REPORT TO REGION X

ON THE RESULTS OF

THE SPOKANE RIVER ALGAL ASSAYS

by

Joseph C. Greene, William E. Miller,

and Ellen Merwin

NATIONAL EUTROPHICATION RESEARCH PROGRAM
Corvallis, Oregon

INTRODUCTION

The Spokane River system is beset by three major water pollution problems in the reach from Post Falls, Idaho to Long Lake Dam, Washington. They are: 1) over-enrichment by plant nutrients, 2) presence of toxic materials, and 3) low dissolved oxygen content.

Corrective water quality management practices have been initiated by the Washington State Department of Ecology in cooperation with the state of Idaho and Region X of the U. S. Environmental Protection Agency to maintain and/or obtain Class A water quality standards throughout the Spokane River System--below Post Falls--for both dissolved oxygen (8.0 mg/l) and total coliform content (median of 240--with 20 percent not to exceed 1000). This goal is to be met by upgrading the City of Spokane's sewage treatment plant (STP) from primary to secondary level treatment. While secondary treatment would enable compliance with the Class A dissolved oxygen and total coliform criteria it would not solve the nutrient over-enrichment problem which exists downstream from the STP.

Assessment of the nutrient over-enrichment problem in the Spokane River Basin is complicated by the occurrence of heavy metals (predominantly zinc) in the upper reaches of the Coeur d' Alene Lake watershed. Most of the zinc entering the Spokane drainage basin is from mining and smeltering wastewater effluents or is leached from mine tailings. Zinc

is found in the surface and ground waters confluent to the South and to some extent the North Fork of Coeur d' Alene River. Proposed and existing smelter wastewater treatment measures are currently being upgraded and implemented by the Bunker Hill Mining Company in an effort to solve the existing pollution problems.

The impact of the proposed municipal and industrial wastewater treatment measures upon the growth of algae in the Spokane River System has been under considerable debate.

At the request of Region X of EPA, algal assays were conducted on seven Spokane River Basin samples by the National Eutrophication Research Program at the Pacific Northwest Environmental Research Laboratory, National Environmental Reseach Center, Corvallis, Oregon, to determine the following: 1) the algistatic concentration of zinc that would prevent the growth of planktonic algae, 2) the nutritional--phosphorus and nitrogen--status of the Spokane River System, and 3) the critical nutrient responsible for the support of algal growth within the Spokane River System.

METHODOLOGY

The "Algal Assay Procedure, (AAP) Bottle Test" August, 1971, using Selenastrum capricornutum Prinz as the test alga, was used to assess the algal growth response of the Spokane River samples. Prior to assaying the Spokane River samples were autoclaved to solubilize the nutrients tied up in the indigenous biomass, carbonated with a mixture of 1 percent CO_2 in air until the original pH was obtained, and filtered through a

0.45μ porosity membrane filter to remove particulate material which would interfere with electronic particle measurement of algal biomass in the inoculated test samples. Results of the algal assay are reported as the maximum yield, in mg dry weight/l, of the test alga obtained during a 14 day incubation period.

DISCUSSION AND RESULTS

The growth response of S. capricornutum to known levels (0.0 to 186.0 μg/l) of available phosphorus with and without the addition of selected concentration levels of zinc (20, 40 and 100 μg/l) was evaluated. The results indicate that, in the presence of all other essential nutrients, the addition of one μg ortho-P/l will support 0.43 mg dry weight/l of test alga in waters containing > 10 μg P/l. A natural water containing 15 μg P/l supported up to 6.4 mg dry weight/l of S. capricornutum, providing sufficient nutrients other than phosphorus were available in sufficient quantity.

