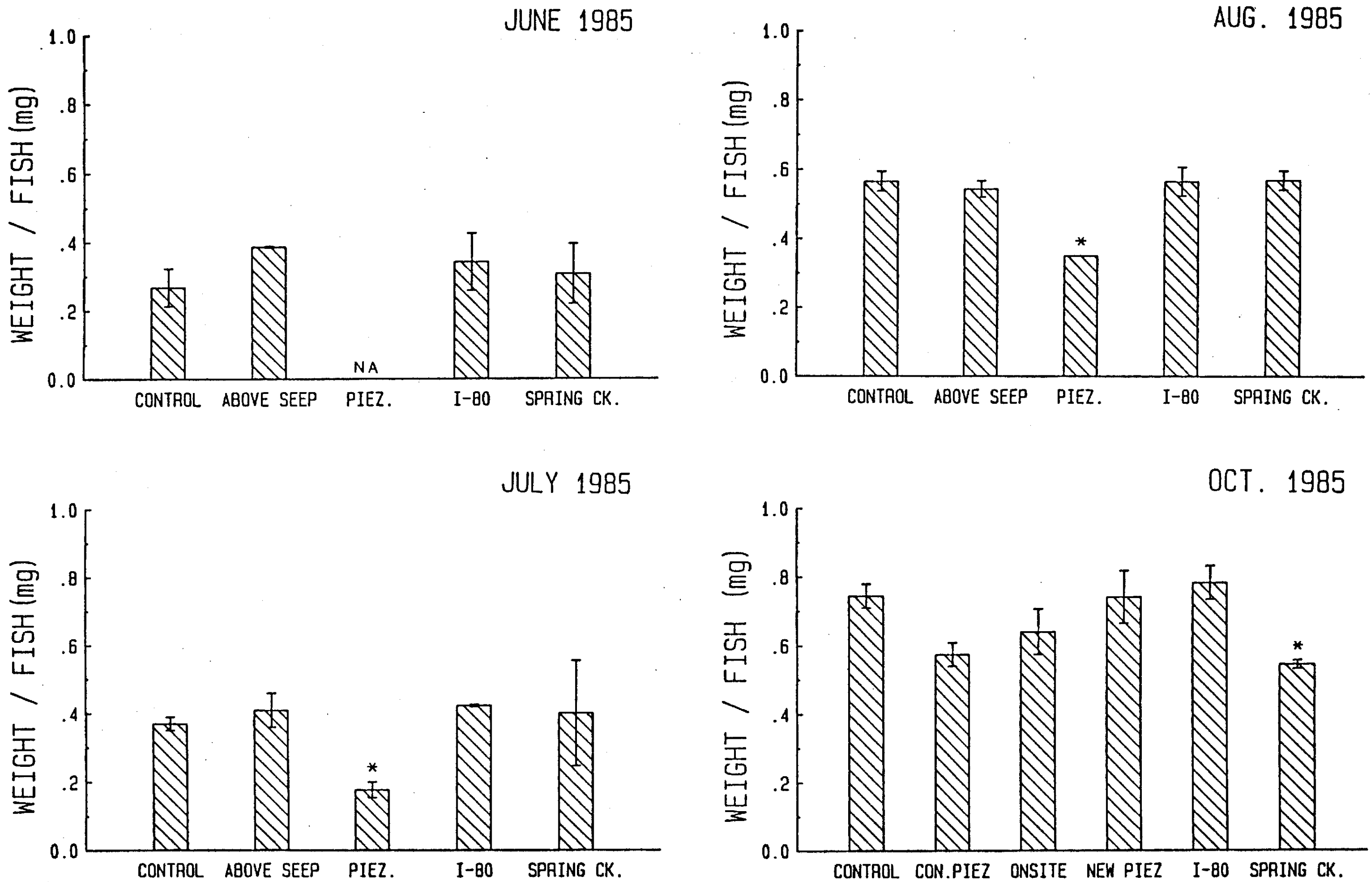


Figure 6. Fathead minnow (Pimephales promelas) growth (mean ± one standard error of the mean) in Laramie River water and interstitial water (PIEZ.) from June to October 1985. NA = value could not be calculated because all larvae died; * = significantly lower weight/fish than upstream control ($P < 0.05$).

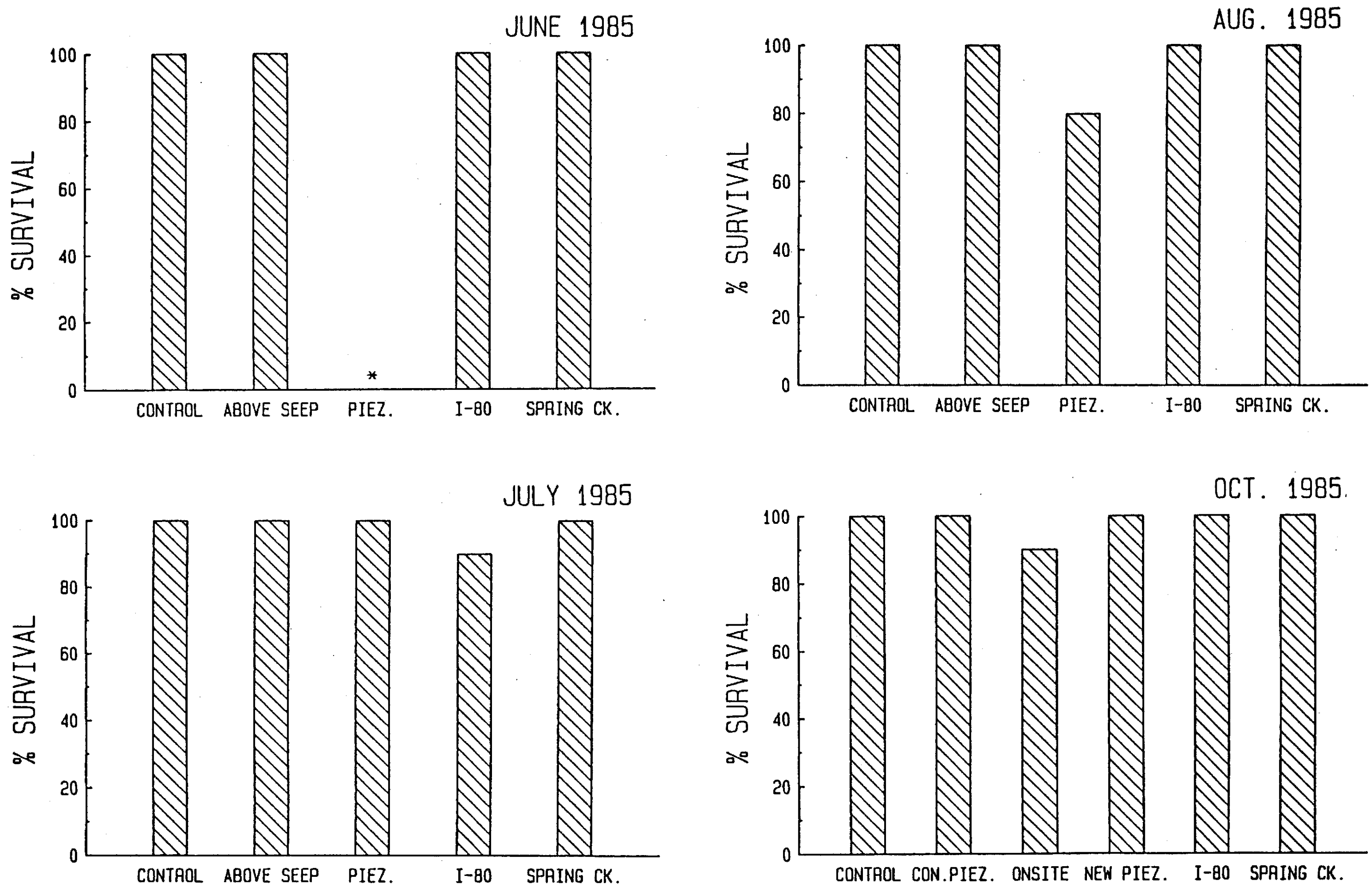


Figure 7. Ceriodaphnia dubia survival in Laramie River water and interstitial water (PIEZ.) from June to October 1985. * = significantly lower survival than upstream control ($P < 0.05$).

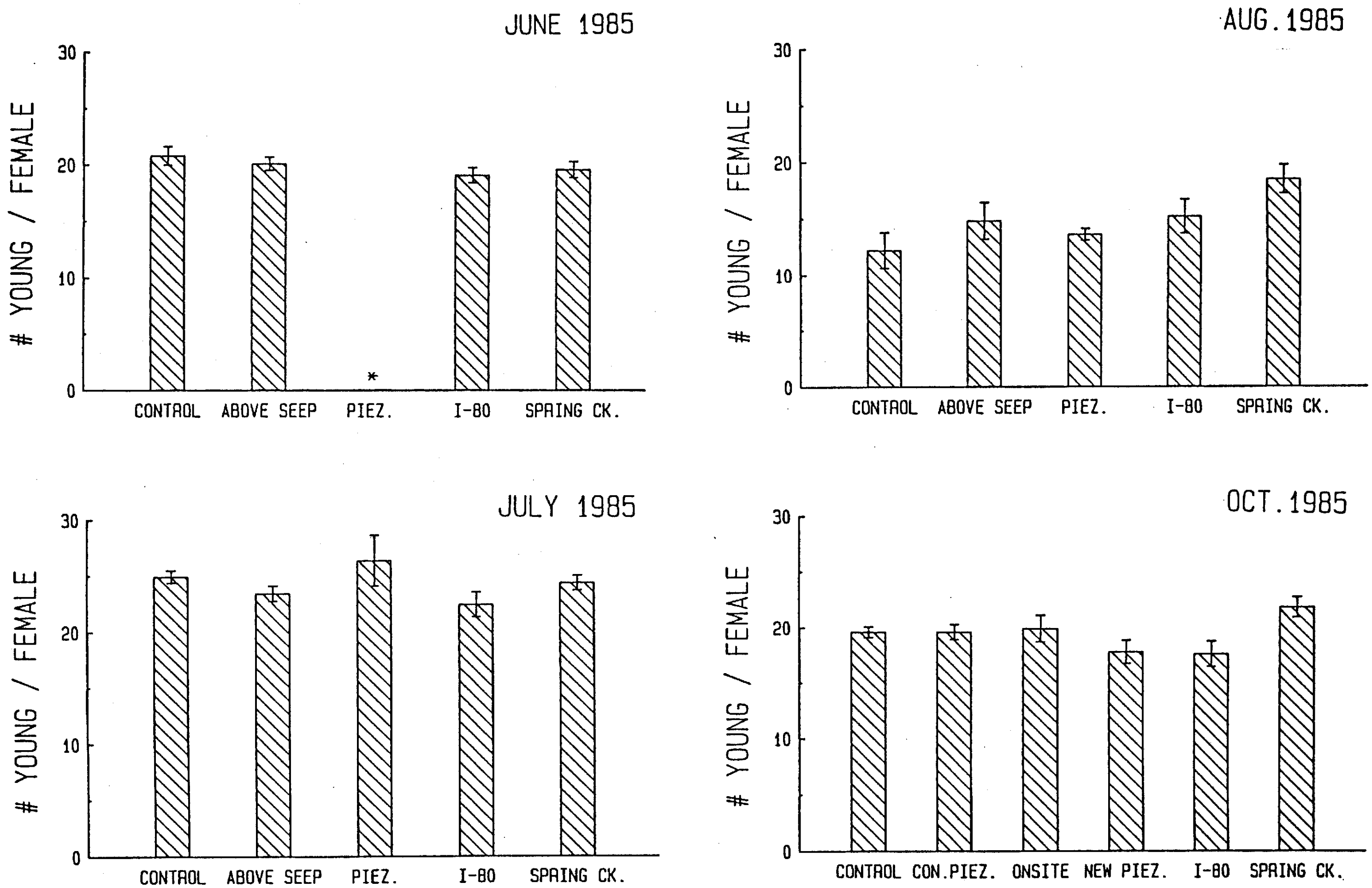


Figure 8. Ceriodaphnia dubia MOA reproduction (mean ± one standard error of the mean) in Laramie River water and interstitial water (PIEZ.) from June to October 1985. * = significantly lower # young/female than upstream control ($P < 0.05$).

at corresponding locations in the new river channel adjacent to the tie treating plant (Figs. 5, 6, 7 and 8 and Appendix Table A-1). However, fathead minnow growth was significantly lower in Laramie River water below the downstream confluence with Spring Creek.

Chemical Analyses. Routine water chemistry parameters and major inorganic ions at all Laramie River sampling locations were within normal ranges and were similar to the upstream control (Table 2 and Appendix Tables B-1 and B-2). Of the 11 trace elements analyzed, concentrations of Al, As, Cd, Fe, Hg, Ni, Pb and Se remained relatively low and did not vary considerably (Table 2 and Appendix Table B-3). Most concentrations of chromium and copper also were low; however, Cr concentration was 0.0139 mg/L in the Laramie River below its confluence with Spring Creek in October 1985, and Cu concentration was 0.0261 mg/L in the Laramie River at the I-80 bridge in June 1985. Zn concentrations varied considerably (Table 2) and were > 0.005 mg/L at least once at each sampling location.

Low concentrations of anthracene, phenanthrene and chrysene were detected in reverse-phase HPLC gradients of the toxic interstitial water in June 1985 (Fig. 9(a)). These three organic compounds were also the three highest peaks detected in reverse-phase HPLC gradients of the creosote oil that underlaid the river sediments (Fig. 9(b); see also Crossey and Bergman 1985). However, organics were not detected in interstitial water using HPLC on the other sampling dates. And no priority pollutants were detected in GC-MS analyses of the base-neutral fraction of interstitial water collected in June 1985.

Table 2. Ranges of values for chemical parameters measured in Laramie River water and interstitial water from June 1985 to October 1985 and in Crow Creek water from June 1985 to April 1986.[a]

| | Range of values | |
|---|---|---|
| Parameter[b] | Laramie River | Crow Creek |
| Routine chemical parameters | | |
| pH (units) | 7.6 - 8.4 | 7.7 - 8.6 |
| Conductivity (µS/cm at 25°C) | 607 - 1220 | 347 - 934 |
| Alkalinity (as $CaCO_3$) | 103 - 172 | 134 - 280 |
| Hardness (as $CaCO_3$) | 230 - 499 | 95 - 336 |
| Ammonia, total (as N) | < 0.10 | < 0.10 - 12.0 |
| Ammonia, unionized (as $NH_3$) | < 0.01 | < 0.01 - 0.90 |
| DOC | 2.1 - 32.9 | 2.0 - 24.9 |
| Major inorganic ions | | |
| $Na^+$ | 38 - 86 | 12 - 68 |
| $Ca^{2+}$ | 67 - 137 | 52 - 146 |
| $Mg^{2+}$ | 10 - 38 | 4 - 22 |
| $K^+$ | 2.6 - 5.8 | 4 - 19 |
| $Sr^{2+}$ | 0.5 - 1.2 | 0.2 - 0.6 |
| $NH_4^+$ | < 0.13 | < 0.13 - 14.8 |
| $Cl^-$ | 7 - 48 | 7 - 97 |
| $SO_4^{2-}$ | 171 - 514 | 17 - 130 |
| $NO_3^-$ | < 1.0 | 1.0 - 18.5 |
| $F^-$ | 0.4 - 0.8 | 0.4 - 7.4 |
| $HCO_3^-$ | 125 - 206 | 161 - 337 |
| Trace elements | | |
| Al | ≤ 0.1 | ≤ 0.1 |
| As | ≤ 0.1 | ≤ 0.1 |
| Cd | 0.0007 - 0.0035 | 0.0002 - 0.0021 |
| Cr | < 0.001 - 0.0139 | < 0.001 - 0.0399 |
| Cu | < 0.001 - 0.0261 | < 0.001 - 0.0417 |
| Fe | 0.01 - 0.15 | < 0.01 - 0.10 |
| Hg | < 0.1 | < 0.1 |
| Ni | < 0.01 | < 0.01 - 0.04 |
| Pb | < 0.1 | ≤ 0.1 |
| Se | ≤ 0.1 | ≤ 0.1 |
| Zn | 0.0003 - 0.0187 | < 0.0001 - 0.0099 |

[a]See Appendix Tables B-1 to B-6 for detailed listings of values.