Three levels of zinc (20, 40 and 100 μg/l were added to AAP culture medium containing varying amounts of phosphorus ranging from 10-186 μg P/l. In general, the algistatic effect of zinc decreased as phosphorus content increased. Table 1 shows 20 μg Zn/l to be algistatic in waters contining less than 10 μg P/l. Zinc concentrations of 40 and 100 μg/l inhibited algal growth in waters containing 46 and 93 μg P/l respectively. Table 1 also shows the percentage of algal growth inhibition of the three zinc concentration levels in waters containing 10 to 186 μg P/l. Twenty μg Zn/l decreased algal growth from

Table 1. EFFECT OF ZINC UPON 14 DAY MAXIMUM YIELDS OF SELENASTRUM CAPRICORNUTUM

ug/l Phosphorus Content	14 Day* Maximum Yield	Zinc Depression (mg dry weight/l)					
		20 ug/l	Percent Inhibition	40 ug/l	Percent Inhibition	100 ug/l	Percent Inhibition
10	<0.10	<0.10	100	0.10	100	0.10	100
12	5.16	3.00	58	5.16	100	5.16	100
23	9.89	3.00	30	9.49	96	9.89	100
46	19.78	3.00	15	15.78	80	19.78	100
93	39.99	0.00**	0	8.99	22	39.99	100
186	79.98	0.00**	0	6.98	9	77.48	97

*mg dry weight/l. **This concentration of zinc has been shown to be stimulatory.

9.89 mg dry weight/l to 6.89 mg dry weight/l or 30 percent in waters containing 23 µg P/l. These data indicate the sensitivity of S. capricornutum to phosphorus and zinc concentrations normally found within the waters of the Spokane River Basin. As a result, another study was undertaken to define the problems of nutrient over-enrichment and the presence of toxic materials in the Spokane River System.

Seven sampling sites (Figure 1) were chosen in the Spokane River Basin which represented varying types of water quality with respect to both nutrients and the presence of toxic materials. The South Fork Coeur d' Alene River at Mullan, Idaho is a low nutrient high quality water, uncontaminated by mine waste discharge. An autoclaved and filtered, sample collected in November 1972, contained 7 µg orthophosphorus/l, 3 µg total soluble inorganic nitrogen/l (NO_2+NO_3+NH_3) and 18 µg Zn/l. The orthophosphorus content indicated that, theoretically, it would support algal growth in an amount not greater than 0.10 mg dry weight/l (Table 1). The actual algal yield in the sample was 0.03 mg dry weight/l (Figure 2). The addition of 20 µg P/l to the sample produced 0.31 mg dry weight/l of S. capricornutum. The predicted algal yield for this phosphorus concentration (27 µg P/l) in the presence of all other essential nutrients was 11.6 mg dry weight/l of the test alga (27 x 0.43). The failure of the test water to support this amount of algal growth indicated that the South Fork of the Coeur d' Alene River may become limited by other essential nutrients when sufficient phosphorus is added to the test water. The addition of 1000 µg N/l and 20 µg P/l

FIGURE 1. Identification of Sampling Sites for the Spokane River Basin Survey

1. So. Fork Coeur d' Alene at Mullan, Id.
2. So. Fork Coeur d' Alene at Smelterville, Idaho
3. Coeur d' Alene River at Lane, Id.
4. Coeur d' Alene Lake at Driftwood Point, Idaho
5. Spokane River at Post Falls, Id.
6. Spokane River at Seven Mile Road Bridge, Washington
7. Spokane River at Long Lake Dam, Washington

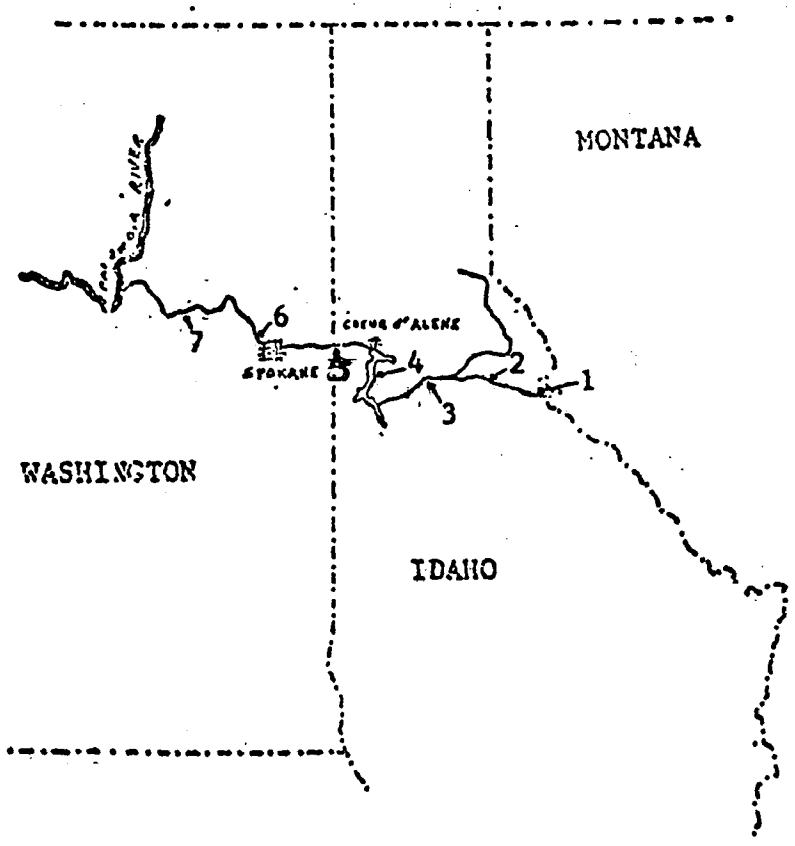
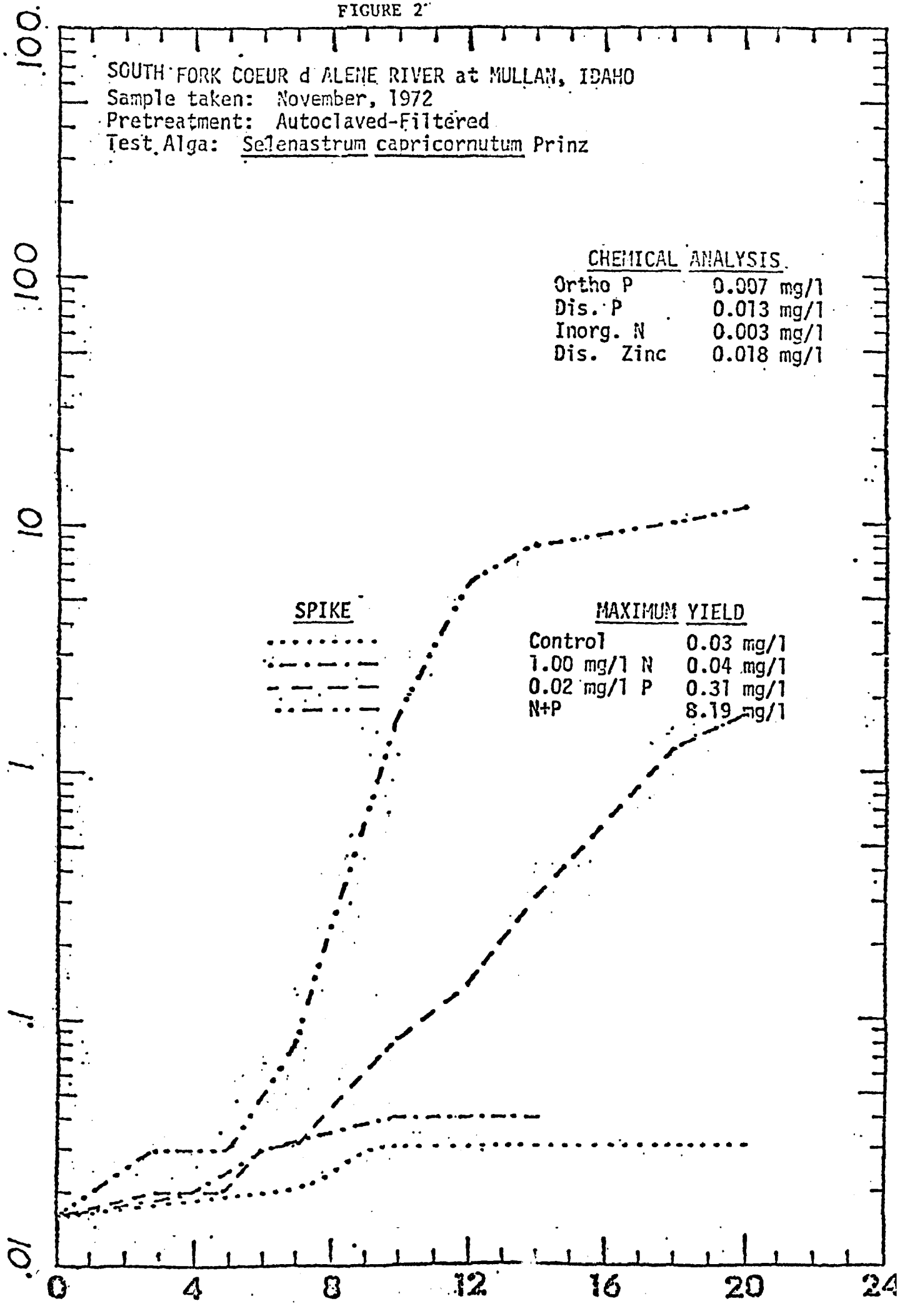