[b]Values expressed as mg/L, unless otherwise noted.

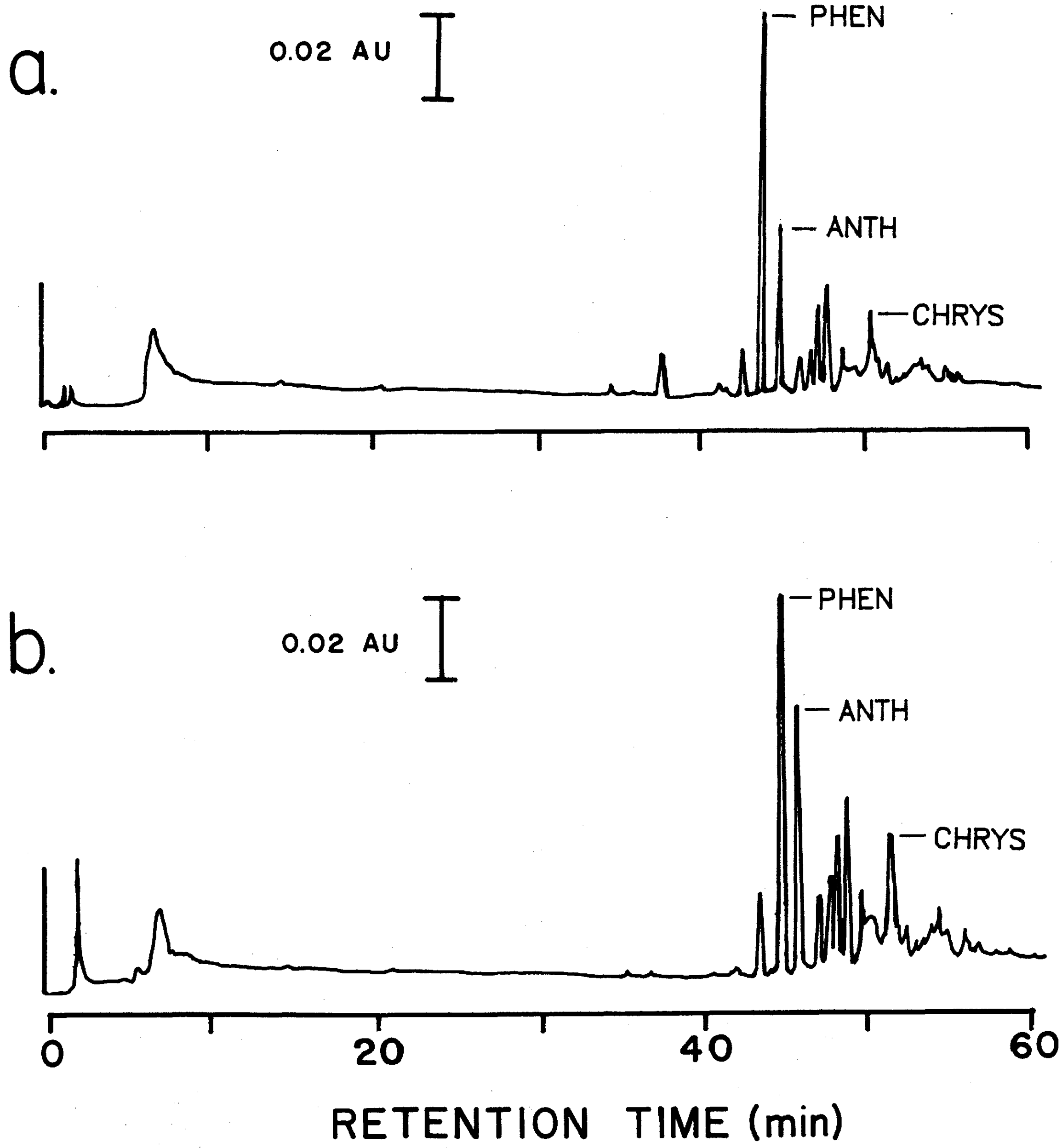


Figure 9. Reverse-phase HPLC chromatograms of (a) June 1985 interstitial water collected from a mini-piezometer inserted 1 m deep in Laramie River sediments, 30 m downstream of the oil body (see Fig. 2 for sampling location); and (b) creosote oil. Phen = phenanthrene, Anth = anthracene, Chrys = chrysene.

Crow Creek

Toxicity Tests. All fathead minnow larvae and Ceriodaphnia tested in Crow Creek water below the oil refinery's NPDES discharge in June, July and October 1985 and February 1986 died by Day 7 of the tests (Figs. 10 and 12 and Appendix Table A-2). In June 1985 the 96-h LC50 of Crow Creek water below the NPDES discharge was 53% for fathead minnows, and the 48-h LC50 for Ceriodaphnia was between 56% and 100%. Corresponding July 1985 LC50 values were 26% for fathead minnows and 73% for Ceriodaphnia. Additionally, all Ceriodaphnia died and fathead minnow survival was significantly less than in the upstream control when they were tested in Crow Creek water below the NPDES discharge in December 1985 (Figs. 10 and 12 and Appendix Table A-2). In August 1985 and April 1986, fathead minnow growth and Ceriodaphnia MIM reproduction below the NPDES discharge were significantly lower than in the upstream control, even though survival was not significantly decreased (Figs. 10, 11, 12 and 13 and Appendix Table A-2). Thus, the NPDES discharge adversely affected fathead minnows and Ceriodaphnia on every sampling date.

Crow Creek water collected at the refinery site (adjacent to the refinery but upstream from the NPDES discharge) significantly reduced fathead minnow growth in July 1985 and February 1986, whereas it killed all Ceriodaphnia by Day 7 of the test and significantly reduced their reproduction only in August 1985 (Figs. 11, 12 and 13 and Appendix Table A-2).

Water collected at the Morrie Avenue bridge (the upstream boundary of the oil refinery property, adjacent to the SWSI Site) in June 1985 killed all Ceriodaphnia between Days 6 and 7 of the test (Fig. 12 and Appendix Table A-2). And water collected at the Morrie Avenue bridge in

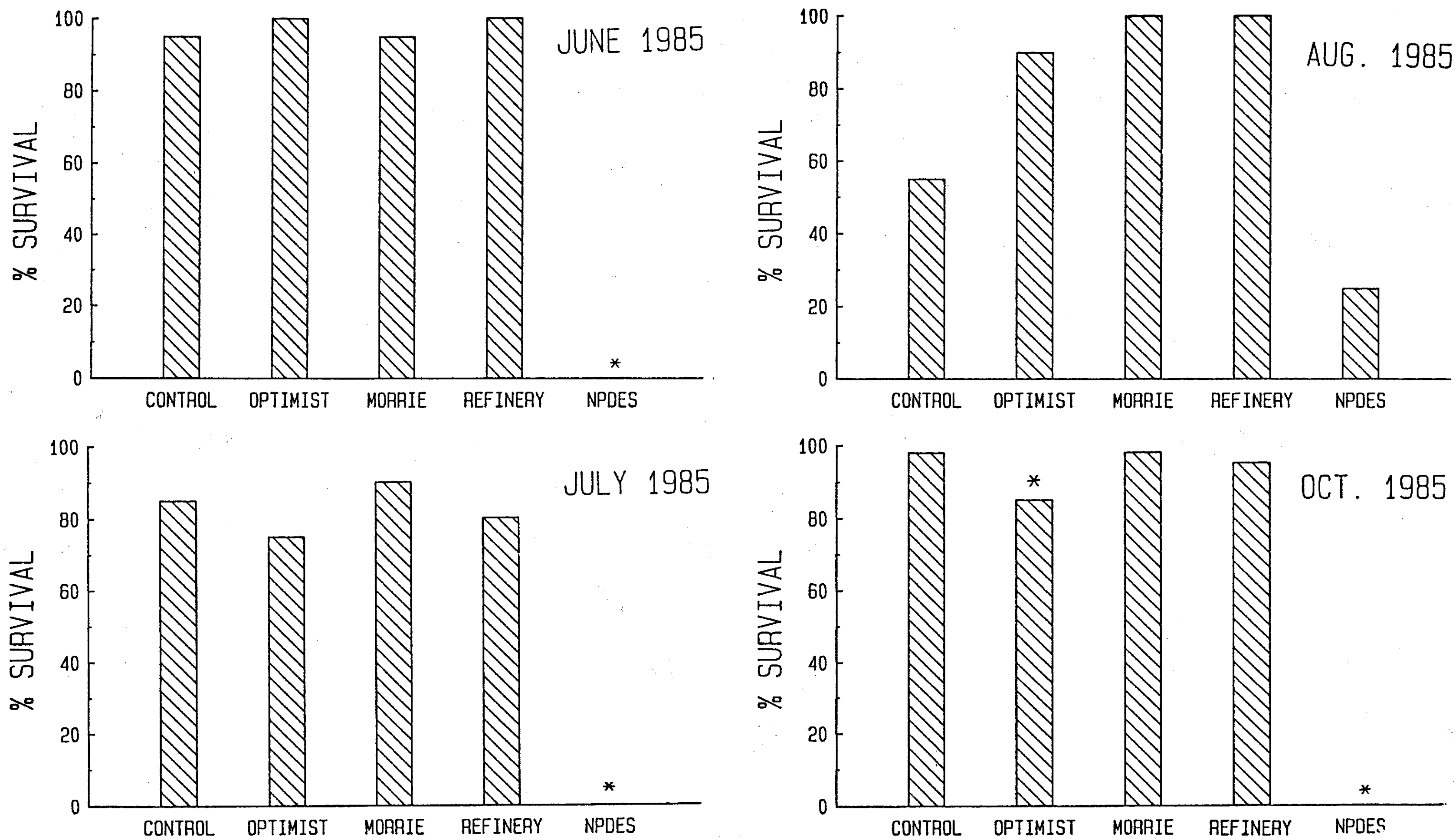


Figure 10. Fathead minnow (Pimephales promelas) survival in Crow Creek water from June 1985 to April 1986. * = significantly lower survival than upstream control ($P < 0.05$).

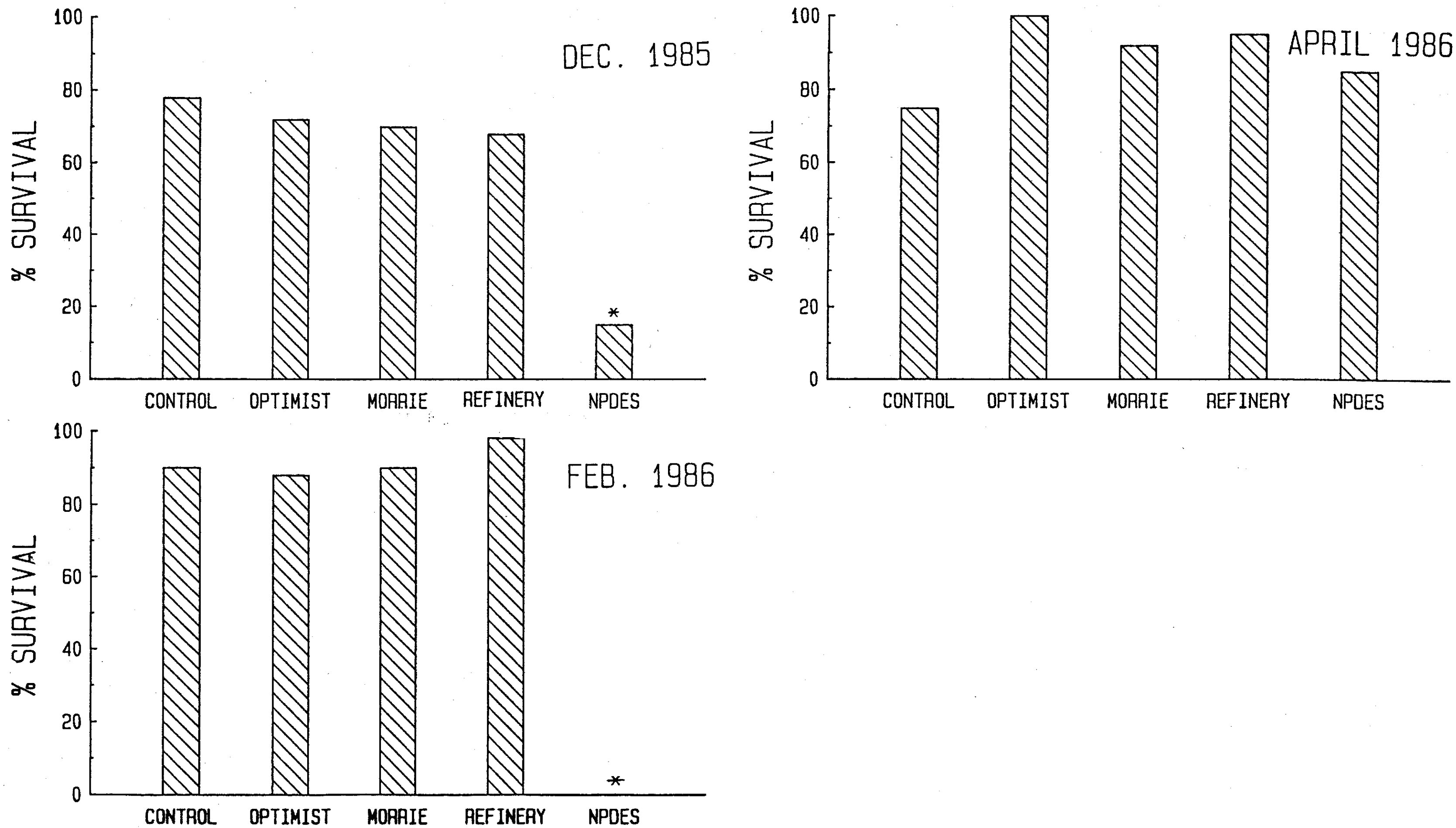


Figure 10 (continued).