FIGURE 2


SOUTH FORK COEUR d ALENE RIVER at MULLAN, IDAHO
Sample taken: November, 1972
Pretreatment: Autoclaved-Filtered
Test Alga: Selenastrum capricornutum Prinz
CHEMICAL ANALYSIS
Ortho P 0.007 mg/l
Dis. P 0.013 mg/l
Inorg. N 0.003 mg/l
Dis. Zinc 0.018 mg/l
SPIKE
MAXIMUM YIELD
Control 0.03 mg/l
1.00 mg/l N 0.04 mg/l
0.02 mg/l P 0.31 mg/l
N+P 8.19 mg/l
100
10
1
.1
.01
0
4
8
12
16
20
24

increased algal growth to 8.2 mg dry weight/l or 71 percent of the expected yield of 11.6 mg dry weight/l. This indicates that when the nitrogen and phosphorus requirements for algal growth are satisfied either other essential nutrients or the presence of toxic materials limits maximum algal growth in the test water. A concentration of 20 µg Zn/l added to waters containing less than 20 µg P/l reduced the algal yield approximately 3.0 mg dry weight/l (Table 1). The actual yield of 8.2 mg dry weight/l plus the 3.0 mg dry weight/l lost due to zinc toxicity was equal to 11.2 mg dry weight/l or 97 percent of the expected theoretical yield when nitrogen and phosphorus were added to the South Fork Coeur d' Alene River water sample. This suggests that a concentration level of 20 µg Zn/l may inhibit planktonic algal growth in waters containing less than 10 µg P/l.

The Coeur d' Alene Lake watershed is the main contributor of zinc to the Spokane River, contributing about 83 percent of the total load during September 1972 low flow conditions. Samples collected at the South Fork of the Coeur d' Alene River at Smeltersville, the Coeur d' Alene River at Lane and Coeur d' Alene Lake (off Driftwood Point) in November 1972 contained concentrations of dissolved zinc ranging from 7500 µg/l at Smeltersville to 118 µg/l off Driftwood Point. The algal assay growth responses (Figures 3, 4 and 5) of these waters reflects the toxicity of zinc upon the growth of S. capricornutum. Each of these autoclaved and filtered test waters supported less than 0.10 mg dry weight/l of the test alga. This growth response was