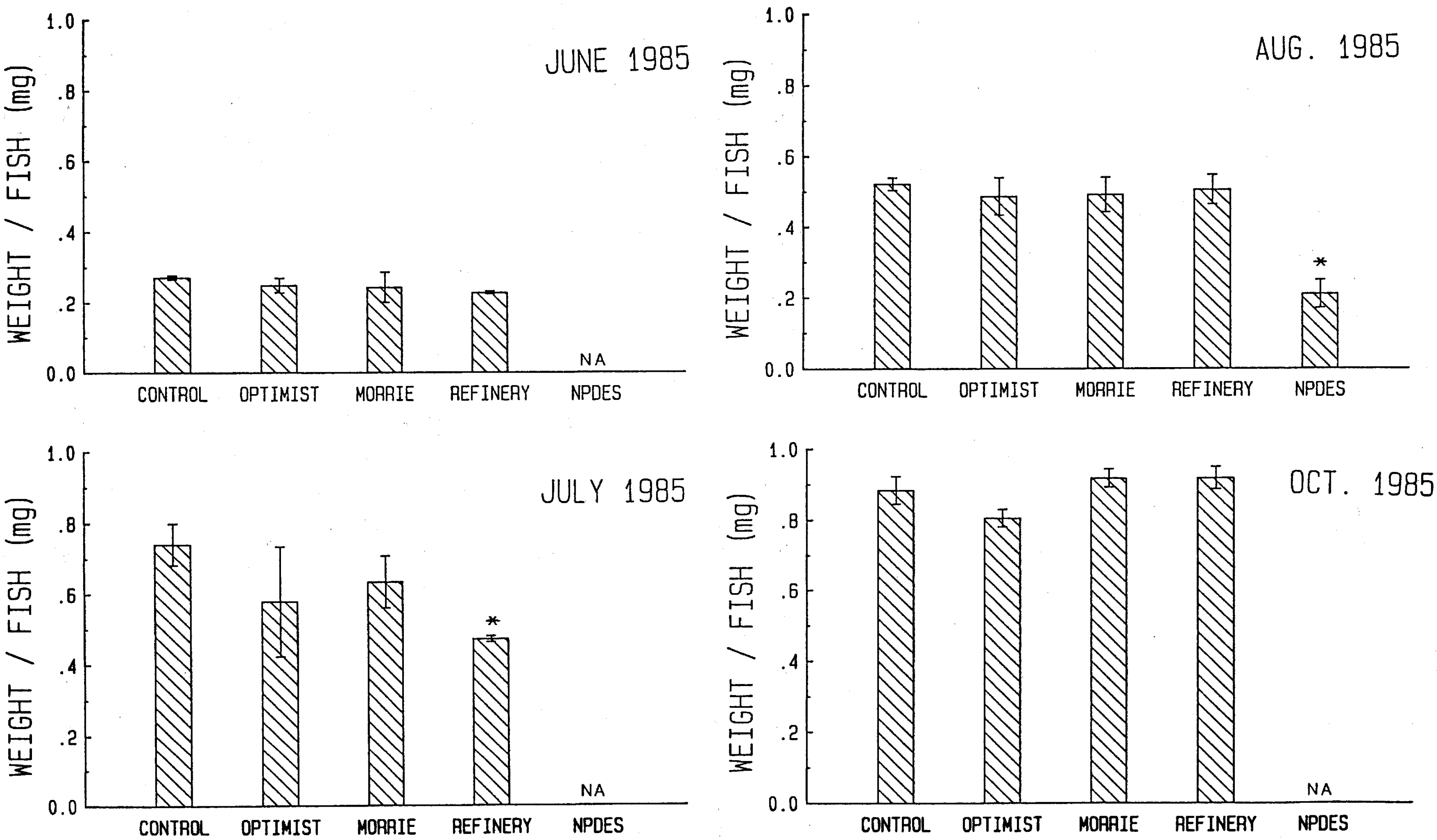


Figure 11. Fathead minnow (Pimephales promelas) growth (mean ± one standard error of the mean) in Crow Creek water from June 1985 to April 1986. NA = value could not be calculated because all larvae died; * = significantly lower weight/fish than upstream control ($P < 0.05$).

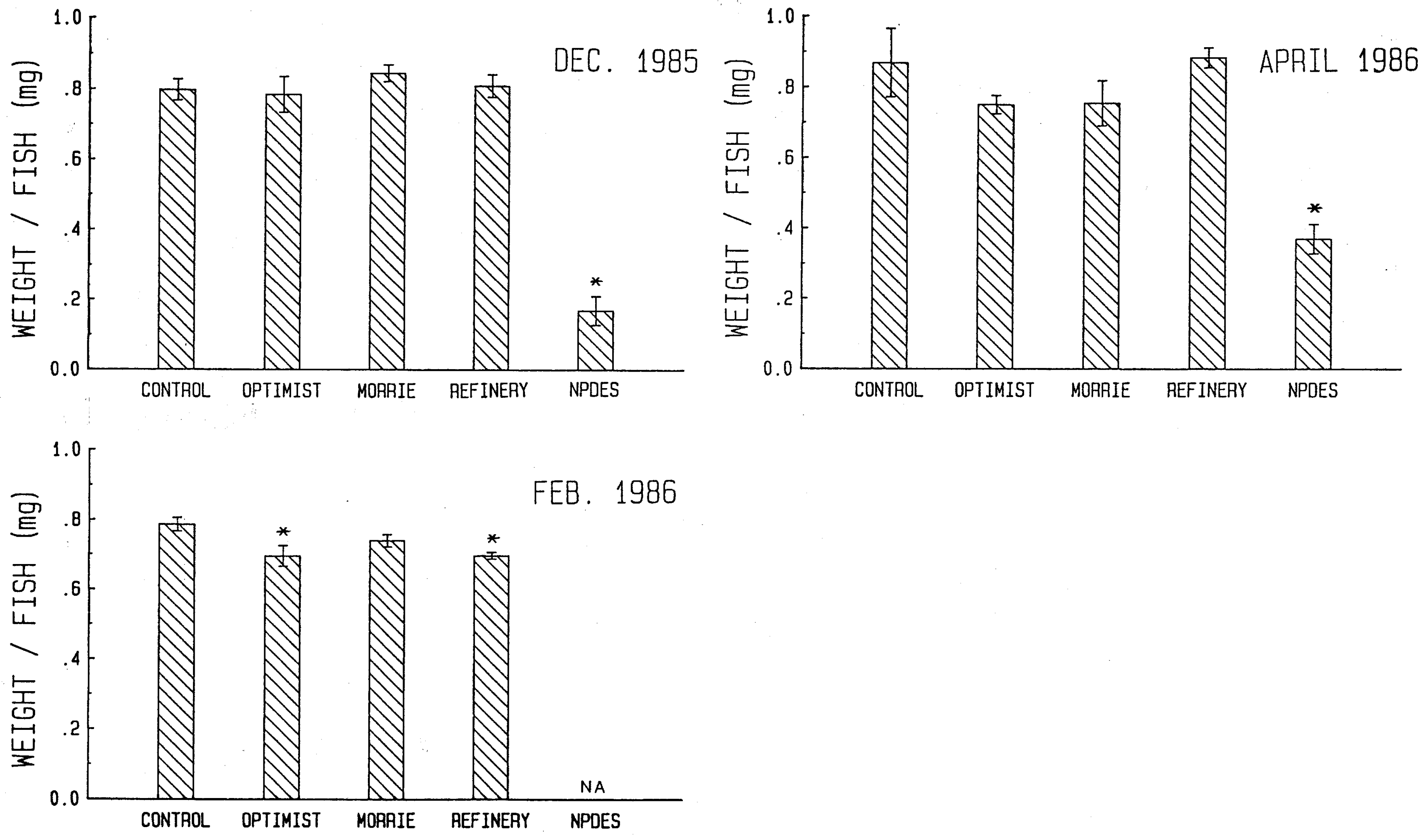


Figure 11 (continued).

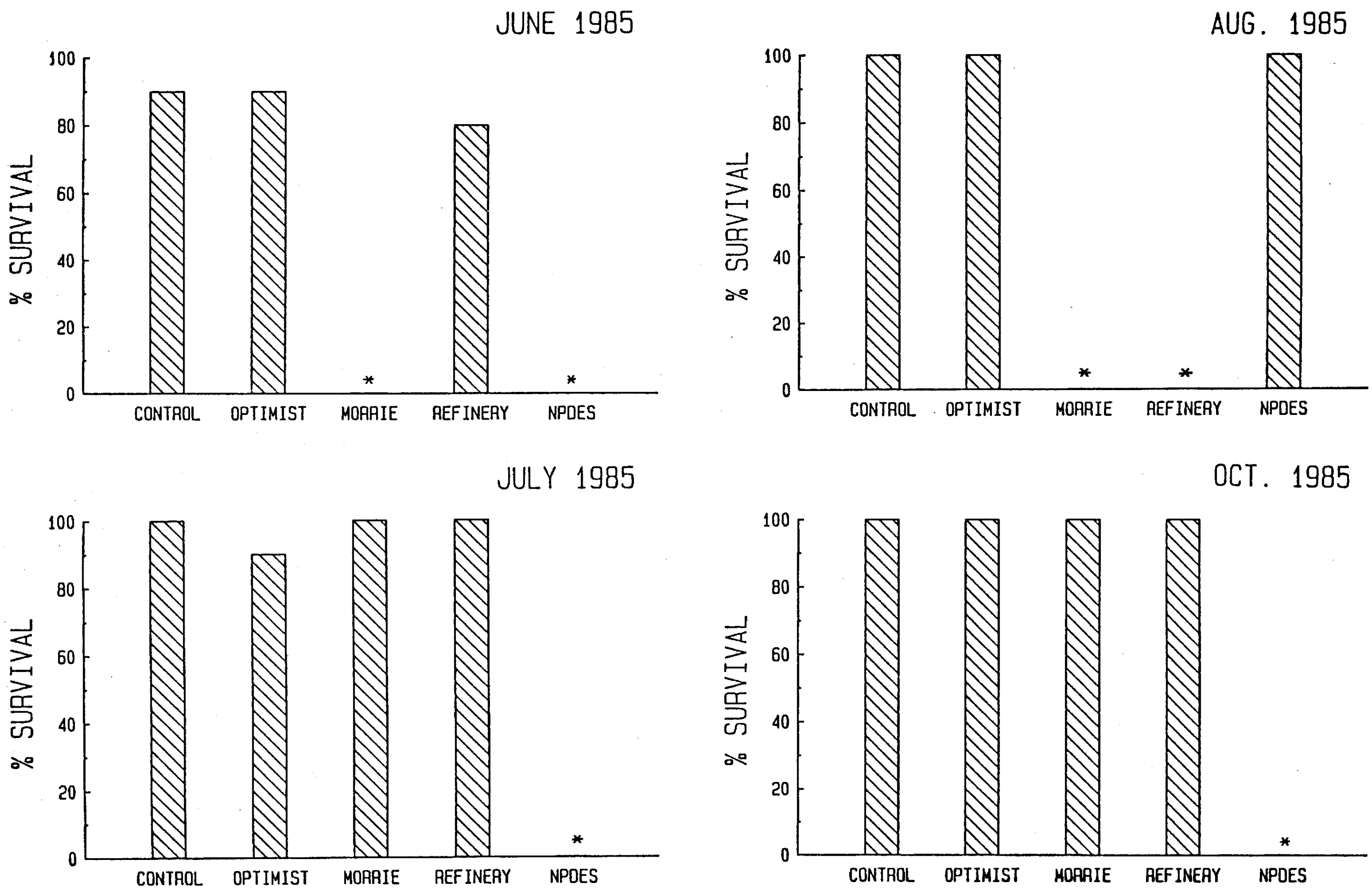


Figure 12. Ceriodaphnia dubia survival in Crow Creek water from June 1985 to April 1986.
* = significantly lower survival than upstream control ($P < 0.05$).

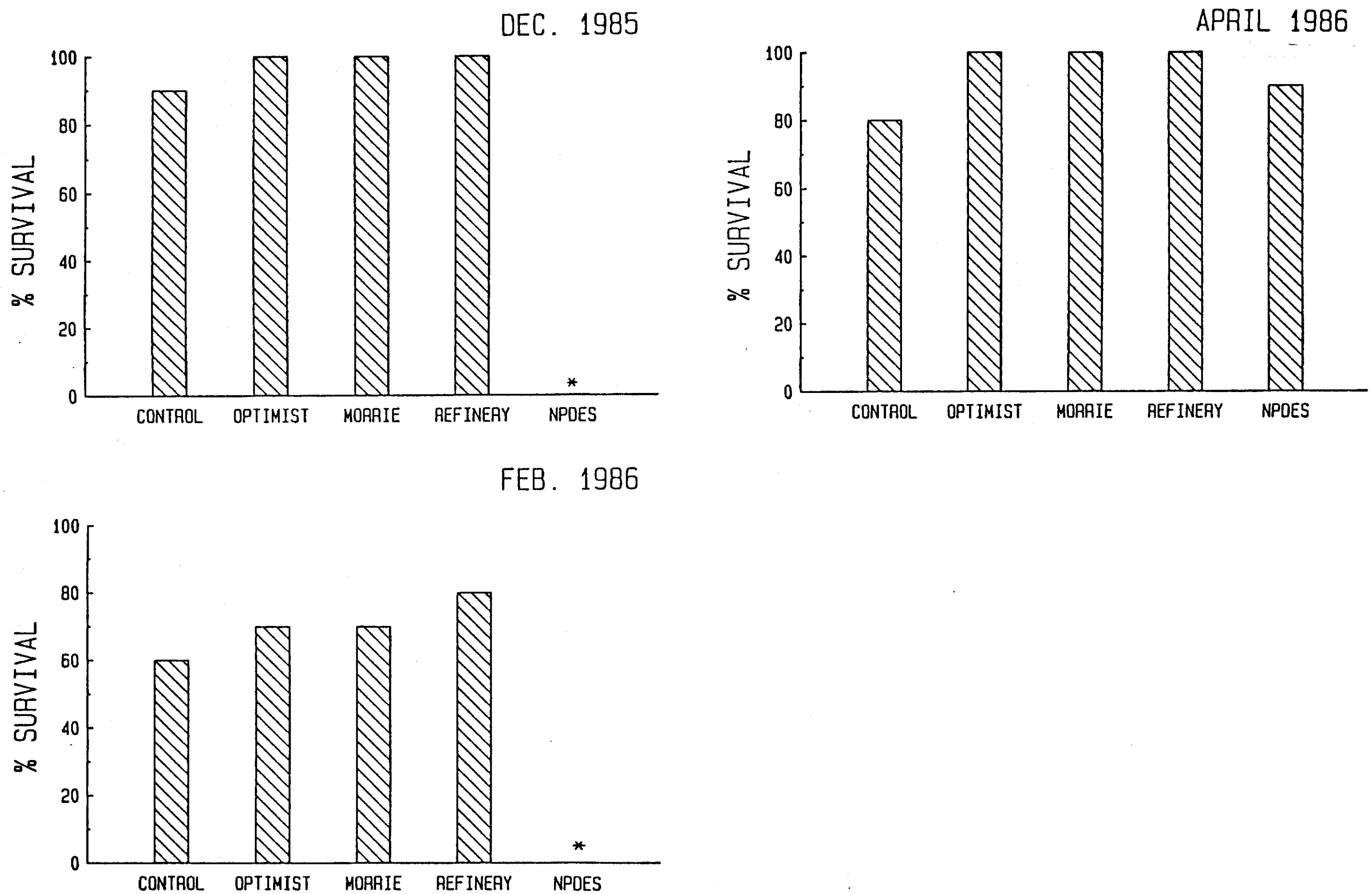


Figure 12 (continued).

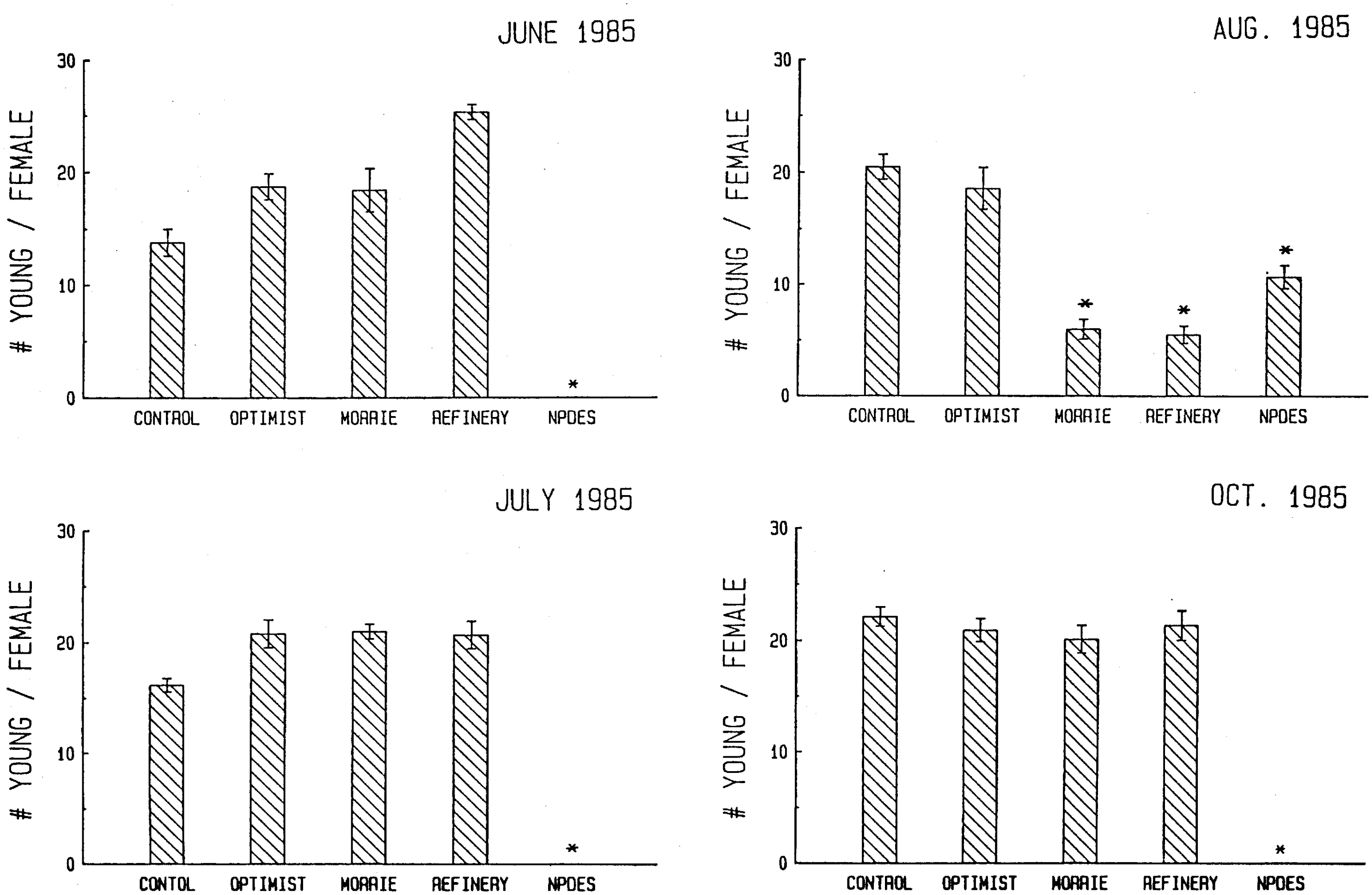


Figure 13. Ceriodaphnia dubia MOA reproduction (mean ± one standard error of the mean) in Crow Creek water from June 1985 to April 1986. * = significantly lower survival than upstream control ($P < 0.05$).

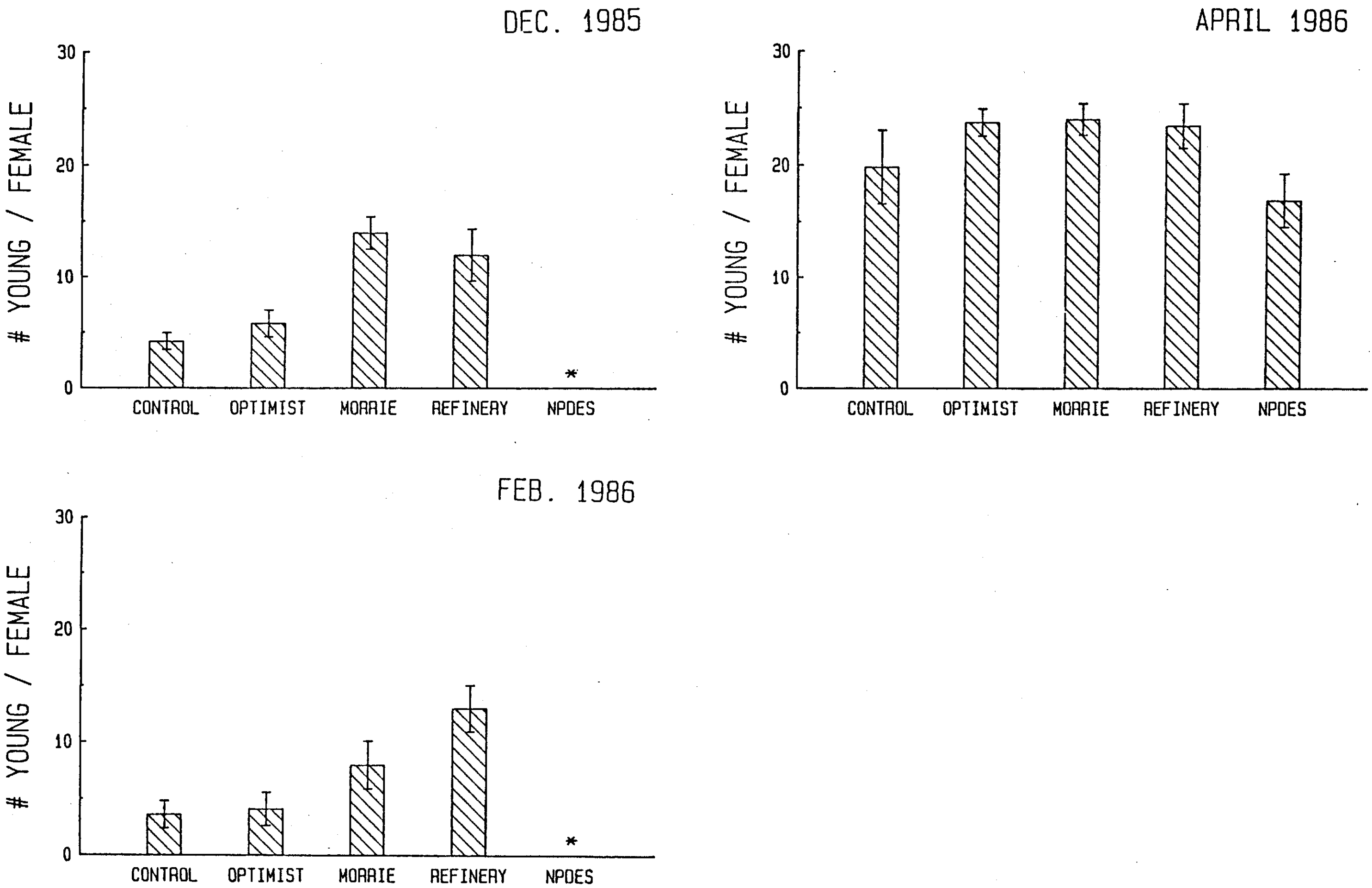


Figure 13 (continued).

August 1985 also killed all Ceriodaphnia by Day 7 of the test and significantly reduced their reproduction (Figs. 12 and 13 and Appendix Table A-2). However, samples from Morrie Avenue bridge never adversely affected fathead minnows (Figs. 10 and 11 and Appendix Table A-2).

At Optimist Park, fathead minnow growth was significantly lower than in the upstream control in February 1986 (Fig. 11 and Appendix Table A-2). Additionally, fathead minnow survival was significantly decreased in October 1985 (Fig. 10 and Appendix Table A-2). However, that decrease in survival was not large (85% survival at Optimist Park vs. 98% survival in upstream control), and growth was not significantly lower (Fig. 11 and Appendix Table A-2). Therefore, the October 1985 significant decrease in fathead minnow survival at Optimist Park was probably an artifact of unusually small variances in survival among replicate beakers in the ANOVA computations. Optimist Park samples never adversely affected Ceriodaphnia survival or reproduction (Figs. 12 and 13 and Appendix Table A-2).

Chemical Analyses. Except for unionized ammonia ($NH_3$) and ammonium ion ($NH_4^+$), routine water chemistry parameters and major inorganic ions at all Crow Creek sampling locations were within normal ranges (Table 2 and Appendix Tables B-4 and B-5). $NH_3$, the species of ammonia most toxic to aquatic animals, was calculated to be $\geq$ 0.07 mg/L and as high as 0.90 mg/L below the refinery's NPDES discharge in every month total ammonia was measured (Appendix Table B-4). Total ammonia was not measured in July and August 1985 due to instrument malfunction. Concentrations of $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $K^+$, $Cl^-$, $SO_4^{2-}$, $NO_3^-$ and $F^-$ tended to increase downstream from the control, especially $Na^+$, $K^+$, $Cl^-$, $SO_4^{2-}$ and $F^-$ below the refinery's NPDES discharge (Appendix Table B-5).

Of the 11 trace elements analyzed, only chromium and copper were unusually high in a few samples (Appendix Table B-6). Total Cr concentration was 0.0399 mg/L below the refinery's NPDES discharge in June 1985; however, $Cr^{6+}$ (the most toxic chromium species) was not analyzed in any samples. All other total Cr values below the NPDES discharge were $\leq$ 0.0056 mg/L. Concentrations of Cu were 0.0417 mg/L in the upstream control in July 1985 and 0.0165 mg/L along the oil refinery in August 1985. Since their respective downstream samples had much lower Cu concentrations, those two high values may have been caused by sample contamination.

No organic compounds were detected in any Crow Creek samples using reverse-phase HPLC in our laboratory. Similarly, none of the 11 phenolic priority pollutants monitored by GC-MS analyses in Crow Creek water in October and December 1985 was above detection limits (Rocky Mountain Analytical Laboratory 1986a, 1986b). Dissolved organic carbon concentrations ranged between 2.0 and 24.9 mg/L, and DOC concentrations usually were higher downstream from the upstream control. However, the range of DOC values in Crow Creek from June 1985 to April 1986 was narrower than the range of DOC values recorded for the Laramie River from June 1985 to October 1985 (Table 2).

# DISCUSSION

## Laramie River

The Union Pacific Tie Treatment Plant illustrates several common problems encountered at hazardous waste sites. This industrial site was operated adjacent to a major river in southeast Wyoming for nearly 100 years. Waste management practices for the various liquids and solids used in several wood preservation processes did not exist or were haphazard. Accumulation of this material on the surface and below ground led to severe groundwater/riverine pollution. Because the contaminants are a complex mixture of organic and inorganic chemicals, potential environmental fates and effects are difficult to predict at this site.

In this study, we used aquatic organisms to integrate the effects of the numerous biologically available pollutants in river water and interstitial sediment water. Fathead minnow 96-h acute toxicity and 7-d survival and growth tests demonstrated that toxic ground waters underlaid the Laramie River adjacent to the UPTTP. During June, July and August 1985, interstitial water withdrawn from river sediments decreased either survival or growth of the fish. Relocating the Laramie River in September 1985 to a new channel west of its previous location appeared to remove the immediate sediment pollution problem, as evidenced by no adverse effect on survival or growth of fathead minnows in the October groundwater sample. However, further studies would be required to confirm that groundwater contaminants do not migrate to the new river channel in the future.

Although the Ceriodaphnia 48-h LC50 for interstitial water in June 1985 was approximately equal to the fathead minnow 96-h LC50, Ceriodaphnia 7-d survival and reproduction appeared to be less sensitive than fathead minnow 7-d survival and growth at the Laramie River site. Ceriodaphnia survival and reproduction were significantly decreased only in the June interstitial water. Because the waters used for the Ceriodaphnia tests were the same as those used for the fathead minnow tests, it appears that Ceriodaphnia were simply more tolerant of the pollutants at the UPTTP. Therefore, based on Ceriodaphnia tests only, it was not possible to determine whether rechannelization changed the quality of ground water underlying the two river channels in August and October 1985.

Chemistry data suggest that trace organic compounds, as indicated by higher dissolved organic carbon concentrations (Appendix Table B-1) and the polynuclear aromatics identified in the HPLC scan of the June 1985 interstitial water (Fig. 9), may have been a major cause of toxicity in the interstitial waters. No routine water chemistry parameters or trace elements in the interstitial water and river water differed considerably from their concentrations in corresponding upstream control waters.

Survival and reproduction of control animals in the Ceriodaphnia 7-d tests were less variable than survival and growth of animals in the fathead minnow 7-d tests at the Laramie River study site. Control Ceriodaphnia survival was always 100%, and average reproduction ranged from 25 offspring/female in July to 12 offspring/female in August. Control fathead minnow survival ranged from 55% in June to 85% in August, whereas average weights ranged from 0.27 mg/fish in June to 0.74 mg/fish in August.

Monthly sampling during the summer of 1985 demonstrated two important aspects of groundwater/riverine systems, such as the Laramie River. First, ground water entering the river adjacent to the UPTTP was consistently more toxic than river water, indicating considerable dilution by the river water. Second, toxicity at all sampling locations, including the groundwater (mini-piezometer) sample, varied temporally. This is not surprising, because the flow rate of the Laramie River (Fig. 14) follows a hydrographic pattern typical of surface waters in the western United States, wherein flow rates are much higher during late spring and early summer than during other seasons. Thus, stream discharge and hydrologic flow of ground water into the adjacent river vary considerably. There are periods during high flow when the UPTTP site gains water from the river (CH2M/Hill 1985), temporarily reversing the normal flow of ground water. Hence, toxicity of ground water and river water can be expected to vary temporally.