Figure 3

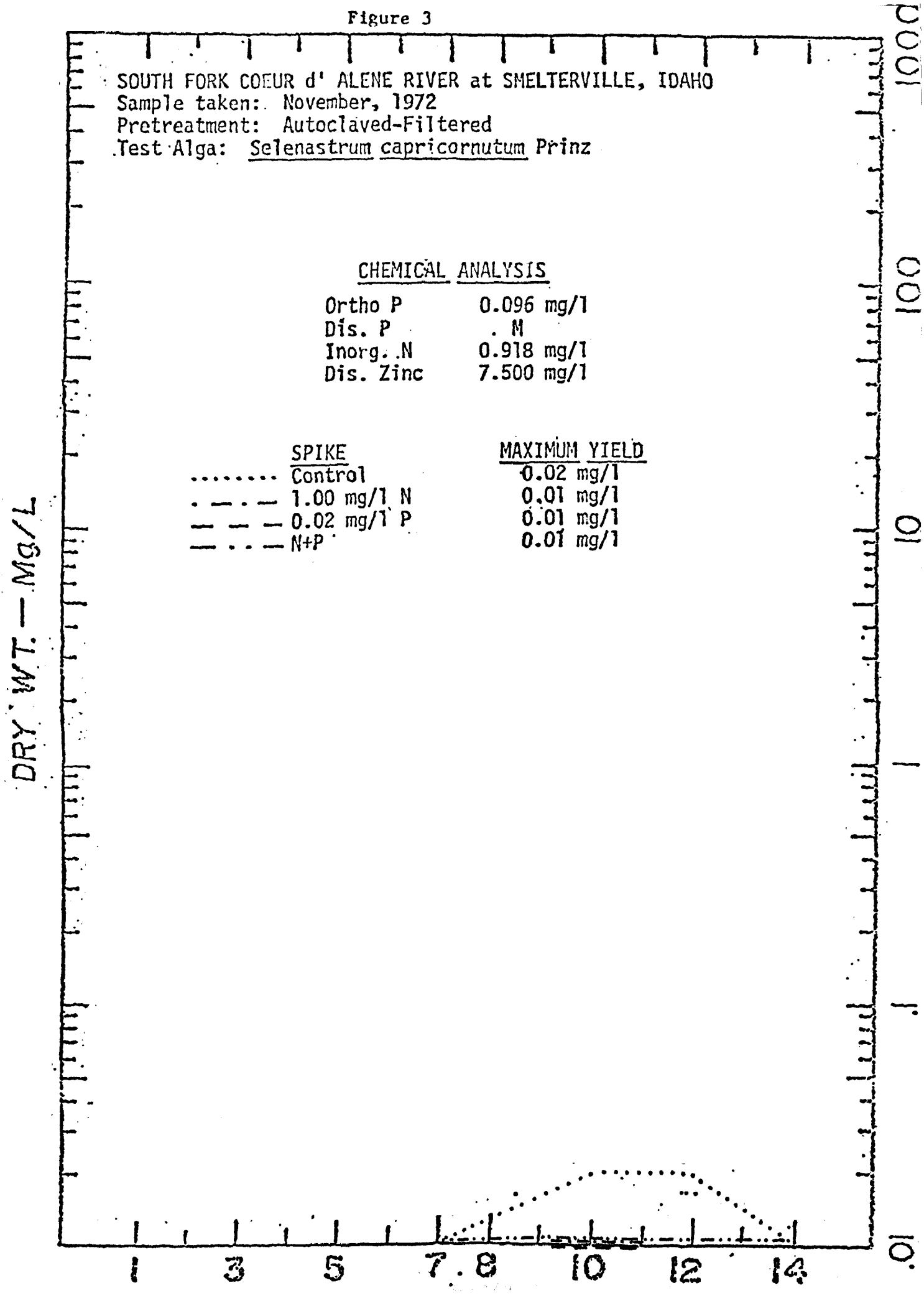

SOUTH FORK COEUR d' ALENE RIVER at SMELTERVILLE, IDAHO
Sample taken: November, 1972
Pretreatment: Autoclaved-Filtered
Test Alga: Selenastrum capricornutum Prinz
CHEMICAL ANALYSIS
Ortho P 0.096 mg/l
Dis. P . M
Inorg. N 0.918 mg/l
Dis. Zinc 7.500 mg/l
SPIKE
Control
1.00 mg/l N
0.02 mg/l P
N+P
MAXIMUM YIELD
0.02 mg/l
0.01 mg/l
0.01 mg/l
0.01 mg/l
DRY WT. — Mg/L
1000
100
10
1
.1
.01
1
3
5
7.8
10
12
14