Crow Creek

At Frontier Oil Refinery adjacent to Crow Creek, surface water may be contaminated due to groundwater pollutants from the old refinery facilities and due to current surface-water releases at a permitted NPDES discharge. Crow Creek has been judged by the Wyoming Game and Fish Department to be without sufficient hydrologic qualities to support fish life (John Wagner, Wyoming Department of Environmental Quality, personal communication). Because of that assessment, Crow Creek is classified as a Class IV (lowest ranking) stream by the Wyoming Department of Environmental Quality and is not protected for aquatic life. Instead, NPDES discharge limitations for the refinery are

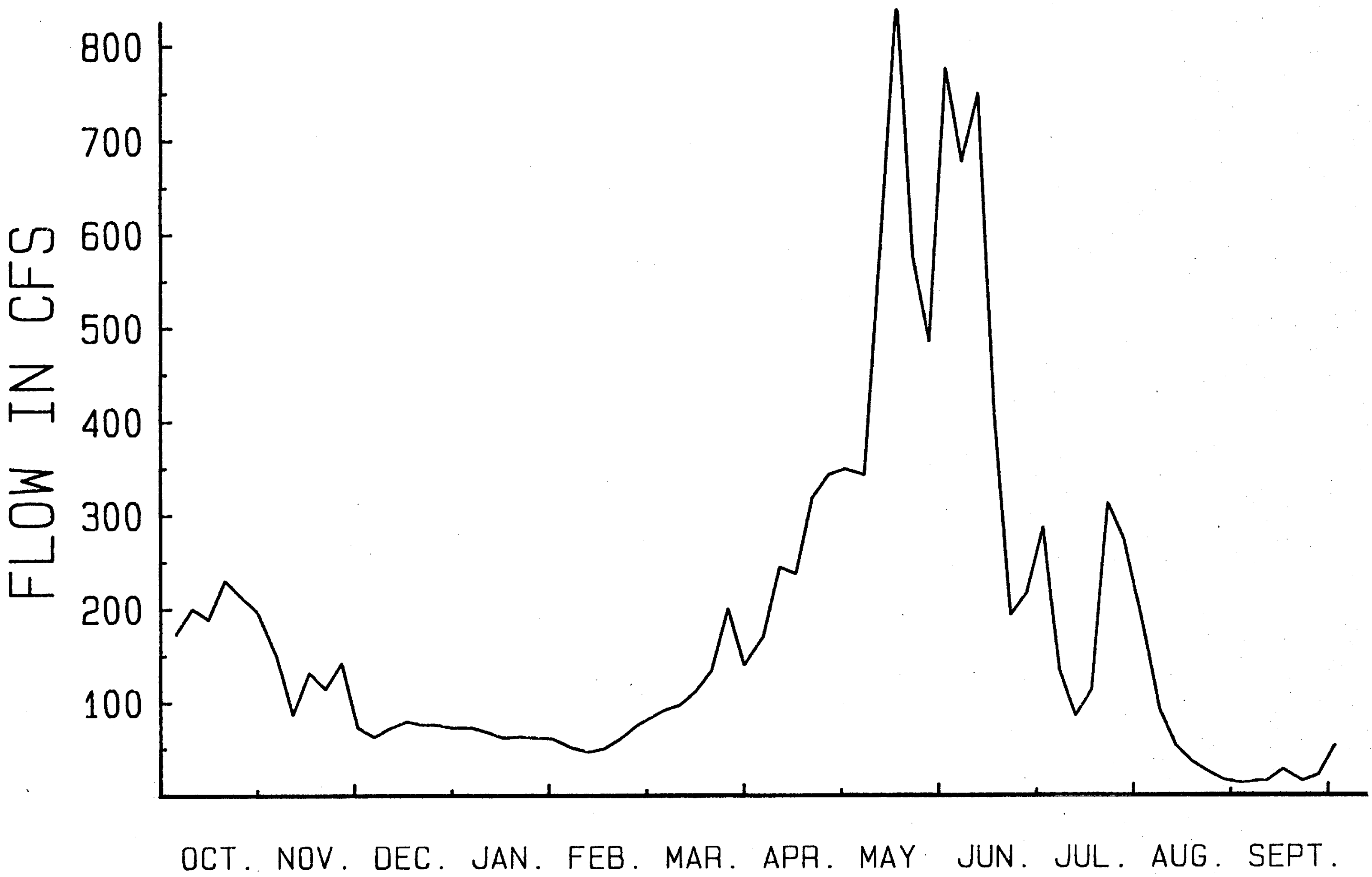


Figure 14. Laramie River hydrograph from October 1984 to September 1985. Data were compiled from unpublished files at the USGS office in Cheyenne, Wyoming.

computed according to U.S EPA Best Available Treatment (BAT) technology guidelines for a refinery of that design and size. BAT guidelines are based on concentrations of individual chemicals in effluents and not on biological effects in receiving waters. For the refinery effluent, limitations are placed on average and maximum discharges for several parameters including pH, biological oxygen demand, chemical oxygen demand, total phenols, ammonia, sulfide, oil and grease, total suspended solids, total chromium, and hexavalent chromium.

Although monthly NPDES reports filed by Frontier Oil Refinery (available for inspection at the Wyoming Department of Environmental Quality, Cheyenne, Wyoming) indicate that the NPDES discharge was always in compliance with limitations imposed by the Wyoming Department of Environmental Quality, acute toxicity tests and 7-d ambient toxicity tests indicated consistent adverse effects on survival, growth, or reproduction of fathead minnows and Ceriodaphnia in Crow Creek water downstream from the discharge. The intensity of the biological responses appeared to be approximately inversely related to the concentration of unionized ammonia in the water (see Appendix Table B-4). Thurston et al. (1983) reported 96-h LC50 values between 1.8 and 3.4 mg/L of unionized ammonia at 22$^{o}$C for fathead minnow fry and adults, while John W. Arthur and coworkers (U.S. EPA, Monticello, Minnesota, unpublished data) determined a 96-h LC50 of 2.6 mg/L of unionized ammonia at 26$^{o}$C for fathead minnow fry. Thus, there appeared to be sufficient unionized ammonia (0.07-0.63 mg/L) present below the NPDES discharge to account for sublethal effects on the fish. We are aware of no similar toxicity test data for Ceriodaphnia. However, Arthur and coworkers determined a 96-h LC50 of 1.3 mg/L of unionized ammonia at

20°C for adults of another cladoceran, Simocephalus vetulus. Although it is difficult to infer toxic effects concentrations across species, those data suggest that there may also have been sufficient unionized ammonia present to account for the sublethal effects on the Ceriodaphnia. And because of this apparent dominance of ammonia toxicity, it is difficult to infer whether other inorganic or organic contaminants also contributed to the adverse effects on survival, growth, and reproduction.

The consistent adverse biological effects observed in Crow Creek water below the NPDES discharge demonstrate that the fathead minnow and Ceriodaphnia 7-d ambient toxicity tests were capable of detecting the presence of instream contaminants. However, no ground waters were tested during Year 1 at this site, so potential groundwater contamination of Crow Creek can only be inferred from surface-water toxicity tests.

Several times, Crow Creek water upstream from the NPDES discharge, but still adjacent to the refinery, caused adverse biological effects. For example, fathead minnow growth was significantly lower at the refinery sampling location compared to the upstream control in July 1985 and February 1986, whereas Ceriodaphnia survival and growth were lower at the refinery and at Morrie Avenue bridge (adjacent to the SWSI Site) in August 1985. Additionally, no Ceriodaphnia survived at Morrie Avenue bridge in June 1985. On each of those dates, there was no obvious chemical constituent responsible for the observed biological effects. Storm sewer runoff or unknown spills and discharges upstream may account for some of the toxicity. However, the August 1985 samples were collected following the massive flood in Crow Creek. The SWSI Site, where wastes from previous refinery operations are buried or stored at the surface, was most likely saturated during the torrential rain and hail storms. Hence, polluted ground water from that site may have contributed at least some of the contamination that was detected biologically in Crow Creek in August 1985. And although Crow Creek water killed all Ceriodaphnia at Morrie Avenue bridge and the refinery sampling locations, its toxic and reproductive effects were lessened below the NPDES discharge less than 1 km downstream from the Morrie Avenue bridge (Figs. 3 and 4). Either physical/chemical processes (e.g., sediment adsorption, photolysis, volatilization, complexation with chemical constituents in the NPDES discharge) or biological processes (e.g., microbial degradation) are probably responsible for the decreased downstream effects.

Fathead minnows and Ceriodaphnia varied in their relative sensitivity to toxicants in Crow Creek water, depending on sampling location and sampling date. Potential reasons for this variability in sensitivity include different contaminants present at different sites and at different times of the year, and seasonally variable responses of test species to toxicants (see data of John W. Arthur and coworkers). But results from Crow Creek illustrate that it is useful to have data from more than one species when evaluating toxic effects in receiving waters. As a minimum, we believe that the fathead minnow and an invertebrate should be tested.

As discussed for the Laramie River study site, monthly variability in toxicity at Crow Creek sites would be expected to depend on stream flow rates and amount of groundwater infiltration. The variability in storm sewer and surface runoff from a municipal setting such as Cheyenne increases the difficulty of ascribing adverse instream biological effects to permitted discharges or specific groundwater pollution sources. Without detectable chemical "fingerprints" of contaminants to complement the toxicity test results, statements can only be made concerning the quality of the receiving water for supporting aquatic life. Such high-sensitivity chemical analyses are not routinely performed in the initial phases of a pollution investigation and thus may limit the extent of responsibility that can be attributed to potential pollution sources.

We encountered one major problem with Ceriodaphnia tests at Crow Creek. Although survival was always $\geq$ 60% at the upstream control, MOA reproduction varied from over 20 offspring/female in August 1985 to 4 offspring/female in December 1985 and February 1986. Because of low upstream control reproduction during the winter months, it was difficult to demonstrate adverse reproductive effects at downstream sampling locations. This may have been due to a chemical constituent that was present in the water at the upstream control, but was degraded or not bioavailable by the time the stream water reached the downstream sampling locations. Or it may also have been due to fewer bacteria in upstream control water during winter, thus providing less food for Ceriodaphnia adults to eat. We did not notice a similar problem of low reproduction in upstream control water at the Laramie River study site, probably because we did not test that water during the winter months.

## Toxicity Test Evaluation

In addition to establishing the potential for migration of contaminated ground water into surface waters at the Laramie River and

Crow Creek study sites, an important objective of this study was to evaluate the utility of fathead minnow and Ceriodaphnia ambient toxicity tests as routine biological monitoring techniques. In the following paragraphs, we address difficulties with current procedures for culturing and testing these animals.

A large amount of fathead minnow acute and chronic toxicity test data for single compounds and effluents is available in the published literature (e.g., Brooke et al. 1984). Fathead minnows are easily maintained in a laboratory, and an abundant supply of newly hatched larvae can be produced routinely for starting ambient toxicity tests. Larvae are easy to count with an unaided eye as long as the test water is not turbid. Siphoning the exposure chambers without removing and/or injuring the fish is tedious, but with practice the daily time requirement for handling a test comprising four replicate beakers for each of six test waters is approximately three hours. Necessary equipment to conduct the fathead minnow test is available or can be easily fabricated in most aquatic biology laboratories.

An important aspect of the fathead minnow test that we changed during Year 1 of this study was the number of replicates per exposure water. For all of the Laramie River sampling dates and for June, July and August 1985 at Crow Creek, we tested only two replicate chambers containing ten fish for each test water. However, variability of average fish weights between replicates was sometimes high. Furthermore, variances among exposure waters often were not homogeneous. Therefore, we changed to four replicates per exposure water in the Crow Creek study after August 1985 and obtained much more consistent results. This allowed us to simplify the statistical analyses of fish weights and increased our theoretical statistical power by a factor of approximately 1.7. We are awaiting results of a round-robin interlaboratory study of the fathead minnow 7-d growth and reproduction test that was conducted recently by Battelle Columbus Laboratories (see RELATED RESEARCH) for additional guidance on the most cost-effective number of replicates for that test.

Not as much acute and chronic toxicity data are available in the published literature for *Ceriodaphnia dubia* as there are for fathead minnows. But due to the increasing popularity of the *Ceriodaphnia* 7-d test, this will not be a major limitation in the near future.

A major drawback to the *Ceriodaphnia* test is that nutritional requirements for *Ceriodaphnia* are not well known. Occasionally, cultures in our laboratory and laboratories of other investigators around the country "crash" (die off) or produce males and diapause eggs, both of which indicate stress. New cultures must be started when that occurs. But with proper rotation of cultures, there are usually enough neonates available to begin a test at any time. Current research at several laboratories across the country should help to resolve problems related to *Ceriodaphnia* nutrition and culturing (see RELATED RESEARCH).

Related to the culturing problem, we also had difficulty maintaining adequate laboratory-water controls during the *Ceriodaphnia* 7-d toxicity tests. Survival and reproduction were erratic and often much less than in the upstream control waters. When upstream controls perform well, there is no need for laboratory controls. However, good survival and reproduction in laboratory water are needed to demonstrate that experimental techniques are not to blame when survival or reproduction in upstream controls is low.

Daily observation of adult survival and numbers of offspring is not difficult, but it requires a low-power dissecting microscope to view the animals. Adults can be transferred to fresh test water every other day fairly quickly, so the daily requirement for a test with ten replicates of six or seven test waters is approximately two hours. As with the fathead minnow test, equipment needed for the *Ceriodaphnia* 7-d test is available in most aquatic biology laboratories.

## Toxicity Testing vs. Chemical Analyses

The National Pollutant Discharge Elimination System (NPDES) was originally established by the U.S. EPA to control the discharge of "toxics in toxic amounts" into the nation's waterways. In the past, it has been based on water quality criteria for 129 named pollutants. Many contract analytical laboratories are now capable of routinely analyzing soil and water samples for these compounds. In addition, regulatory agencies and environmental consultants have used the 129 priority pollutants as a focus for assessing a wide range of environmental contamination problems.

Yet cumulative experience with this system has indicated that many pollution problems are not addressed adequately. Although 129 priority pollutants are identified, thousands of other chemicals are discharged to aquatic systems and can cause adverse biological effects. And because the NPDES system is currently based on laboratory toxicity data for single compounds, discharge limitations are not always environmentally realistic. Contaminant exposures in aquatic systems often occur as complex mixtures of compounds, containing perhaps some priority pollutants and many compounds not on the priority list.

Therefore, previous methods for determining discharge limitations based on Best Available Technology and concentrations of individual chemicals may have underprotected or overprotected aquatic life in receiving waters.

Interest has now turned toward addressing the biological impacts of receiving water contamination. For example, assessing the hazard of effluent mixtures was the topic of a recent workshop attended by many prominent aquatic toxicologists (Bergman et al. 1986). And results of field research and test standardization related to effluent testing have been published by the U.S. EPA (e.g., Mount et al. 1984, Horning and Weber 1985). Results of those meetings and toxicity studies indicate that biological tests contribute considerable information cost-effectively for evaluating the potential or realized effects of surface-water contamination. And our studies on the Laramie River and Crow Creek demonstrate that ambient toxicity tests can be used to detect contaminated ground water and its migration into surface waters. We do not believe that toxicity tests will supplant chemical analyses in pollutant studies. Instead, toxicity tests complement chemical analyses. Without chemical analyses, it is difficult to identify sources of toxicity; without toxicity tests, it is difficult to interpret the biological significance of the presence of pollutants in an aquatic system.

## Cost Comparisons

Current costs of fathead minnow and *Ceriodaphnia* 7-d ambient toxicity tests, fathead minnow and invertebrate acute toxicity tests, and various chemical analyses are listed in Table 3. Ranges of prices

Table 3. Comparison of costs for toxicity tests and chemical analyses.

| Test | Cost[a] |
|---|---|
| *Toxicity* | |
| Fathead minnow 7-d survival and growth (4 replicates x 6 exposure waters) | \$1100 - \$1800 |
| *Ceriodaphnia* 7-d survival and reproduction (10 replicates x 6 exposure waters) | \$800 - \$1800 |
| Fathead minnow 96-h LC50 (3 replicates x 6 exposure waters) | \$550 - \$750 |
| Invertebrate 48-h LC50 -- *Ceriodaphnia* or *Daphnia* (3 replicates x 6 exposure waters) | \$400 - \$650 |
| *Chemistry* | |
| Routine chemistry parameters (pH, conductivity, alkalinity, hardness, ammonia, total phenols, oil and grease, suspended solids; 6 samples at \$80/sample) | \$480 |
| Major inorganic ions ($K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$ by ICP and $Cl^-$, $NO_3^-$, $SO_4^{2-}$ by ion chromatography; 6 samples at \$20/sample) | \$120 |
| Trace elements (20 elements by AA; 6 samples at \$10/element/sample) | \$1200 |
| Dissolved organic carbon (6 samples at \$15/sample) | \$90 |
| Reverse-phase HPLC gradient fingerprints (6 samples at \$50/sample) | \$300 |
| GC-MS scan of major organics (6 samples at \$500/sample) | \$3000 |
| Priority pollutant analysis (6 samples at \$1500/sample) | \$9000 |

[a]Toxicity test costs were compiled from price lists and a telephone survey of five university and private toxicity testing laboratories.

for toxicity tests were obtained from price lists and a telephone survey of five university and private toxicity testing laboratories. Higher prices were quoted by laboratories that anticipated having to run a test more than once to satisfy some clients.

Prices in Table 3 indicate that the 7-d ambient tests cost approximately two to three times as much as corresponding acute toxicity tests. Based on results of this study, we believe that 7-d ambient tests are cost-effective compared to shorter-duration acute tests. For example, fathead minnow and Ceriodaphnia 7-d tests showed an adverse effect of Crow Creek water collected below the refinery discharge on all seven sampling dates. However, 96-h fathead minnow and 48-h Ceriodaphnia acute tests would have identified an LC50 < 100% of full-strength stream water in only five of those seven tests. And in upstream waters where only fathead minnow growth or Ceriodaphnia reproduction was adversely affected, acute toxicity tests would not have indicated the presence of toxicants.

A suite of routine chemistry parameters (pH, conductivity, alkalinity, hardness, etc.) and major inorganic ions would cost approximately $600 for six water samples, the same number analyzed in an acute or ambient toxicity test. The cost of one acute test is therefore approximately equal to this suite of routine chemical analyses, and one ambient toxicity test only costs two to three times as much. Since total ammonia below the NPDES discharge on Crow Creek was the only major inorganic toxicant that we could identify in this study, much of the observed toxicity would not have been predicted from routine chemical analyses. Trace elements did not account for much of the toxicity either, yet a suite of 20 trace elements would have cost as much as one ambient toxicity test.

Organic chemicals explained much of the toxicity of ground water at the Laramie River site. Relatively simple dissolved organic carbon analyses and reverse-phase HPLC fingerprints would have cost about $400 total for 6 samples and would have indicated the presence of potentially toxic organics, although their identities would still not have been known. A GC-MS scan of only the major organics in all 6 water samples would have cost at least $3000, equal to the average cost of two 7-d ambient toxicity tests. And finally, a complete priority pollutant scan of six water samples, which would probably still not have identified all potential inorganic and organic toxicants in Laramie River or Crow Creek waters, would have cost approximately $9000.

Therefore, we believe that ambient toxicity tests are cost-competitive with chemical analyses and provide additional information concerning potential biological effects of toxicants that cannot be predicted reliably from a list of all chemical constituents in a water sample.

## Research Planned for Year 2

Because the Laramie River was rechanneled in September 1985 to avoid groundwater pollution from the UPTTP, our Year 1 investigations of the Laramie River study site were completed in October 1985. No new samples will taken from the Laramie River in Year 2.

Since December 1985 (Year 1 of the current study), we have intensified our investigations at the Crow Creek study site. In June 1986 (Year 2 of the current study) we began collecting interstitial water samples from Crow Creek sediments adjacent to Frontier Oil

Refinery, in order to more accurately identify potential sources of groundwater toxicity found in Year 1. Based on Year 1 results, we will only collect Crow Creek samples from June to September 1986. That was the period when potential groundwater effects were most evident in Crow Creek waters. Additionally, sampling will be conducted at closer time intervals (e.g., twice a month) during Year 2 in order to better quantify temporal variability of instream toxicity and correlate instream toxicity with stream flow rate.

## SUMMARY AND CONCLUSIONS

In this two-year study, we are (1) evaluating the utility of U.S. EPA fathead minnow and Ceriodaphnia dubia ambient toxicity tests as monitors of the effects of groundwater pollution that enters surface waters, (2) comparing the sensitivity of those biological tests to the sensitivity of chemical analyses for detecting the presence of groundwater contaminants, and (3) assessing temporal variability of groundwater and surface-water contamination in the Laramie River and Crow Creek in southeast Wyoming. Results of Year 1 studies are as follows:

- Toxic ground water underlaid Laramie River sediments adjacent to the former Union Pacific Tie Treatment Plant. This ground water was heavily contaminated with water soluble organic compounds typical of creosote oil that permeated the soils adjacent to the river and also underlaid Laramie River sediments approximately 30 m upstream from the groundwater sampling location.
- Laramie River water flowing directly over the sediments in which the oil body lay and at two downstream locations did not adversely affect survival, growth or reproduction of fathead minnows and Ceriodaphnia, compared to the upstream control during June, July and August 1985.
- The Laramie River was rechanneled in September 1985 to avoid oil seeps and contaminated ground water. Ground water and river water collected at corresponding locations in the new river channel in October 1985 did not adversely affect survival, growth, and reproduction, but river water below the downstream

confluence with Spring Creek significantly decreased fathead minnow growth relative to the upstream control.

- Low concentrations of anthracene, phenanthrene and chrysene were detected in the toxic interstitial water withdrawn from Laramie River sediments in June 1985, using reverse-phase HPLC gradients. However, organics were not detected using HPLC on other sampling dates. And no trace elements, major inorganic ions or routine water chemistry parameters differed considerably from the upstream control on any sampling date.
- Crow Creek water collected 50 m downstream from Frontier Oil Refinery's NPDES discharge either killed all fathead minnows and Ceriodaphnia or significantly reduced fathead minnow growth and Ceriodaphnia reproduction relative to the upstream control on every sampling date. This toxicity was predominantly caused by high ammonia concentrations allowed in the NPDES permit for that discharge.
- Crow Creek waters collected in August 1985 upstream from the NPDES discharge, but still adjacent to the oil refinery property, were toxic to Ceriodaphnia. Those samples were collected after Crow Creek flooded because of intense hail and rain storms on August 1, 1985; hence, the toxicity may have been caused by contaminated ground water emanating from buried wastes at the old refinery facility or by storm-sewer runoff entering Crow Creek upstream from the refinery site. No inorganic or organic contaminants could be identified as possible toxicants in those samples.

These results indicate that (1) ambient toxicity tests can be used in alkaline surface waters of the western U.S.; (2) they are sensitive enough to detect migration of contaminated ground water into surface waters; (3) they may be more sensitive in some cases than routine, inexpensive chemical analyses for detecting the presence of contaminants; and (4) instream toxicity of contaminated ground water and an industrial discharge varied considerably during Year 1. In the summer of Year 2 we will collect surface-water and groundwater samples from Crow Creek adjacent to the Frontier Oil Refinery, in order to more accurately identify potential sources of groundwater toxicity found in Year 1 and correlate instream toxicity with stream flow rate.

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# APPENDIX A

## Chronic Toxicity Test Results

- Laramie River: June 1985 - October 1985
- Crow Creek: June 1985 - April 1986

Table A-1. Seven-day survival and growth of fathead minnows (Pimephales promelas) and seven-day survival and reproduction of Ceriodaphnia dubia in Laramie River water and interstitial (piezometer) water from June 1985 to October 1985.[a]

| | | Fathead minnows | | Ceriodaphnia | | |
|---|---|---|---|---|---|---|
| Date | Site | Percent survival | Weight (mg)[b] | Percent survival | MOA total offspring/ female[b,c] | MIM total offspring/ female[b,c] |
| June 1985 | Upstream control | 55 | 0.27 ± 0.055 | 100 | 20.8 ± 0.84 | 20.8 ± 0.84 |
| | Above seep | 25 | 0.39 ± 0.003 | 100 | 20.1 ± 0.60 | 20.1 ± 0.60 |
| | Piezometer onsite | 0 * | ---[d] --- | 0 * | 0 ± 0 * | --- --- |
| | I-80 | 30 | 0.34 ± 0.084 | 100 | 19.1 ± 0.69 | 19.1 ± 0.69 |
| | Spring Creek | 70 | 0.31 ± 0.088 | 100 | 19.6 ± 0.73 | 19.6 ± 0.73 |
| July 1985 | Upstream control | 60 | 0.37 ± 0.020 | 100 | 24.9 ± 0.57 | 24.9 ± 0.57 |
| | Above seep | 60 | 0.41 ± 0.050 | 100 | 23.4 ± 0.69 | 23.4 ± 0.69 |
| | Piezometer onsite | 35 | 0.18 ± 0.023 * | 100 | 26.3 ± 2.27 | 26.3 ± 2.27 |
| | I-80 | 90 | 0.42 ± 0.004 | 90 | 20.5 ± 2.18 | 22.4 ± 1.11 |
| | Spring Creek | 55 | 0.40 ± 0.154 | 100 | 24.3 ± 0.67 | 24.3 ± 0.67 |
| August 1985 | Upstream control | 85 | 0.56 ± 0.029 | 100 | 12.2 ± 1.60 | 12.2 ± 1.60 |
| | Above seep | 55 | 0.54 ± 0.024 | 100 | 14.8 ± 1.64 | 14.8 ± 1.64 |
| | Piezometer onsite | 5 * | 0.35 ± 0 * | 80 | 11.8 ± 1.29 | 13.6 ± 0.53 |
| | I-80 | 65 | 0.56 ± 0.042 | 100 | 15.2 ± 1.52 | 15.2 ± 1.52 |
| | Spring Creek | 75 | 0.57 ± 0.028 | 100 | 18.5 ± 1.28 | 18.5 ± 1.28 |
| October 1985[e] | Upstream control | 60 | 0.74 ± 0.035 | 100 | 19.6 ± 0.50 | 19.6 ± 0.50 |
| | Upstream piezometer | 74 | 0.57 ± 0.035 | 100 | 19.6 ± 0.69 | 19.6 ± 0.69 |
| | New channel onsite | 53 | 0.64 ± 0.066 | 90 | 18.4 ± 1.83 | 19.9 ± 1.20 |
| | New piezometer onsite | 75 | 0.74 ± 0.076 | 100 | 17.8 ± 1.06 | 17.8 ± 1.06 |
| | I-80 | 50 | 0.78 ± 0.049 | 100 | 17.6 ± 1.17 | 17.6 ± 1.17 |
| | Spring Creek | 75 | 0.54 ± 0.013 * | 100 | 21.8 ± 0.92 | 21.8 ± 0.92 |

[a]* = significantly less than upstream control (α = 0.05).

[b]Values expressed as mean ± one standard error of the mean.

[c]MOA = mean reproduction of all females that started the test; MIM = mean reproduction of surviving females (see Toxicity Tests in METHODS for calculation procedures).

[d]--- = value could not be calculated because all of the test animals died.

[e]Laramie River was rechanneled in September 1985 (see Site Descriptions in METHODS); October 1985 stream samples were collected at corresponding locations along the new river channel.

Table A-2. Seven-day survival and growth of fathead minnows (Pimephales promelas) and seven-day survival and reproduction of Ceriodaphnia dubia in Crow Creek water from June 1985 to April 1986.[a]

| | | Fathead minnows | | Ceriodaphnia | | |
|---|---|---|---|---|---|---|
| Date | Site | Percent survival | Weight (mg)[b] | Percent survival | MOA total offspring/ female[b,c] | MIM total offspring/ female[b,c] |
| June 1985 | Upstream control | 95 | 0.27 ± 0.006 | 90 | 13.6 ± 1.20 | 14.1 ± 1.22 |
| | Optimist Park | 100 | 0.25 ± 0.021 | 90 | 18.7 ± 1.16 | 19.7 ± 0.71 |
| | Morrie Avenue | 95 | 0.24 ± 0.043 | 0 * | 18.4 ± 1.91 | --- --- |
| | Refinery | 100 | 0.23 ± 0.005 | 80 | 25.3 ± 0.68 | 25.6 ± 0.60 |
| | Below NPDES | 0 * | ---[d] --- | 0 * | 0 ± 0 * | --- --- |
| July 1985 | Upstream control | 85 | 0.74 ± 0.059 | 100 | 16.2 ± 0.61 | 16.2 ± 0.61 |
| | Optimist Park | 75 | 0.58 ± 0.156 | 90 | 20.8 ± 1.26 | 21.8 ± 0.89 |
| | Morrie Avenue | 90 | 0.63 ± 0.074 | 100 | 21.0 ± 0.67 | 21.0 ± 0.67 |
| | Refinery | 80 | 0.47 ± 0.009 * | 100 | 20.7 ± 1.24 | 20.7 ± 1.24 |
| | Below NPDES | 0 * | --- --- | 0 * | 0 ± 0 * | --- --- |
| August 1985 | Upstream control | 55 | 0.52 ± 0.018 | 100 | 20.5 ± 1.10 | 20.5 ± 1.10 |
| | Optimist Park | 90 | 0.49 ± 0.053 | 100 | 18.6 ± 1.84 | 18.6 ± 1.84 |
| | Morrie Avenue | 100 | 0.49 ± 0.049 | 0 * | 6.0 ± 0.89 * | --- --- |
| | Refinery | 100 | 0.51 ± 0.042 | 0 * | 5.5 ± 0.78 * | --- --- |
| | Below NPDES | 25 | 0.21 ± 0.040 * | 100 | 10.7 ± 1.05 * | 10.7 ± 1.05 * |
| October 1985 | Upstream control | 98 | 0.88 ± 0.039 | 100 | 22.1 ± 0.86 | 22.1 ± 0.86 |
| | Optimist Park | 85 * | 0.81 ± 0.025 | 100 | 20.9 ± 1.04 | 20.9 ± 1.04 |
| | Morrie Avenue | 98 | 0.92 ± 0.026 | 100 | 20.1 ± 1.26 | 20.1 ± 1.26 |
| | Refinery | 95 | 0.92 ± 0.032 | 100 | 21.3 ± 1.32 | 21.3 ± 1.32 |
| | Below NPDES | 0 * | --- --- | 0 * | 0 ± 0 * | --- --- |
| December 1985 | Upstream control | 78 | 0.80 ± 0.030 | 90 | 4.2 ± 0.76 | 4.7 ± 0.67 |
| | Optimist Park | 72 | 0.78 ± 0.051 | 100 | 5.8 ± 1.21 | 5.8 ± 1.21 |
| | Morrie Avenue | 70 | 0.84 ± 0.024 | 100 | 14.0 ± 1.46 | 14.0 ± 1.46 |
| | Refinery | 68 | 0.81 ± 0.032 | 100 | 12.0 ± 2.37 | 12.0 ± 2.37 |
| | Below NPDES | 15 * | 0.17 ± 0.041 * | 0 * | 0 ± 0 * | --- --- |
| February 1986 | Upstream control | 90 | 0.79 ± 0.020 | 60 | 3.6 ± 1.22 | 5.8 ± 1.40 |
| | Optimist Park | 88 | 0.70 ± 0.030 * | 70 | 4.1 ± 1.47 | 5.9 ± 1.71 |
| | Morrie Avenue | 90 | 0.74 ± 0.018 | 70 | 8.0 ± 2.11 | 11.1 ± 2.00 |
| | Refinery | 98 | 0.70 ± 0.010 * | 80 | 13.0 ± 2.08 | 15.9 ± 1.01 |
| | Below NPDES | 0 * | --- --- | 0 * | 0 ± 0 * | --- --- |
| April 1986 | Upstream control | 75 | 0.87 ± 0.089 | 80 | 19.8 ± 3.22 | 24.4 ± 1.28 |
| | Optimist Park | 100 | 0.75 ± 0.026 | 100 | 23.7 ± 1.20 | 23.7 ± 1.20 |
| | Morrie Avenue | 92 | 0.75 ± 0.064 | 100 | 24.0 ± 1.39 | 24.0 ± 1.39 |
| | Refinery | 95 | 0.88 ± 0.028 | 100 | 23.4 ± 1.96 | 23.4 ± 1.96 |
| | Below NPDES | 85 | 0.37 ± 0.042 * | 90 | 16.9 ± 2.37 | 18.7 ± 1.62 * |

[a]* = significantly less than upstream control ($\alpha = 0.05$).