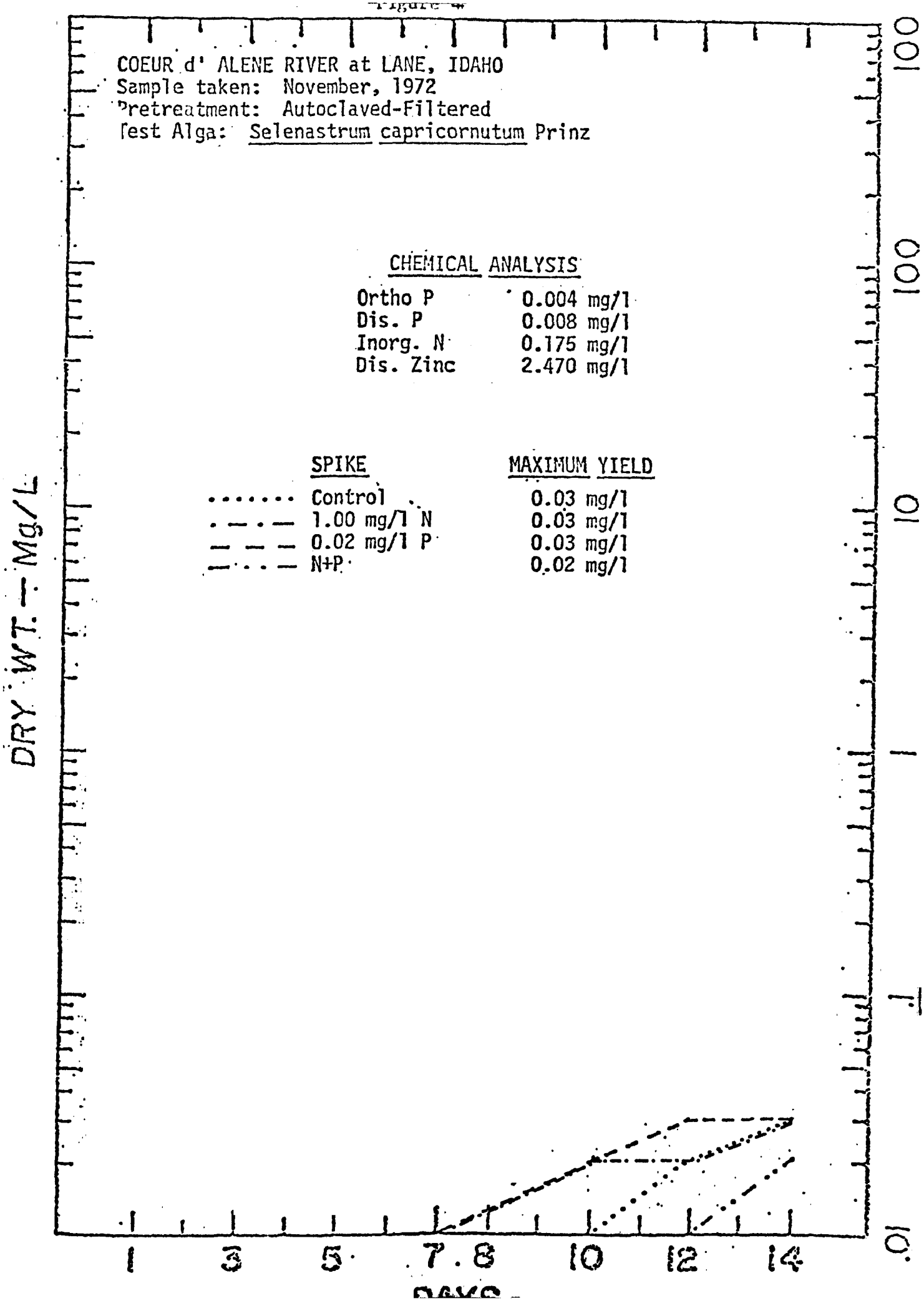
Figure 4

COEUR d' ALENE RIVER at LANE, IDAHO
Sample taken: November, 1972
Pretreatment: Autoclaved-Filtered
Test Alga: Selenastrum capricornutum Prinz

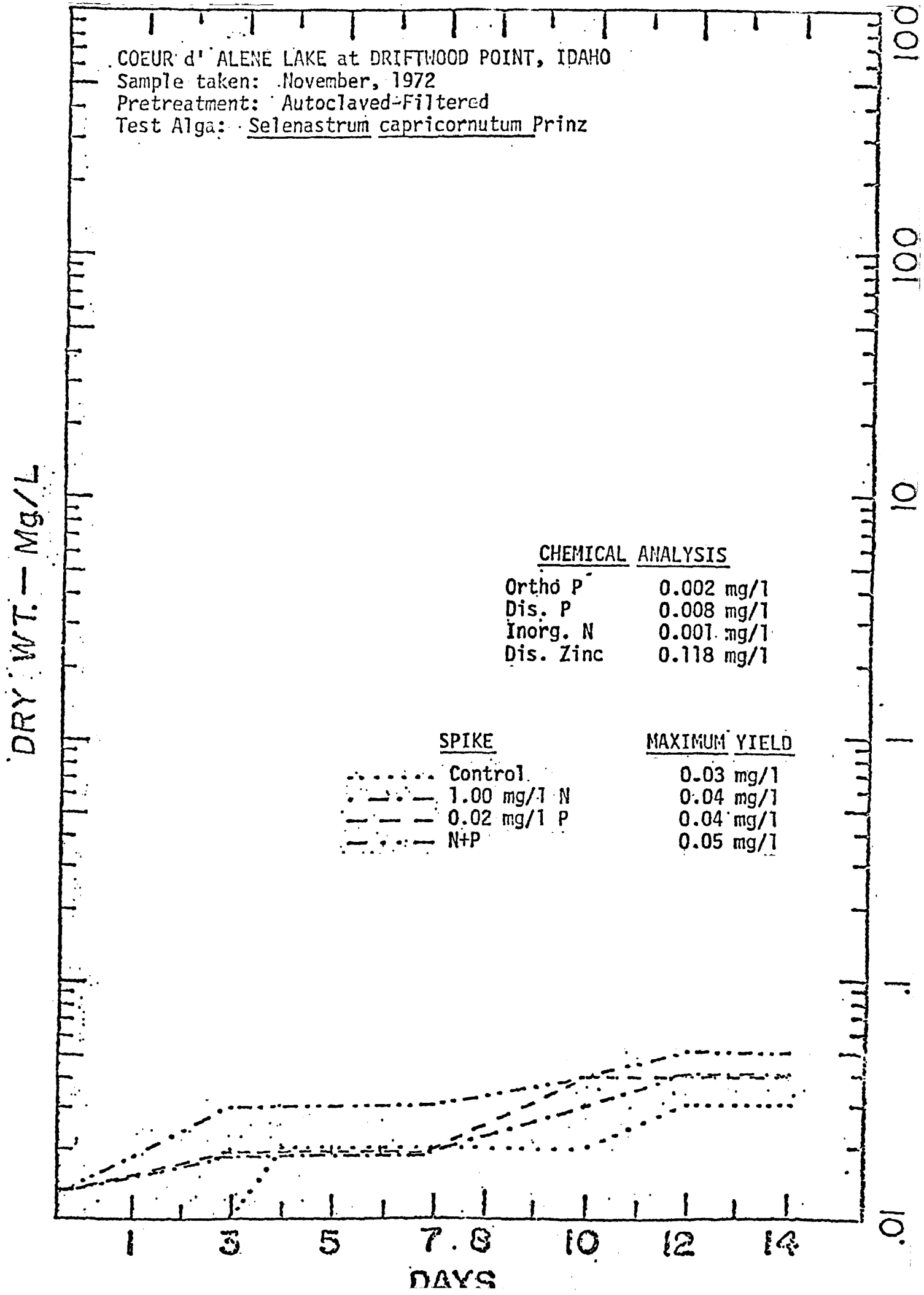
CHEMICAL ANALYSIS

Ortho P	0.004 mg/l
Dis. P	0.008 mg/l
Inorg. N	0.175 mg/l
Dis. Zinc	2.470 mg/l

SPIKE	MAXIMUM YIELD
..... Control	0.03 mg/l
. — . — 1.00 mg/l N	0.03 mg/l
— — — 0.02 mg/l P	0.03 mg/l
— . . — N+P	0.02 mg/l



COEUR d' ALENE LAKE at DRIFTWOOD POINT, IDAHO
Sample taken: November, 1972
Pretreatment: Autoclaved-Filtered
Test Alga: Selenastrum capricornutum Prinz