[b]Values expressed as mean ± one standard error of the mean.

[c]MOA = mean reproduction of all females that started the test; MIM = mean reproduction of surviving females (see Toxicity Tests in METHODS for calculation procedures).

[d]--- = value could not be calculated because all of the test animals died.

APPENDIX B

Water Chemistry

- Laramie River: June 1985 - October 1985
- Crow Creek: June 1985 - April 1986

Table B-1. Routine water chemistry parameters in Laramie River water and interstitial (piezometer) water from June 1985 to October 1985.

| Date | Site | pH | Conductivity (µS/cm) | Alkalinity (mg/L as $CaCO_3$) | Hardness (mg/L as $CaCO_3$) | Total ammonia (mg N/L) | Unionized ammonia (mg $NH_3$/L) | Dissolved organic carbon (mg/L) |
|---|---|---|---|---|---|---|---|---|
| June 1985 | Upstream control | 7.8 | 612 | 106 | 235 | < 0.10 | < 0.01 | 11.7 |
| | Above seep | 7.7 | 622 | 104 | 240 | < 0.10 | < 0.01 | 10.5 |
| | Piezometer onsite | 7.8 | 1158 | 158 | 461 | < 0.10 | < 0.01 | 23.0 |
| | I-80 | 7.6 | 607 | 103 | 230 | < 0.10 | < 0.01 | 10.2 |
| | Spring Creek | 7.8 | 647 | 108 | 250 | < 0.10 | < 0.01 | 10.0 |
| July 1985 | Upstream control | 8.4 | 1150 | 156 | 490 | ---[a] | --- | 6.6 |
| | Above seep | 8.3 | 1160 | 156 | 499 | --- | --- | 6.9 |
| | Piezometer onsite | 8.1 | 1220 | 172 | 482 | --- | --- | 9.9 |
| | I-80 | 8.3 | 1160 | 162 | 459 | --- | --- | 9.8 |
| | Spring Creek | 8.4 | 1150 | 157 | 455 | --- | --- | 32.9 |
| August 1985 | Upstream control | 8.2 | 1036 | 134 | 396 | --- | --- | 9.5 |
| | Above seep | 8.1 | 1038 | 134 | 402 | --- | --- | 7.5 |
| | Piezometer onsite | 7.8 | 1033 | 139 | 402 | --- | --- | 9.4 |
| | I-80 | 8.2 | 1032 | 134 | 392 | --- | --- | 7.9 |
| | Spring Creek | 8.1 | 1026 | 138 | 412 | --- | --- | 8.4 |
| October 1985[b] | Upstream control | 8.1 | 763 | 114 | 313 | < 0.10 | < 0.01 | 6.5 |
| | Upstream piezometer | 8.0 | 741 | 110 | 286 | < 0.10 | < 0.01 | 8.0 |
| | New channel onsite | 8.1 | 788 | 113 | 317 | < 0.10 | < 0.01 | 7.3 |
| | New piezometer onsite | 8.3 | 762 | 112 | 298 | < 0.10 | < 0.01 | 8.0 |
| | I-80 | 8.0 | 797 | 110 | 309 | < 0.10 | < 0.01 | 8.4 |
| | Spring Creek | 8.0 | 798 | 119 | 305 | < 0.10 | < 0.01 | 2.1 |

[a]--- = value not determined.

[b]Laramie River was rechanneled in September 1985 (see Site Descriptions in METHODS); October 1985 stream samples were collected at corresponding locations along the new river channel.

Table B-2. Concentrations of major inorganic ions in Laramie River water and interstitial (piezometer) water from June 1985 to October 1985.[a]

| | | Cations | | | | | | Anions | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Date | Site | $Na^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $K^+$ | $Sr^{2+}$ | $NH_4^+$ | $Cl^-$ | $SO_4^{2-}$ | $NO_3^-$ | $F^-$ | $HCO_3^-$ | $CO_3^{2-}$ |
| June 1985 | Upstream control | 42 | 77 | 10 | 3.7 | 0.6 | < 0.13 | 7 | 176 | < 1 | 0.5 | 128 | 0.5 |
| | Above seep | 43 | 68 | 10 | 2.8 | 0.6 | < 0.13 | 7 | 176 | < 1 | 0.5 | 126 | 0.4 |
| | Piezometer onsite | 73 | 90 | 34 | 5.8 | 1.2 | < 0.13 | 48 | 299 | < 1 | 0.8 | 191 | 0.8 |
| | I-80 | 38 | 67 | 12 | 2.8 | 0.5 | < 0.13 | 7 | 171 | < 1 | 0.5 | 125 | 0.3 |
| | Spring Creek | 38 | 74 | 12 | 2.9 | 0.6 | < 0.13 | 8 | 185 | < 1 | 0.5 | 131 | 0.5 |
| July 1985 | Upstream control | 86 | 137 | 22 | 4.6 | 1.0 | ---[b] | 20 | 508 | < 1 | 0.8 | 184 | 3.2 |
| | Above seep | 83 | 134 | 22 | 4.4 | 1.1 | --- | 21 | 503 | < 1 | 0.8 | 185 | 2.6 |
| | Piezometer onsite | 81 | 136 | 23 | 5.0 | 1.2 | --- | 25 | 510 | < 1 | 0.8 | 206 | 1.8 |
| | I-80 | 82 | 136 | 22 | 4.5 | 1.0 | --- | 21 | 503 | < 1 | 0.8 | 192 | 2.7 |
| | Spring Creek | 76 | 126 | 21 | 4.4 | 0.9 | --- | 21 | 514 | < 1 | 0.7 | 185 | 3.2 |
| August 1985 | Upstream control | 73 | 128 | 20 | 3.9 | 0.9 | --- | 19 | 314 | < 1 | 0.7 | 160 | 1.7 |
| | Above seep | 67 | 128 | 20 | 3.9 | 0.8 | --- | 19 | 312 | < 1 | 0.6 | 161 | 1.4 |
| | Piezometer onsite | 75 | 113 | 22 | 5.0 | 1.0 | --- | 21 | 306 | < 1 | 0.4 | 168 | 0.7 |
| | I-80 | 78 | 124 | 19 | 3.9 | 0.8 | --- | 19 | 309 | < 1 | 0.4 | 160 | 1.7 |
| | Spring Creek | 69 | 128 | 20 | 4.1 | 0.9 | --- | 20 | 306 | < 1 | 0.4 | 165 | 1.4 |
| October 1985[c] | Upstream control | 48 | 66 | 32 | 2.9 | 0.5 | < 0.13 | 10 | 228 | < 1 | 0.6 | 137 | 1.1 |
| | Upstream piezometer | 45 | 65 | 31 | 2.6 | 0.5 | < 0.13 | 10 | 218 | < 1 | 0.5 | 132 | 0.9 |
| | New channel onsite | 49 | 69 | 34 | 2.8 | 0.5 | < 0.13 | 12 | 237 | < 1 | 0.5 | 136 | 1.1 |
| | New piezometer onsite | 48 | 69 | 31 | 2.7 | 0.5 | < 0.13 | 11 | 225 | < 1 | 0.5 | 133 | 1.7 |
| | I-80 | 51 | 67 | 33 | 2.7 | 0.5 | < 0.13 | 12 | 237 | < 1 | 0.5 | 132 | 0.9 |
| | Spring Creek | 47 | 70 | 38 | 2.8 | 0.6 | < 0.13 | 11 | 235 | < 1 | 0.5 | 143 | 0.9 |

[a]Values expressed as mg/L.

[b]--- = value not determined.

[c]Laramie River was rechanneled in September 1985 (see Site Descriptions in METHODS); October 1985 stream samples were collected at corresponding locations along the new river channel.

Table B-3. Concentrations of trace elements in Laramie River water and interstitial (piezometer) water from June 1985 to October 1985.[a]

| | | Element | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Date | Site | Al | As | Cd | Cr | Cu | Fe | Hg | Ni | Pb | Se | Zn |
| June 1985 | Upstream control | < 0.1 | < 0.1 | 0.0015 | 0.0041 | < 0.0010 | 0.12 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0075 |
| | Above seep | < 0.1 | < 0.1 | 0.0030 | 0.0030 | < 0.0010 | 0.14 | < 0.1 | 0.02 | < 0.1 | < 0.1 | 0.0036 |
| | Piezometer onsite | < 0.1 | < 0.1 | 0.0023 | 0.0017 | < 0.0010 | 0.13 | < 0.1 | < 0.01 | < 0.1 | 0.1 | 0.0124 |
| | I-80 | 0.1 | < 0.1 | 0.0019 | 0.0078 | 0.0261 | 0.15 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0018 |
| | Spring Creek | < 0.1 | < 0.1 | 0.0014 | 0.0036 | < 0.0010 | 0.12 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0025 |
| July 1985 | Upstream control | < 0.1 | < 0.1 | 0.0023 | 0.0022 | < 0.0010 | 0.02 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0045 |
| | Above seep | 0.1 | < 0.1 | 0.0022 | 0.0028 | < 0.0010 | 0.02 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0035 |
| | Piezometer onsite | 0.1 | < 0.1 | 0.0029 | < 0.0010 | < 0.0010 | 0.02 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0132 |
| | I-80 | < 0.1 | < 0.1 | 0.0026 | 0.0080 | 0.0023 | 0.02 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0112 |
| | Spring Creek | < 0.1 | < 0.1 | 0.0035 | 0.0043 | 0.0016 | 0.04 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0064 |
| August 1985 | Upstream control | 0.1 | < 0.1 | 0.0022 | 0.0028 | < 0.0010 | 0.04 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0139 |
| | Above seep | < 0.1 | < 0.1 | 0.0029 | < 0.0010 | < 0.0010 | 0.03 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0187 |
| | Piezometer onsite | 0.1 | < 0.1 | 0.0024 | < 0.0010 | < 0.0010 | 0.07 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0096 |
| | I-80 | 0.1 | < 0.1 | 0.0021 | 0.0053 | < 0.0010 | 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0003 |
| | Spring Creek | 0.1 | < 0.1 | 0.0020 | < 0.0010 | < 0.0010 | 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0018 |
| October 1985[b] | Upstream control | < 0.1 | < 0.1 | 0.0007 | < 0.0010 | < 0.0010 | 0.04 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0008 |
| | Upstream piezometer | < 0.1 | < 0.1 | 0.0010 | < 0.0010 | < 0.0010 | 0.02 | < 0.1 | 0.01 | < 0.1 | < 0.1 | 0.0075 |
| | New channel onsite | < 0.1 | < 0.1 | 0.0008 | < 0.0010 | < 0.0010 | 0.02 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0052 |
| | New piezometer onsite | < 0.1 | < 0.1 | 0.0008 | 0.0055 | < 0.0010 | 0.02 | < 0.1 | 0.01 | < 0.1 | < 0.1 | 0.0062 |
| | I-80 | < 0.1 | < 0.1 | 0.0008 | < 0.0010 | < 0.0010 | 0.02 | < 0.1 | 0.01 | < 0.1 | < 0.1 | 0.0130 |
| | Spring Creek | < 0.1 | < 0.1 | 0.0007 | 0.0139 | < 0.0010 | 0.05 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0033 |

[a]Values expressed as mg/L. Al, As, Fe, Hg, Ni, Pb and Se were analyzed by inductively coupled plasma emission spectroscopy (ICP); Cd, Cr, Cu and Zn were analyzed by atomic absorption spectroscopy (detection limits using ICP for these four elements were only 0.01 mg/L).

[b]Laramie River was rechanneled in September 1985 (see Site Descriptions in METHODS); October 1985 stream samples were collected at corresponding locations along the new river channel.

Table B-4. Routine water chemistry parameters in Crow Creek water from June 1985 to April 1986.

| Date | Site | pH | Conductivity (µS/cm) | Alkalinity (mg/L as $CaCO_3$) | Hardness (mg/L as $CaCO_3$) | Total ammonia (mg N/L) | Union-ized ammonia (mg $NH_3$/L) | Dissolved organic carbon (mg/L) |
|---|---|---|---|---|---|---|---|---|
| June 1985 | Upstream control | 8.0 | 403 | 176 | 182 | < 0.10 | < 0.01 | 5.8 |
| | Optimist Park | 8.4 | 543 | 188 | 221 | 0.14 | 0.02 | 12.3 |
| | Morrie Avenue | 8.2 | 560 | 182 | 230 | < 0.10 | < 0.01 | 8.5 |
| | Refinery | 8.1 | 626 | 188 | 336 | < 0.10 | < 0.01 | 8.8 |
| | Below NPDES | 7.9 | 802 | 163 | 288 | 12.00 | 0.63 | 22.4 |
| July 1985 | Upstream control | 8.2 | 347 | 134 | 141 | ---[a] | --- | 22.4 |
| | Optimist Park | 8.4 | 640 | 180 | 240 | --- | --- | 6.5 |
| | Morrie Avenue | 8.3 | 671 | 179 | 249 | --- | --- | 8.3 |
| | Refinery | 7.9 | 696 | 182 | 259 | --- | --- | 8.9 |
| | Below NPDES | 7.7 | 934 | 158 | 232 | --- | --- | 15.1 |
| August 1985 | Upstream control | 8.1 | 492 | 197 | 218 | --- | --- | 4.4 |
| | Optimist Park | 8.2 | 796 | 230 | 305 | --- | --- | 17.8 |
| | Morrie Avenue | 8.1 | 797 | 224 | 306 | --- | --- | 18.5 |
| | Refinery | 8.0 | 802 | 223 | 309 | --- | --- | 21.6 |
| | Below NPDES | 7.9 | 895 | 208 | 290 | --- | --- | 24.9 |
| October 1985 | Upstream control | 8.1 | 539 | 224 | 258 | < 0.10 | < 0.01 | 11.2 |
| | Optimist Park | 8.2 | 746 | 243 | 329 | < 0.10 | < 0.01 | 9.4 |
| | Morrie Avenue | 8.1 | 770 | 226 | 227 | < 0.10 | < 0.01 | 11.1 |
| | Refinery | 7.9 | 807 | 247 | 188 | < 0.10 | < 0.01 | 6.9 |
| | Below NPDES | 8.0 | 906 | 220 | 243 | 6.90 | 0.45 | 2.4 |
| December 1985 | Upstream control | 8.0 | 532 | 230 | 200 | < 0.10 | < 0.01 | 2.2 |
| | Optimist Park | 8.0 | 778 | 266 | 180 | 0.17 | 0.01 | 2.6 |
| | Morrie Avenue | 8.0 | 818 | 275 | 205 | 0.21 | 0.01 | 3.2 |
| | Refinery | 8.0 | 865 | 280 | 182 | 0.28 | 0.02 | 3.4 |
| | Below NPDES | 8.0 | 920 | 262 | 228 | 2.50 | 0.16 | 4.6 |
| February 1986 | Upstream control | 8.1 | 453 | 197 | 194 | < 0.10 | < 0.01 | 2.0 |
| | Optimist Park | 8.2 | 607 | 224 | 220 | < 0.10 | < 0.01 | 2.7 |
| | Morrie Avenue | 8.2 | 643 | 234 | 194 | < 0.10 | < 0.01 | 2.9 |
| | Refinery | 8.2 | 662 | 228 | 197 | < 0.10 | < 0.01 | 3.1 |
| | Below NPDES | 8.6 | 710 | 224 | 273 | 4.00 | 0.90 | 4.6 |
| April 1986 | Upstream control | 8.1 | 497 | 209 | 95 | < 0.10 | < 0.01 | 2.6 |
| | Optimist Park | 8.2 | 618 | 235 | 103 | < 0.10 | < 0.01 | 4.2 |
| | Morrie Avenue | 8.1 | 601 | 224 | 106 | < 0.10 | < 0.01 | 4.0 |
| | Refinery | 8.0 | 675 | 232 | 110 | < 0.10 | < 0.01 | 4.5 |
| | Below NPDES | 8.0 | 790 | 217 | 118 | 1.10 | 0.07 | 6.6 |

[a]--- = value not determined.

Table B-5. Concentrations of major inorganic ions in Crow Creek water from June 1985 to April 1986.[a]

| Date | Site | Cations | | | | | | Anions | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $Na^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $K^+$ | $Sr^{2+}$ | $NH_4^+$ | $Cl^-$ | $SO_4^{2-}$ | $NO_3^-$ | $F^-$ | $HCO_3^-$ | $CO_3^{2-}$ |
| June 1985 | Upstream control | 18 | 67 | 4 | 6 | 0.3 | < 0.13 | 7 | 27 | 5.2 | 0.4 | 212 | 1.3 |
| | Optimist Park | 37 | 81 | 6 | 8 | 0.5 | 0.16 | 30 | 46 | 4.7 | 0.9 | 223 | 3.1 |
| | Morrie Avenue | 40 | 80 | 6 | 8 | 0.5 | < 0.13 | 34 | 51 | 4.7 | 0.9 | 218 | 1.9 |
| | Refinery | 42 | 85 | 6 | 9 | 0.5 | < 0.13 | 39 | 57 | 8.7 | 0.9 | 226 | 1.6 |
| | Below NPDES | 68 | 82 | 5 | 16 | 0.5 | 14.79 | 97 | 108 | 5.2 | 5.9 | 197 | 1.0 |
| July 1985 | Upstream control | 16 | 52 | 4 | 6 | 0.3 | ---[b] | 9 | 17 | 1.7 | 1.0 | 161 | 1.3 |
| | Optimist Park | 36 | 81 | 7 | 10 | 0.5 | --- | 37 | 60 | 3.7 | 0.9 | 213 | 3.3 |
| | Morrie Avenue | 40 | 91 | 8 | 9 | 0.4 | --- | 43 | 64 | 4.2 | 0.9 | 213 | 2.4 |
| | Refinery | 40 | 115 | 8 | 9 | 0.5 | --- | 45 | 66 | 7.2 | 0.9 | 220 | 1.1 |
| | Below NPDES | 62 | 107 | 7 | 19 | 0.4 | --- | 94 | 130 | 5.7 | 7.4 | 191 | 0.6 |
| August 1985 | Upstream control | 19 | 103 | 5 | 7 | 0.4 | --- | 10 | 66 | 2.2 | 0.9 | 236 | 1.8 |
| | Optimist Park | 55 | 145 | 8 | 12 | 0.5 | --- | 58 | 93 | 9.2 | 1.0 | 275 | 2.9 |
| | Morrie Avenue | 50 | 145 | 8 | 12 | 0.5 | --- | 51 | 97 | 9.7 | 0.9 | 269 | 2.2 |
| | Refinery | 48 | 146 | 8 | 12 | 0.5 | --- | 46 | 96 | 9.7 | 0.9 | 268 | 1.8 |
| | Below NPDES | 58 | 137 | 8 | 16 | 0.5 | --- | 66 | 109 | 8.2 | 2.9 | 251 | 1.3 |
| October 1985 | Upstream control | 16 | 86 | 14 | 6 | 0.3 | < 0.13 | 12 | 38 | 1.0 | 0.7 | 269 | 2.1 |
| | Optimist Park | 36 | 106 | 20 | 8 | 0.5 | < 0.13 | 39 | 88 | 8.5 | 0.9 | 290 | 3.0 |
| | Morrie Avenue | 38 | 98 | 21 | 9 | 0.5 | < 0.13 | 43 | 93 | 12.5 | 0.9 | 271 | 2.2 |
| | Refinery | 40 | 103 | 22 | 9 | 0.5 | < 0.13 | 47 | 95 | 14.0 | 0.9 | 298 | 1.5 |
| | Below NPDES | 54 | 95 | 20 | 16 | 0.5 | 8.41 | 48 | 117 | 10.5 | 4.3 | 265 | 1.7 |
| December 1985 | Upstream control | 13 | 84 | 11 | 5 | 0.3 | < 0.13 | 11 | 35 | 3.9 | 0.9 | 277 | 1.7 |
| | Optimist Park | 37 | 101 | 19 | 9 | 0.5 | 0.21 | 40 | 93 | 11.9 | 0.9 | 320 | 2.1 |
| | Morrie Avenue | 40 | 112 | 19 | 8 | 0.6 | 0.26 | 49 | 71 | 16.1 | 0.9 | 331 | 2.1 |
| | Refinery | 44 | 117 | 20 | 9 | 0.6 | 0.34 | 56 | 109 | 18.5 | 0.9 | 337 | 2.2 |
| | Below NPDES | 56 | 114 | 19 | 12 | 0.6 | 3.05 | 61 | 123 | 15.7 | 1.8 | 315 | 2.1 |
| February 1986 | Upstream control | 12 | 72 | 10 | 4 | 0.2 | < 0.13 | 9 | 34 | 1.1 | 1.0 | 237 | 1.8 |
| | Optimist Park | 26 | 84 | 14 | 6 | 0.4 | < 0.13 | 28 | 67 | 4.9 | 0.9 | 268 | 2.7 |
| | Morrie Avenue | 29 | 88 | 15 | 7 | 0.4 | < 0.13 | 34 | 75 | 7.2 | 0.9 | 280 | 2.5 |
| | Refinery | 30 | 89 | 15 | 7 | 0.4 | < 0.13 | 36 | 79 | 8.2 | 0.9 | 273 | 2.4 |
| | Below NPDES | 36 | 88 | 15 | 8 | 0.4 | 4.20 | 48 | 93 | 7.7 | 1.4 | 260 | 6.6 |
| April 1986 | Upstream control | 15 | 78 | 11 | 4 | 0.2 | < 0.13 | 10 | 29 | 5.0 | 1.0 | 251 | 1.7 |
| | Optimist Park | 38 | 87 | 17 | 6 | 0.4 | < 0.13 | 34 | 50 | 3.2 | 0.9 | 281 | 2.5 |
| | Morrie Avenue | 39 | 86 | 18 | 6 | 0.4 | < 0.13 | 38 | 57 | 4.6 | 0.9 | 269 | 2.1 |
| | Refinery | 41 | 88 | 18 | 6 | 0.4 | < 0.13 | 42 | 61 | 5.1 | 1.0 | 279 | 1.8 |
| | Below NPDES | 63 | 83 | 17 | 15 | 0.4 | 1.34 | 97 | 86 | 4.2 | 3.1 | 261 | 1.7 |

[a]Values expressed as mg/L.

[b]--- = value not determined.

Table B-6. Concentrations of trace elements in Crow Creek water from June 1985 to April 1986.[a]

| Date | Site | Element | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Al | As | Cd | Cr | Cu | Fe | Hg | Ni | Pb | Se | Zn |
| June 1985 | Upstream control | < 0.1 | < 0.1 | 0.0015 | 0.0027 | < 0.0010 | 0.07 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0017 |
| | Optimist Park | < 0.1 | < 0.1 | 0.0015 | 0.0054 | 0.0032 | 0.05 | < 0.1 | 0.02 | < 0.1 | < 0.1 | 0.0013 |
| | Morrie Avenue | < 0.1 | < 0.1 | 0.0013 | 0.0024 | < 0.0010 | 0.04 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0095 |
| | Refinery | < 0.1 | < 0.1 | 0.0016 | 0.0032 | < 0.0010 | 0.05 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0072 |
| | Below NPDES | < 0.1 | < 0.1 | 0.0018 | 0.0399 | 0.0011 | 0.10 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0085 |
| July 1985 | Upstream control | < 0.1 | < 0.1 | 0.0010 | < 0.0010 | 0.0417 | 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0005 |
| | Optimist Park | 0.1 | < 0.1 | 0.0013 | 0.0019 | < 0.0010 | 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0062 |
| | Morrie Avenue | < 0.1 | < 0.1 | 0.0015 | 0.0030 | < 0.0010 | 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0078 |
| | Refinery | 0.1 | < 0.1 | 0.0020 | 0.0022 | < 0.0010 | 0.02 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0060 |
| | Below NPDES | < 0.1 | < 0.1 | 0.0019 | < 0.0010 | < 0.0010 | 0.03 | < 0.1 | < 0.01 | < 0.1 | 0.1 | 0.0074 |
| August 1985 | Upstream control | 0.1 | < 0.1 | 0.0009 | < 0.0010 | < 0.0010 | < 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0046 |
| | Optimist Park | < 0.1 | < 0.1 | 0.0021 | 0.0032 | 0.0025 | 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0059 |
| | Morrie Avenue | < 0.1 | < 0.1 | 0.0020 | 0.0022 | 0.0016 | 0.02 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0050 |
| | Refinery | < 0.1 | < 0.1 | 0.0014 | 0.0063 | 0.0165 | < 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0099 |
| | Below NPDES | < 0.1 | < 0.1 | 0.0011 | < 0.0010 | 0.0013 | 0.02 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0051 |
| October 1985 | Upstream control | < 0.1 | < 0.1 | 0.0003 | 0.0068 | 0.0025 | < 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0008 |
| | Optimist Park | < 0.1 | < 0.1 | 0.0007 | 0.0075 | 0.0042 | 0.03 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0034 |
| | Morrie Avenue | < 0.1 | < 0.1 | 0.0008 | < 0.0010 | 0.0068 | < 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0088 |
| | Refinery | < 0.1 | < 0.1 | 0.0008 | < 0.0010 | 0.0016 | 0.04 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0014 |
| | Below NPDES | < 0.1 | < 0.1 | 0.0009 | 0.0056 | 0.0056 | 0.03 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0058 |
| December 1985 | Upstream control | < 0.1 | < 0.1 | 0.0005 | < 0.0010 | 0.0016 | < 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0028 |
| | Optimist Park | < 0.1 | < 0.1 | 0.0006 | < 0.0010 | < 0.0010 | < 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0005 |
| | Morrie Avenue | < 0.1 | < 0.1 | 0.0006 | < 0.0010 | 0.0014 | < 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0006 |
| | Refinery | < 0.1 | < 0.1 | 0.0009 | < 0.0010 | 0.0012 | 0.02 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0019 |
| | Below NPDES | < 0.1 | < 0.1 | 0.0010 | 0.0014 | < 0.0010 | < 0.01 | < 0.1 | < 0.01 | 0.1 | < 0.1 | < 0.0001 |
| February 1986 | Upstream control | < 0.1 | < 0.1 | 0.0002 | < 0.0010 | 0.0019 | < 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | < 0.0001 |
| | Optimist Park | < 0.1 | < 0.1 | 0.0005 | < 0.0010 | 0.0053 | < 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0005 |
| | Morrie Avenue | < 0.1 | < 0.1 | 0.0005 | < 0.0010 | 0.0025 | < 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0021 |
| | Refinery | < 0.1 | < 0.1 | 0.0007 | < 0.0010 | 0.0019 | < 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0049 |
| | Below NPDES | < 0.1 | < 0.1 | 0.0009 | 0.0031 | 0.0020 | 0.03 | < 0.1 | < 0.01 | < 0.1 | < 0.1 | 0.0049 |
| April 1986 | Upstream control | < 0.1 | < 0.1 | 0.0004 | < 0.0010 | < 0.0010 | 0.05 | < 0.1 | 0.02 | < 0.1 | < 0.1 | < 0.0001 |
| | Optimist Park | < 0.1 | < 0.1 | 0.0007 | < 0.0010 | < 0.0010 | 0.05 | < 0.1 | 0.02 | < 0.1 | < 0.1 | 0.0007 |
| | Morrie Avenue | < 0.1 | < 0.1 | 0.0006 | < 0.0010 | < 0.0010 | 0.07 | < 0.1 | 0.03 | < 0.1 | < 0.1 | 0.0020 |
| | Refinery | 0.1 | < 0.1 | 0.0008 | < 0.0010 | < 0.0010 | 0.07 | < 0.1 | 0.03 | < 0.1 | < 0.1 | 0.0067 |
| | Below NPDES | < 0.1 | < 0.1 | 0.0008 | < 0.0010 | < 0.0010 | 0.09 | < 0.1 | 0.04 | < 0.1 | < 0.1 | 0.0044 |

[a]Values expressed as mg/L. Al, As, Fe, Hg, Ni, Pb and Se were analyzed by inductively coupled plasma emission spectroscopy (ICP); Cd, Cr, Cu and Zn were analyzed by atomic absorption spectroscopy (detection limits using ICP for these four elements were only 0.01 mg/L).