CHEMICAL ANALYSIS

Ortho P	0.002 mg/l
Dis. P	0.008 mg/l
Inorg. N	0.001 mg/l
Dis. Zinc	0.118 mg/l

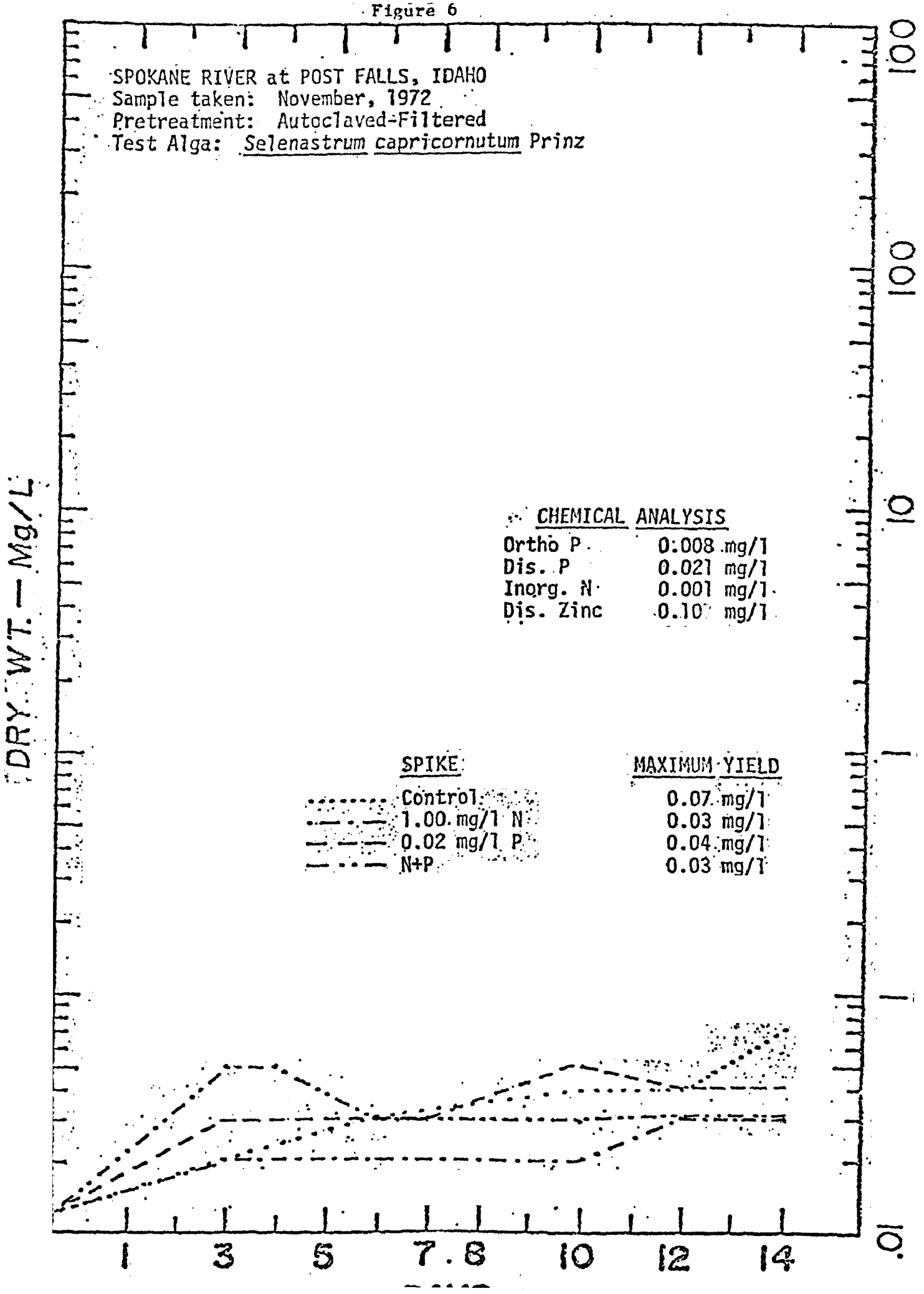
SPIKE	MAXIMUM YIELD
Control	0.03 mg/l
1.00 mg/l N	0.04 mg/l
0.02 mg/l P	0.04 mg/l
N+P	0.05 mg/l

within the anticipated yield based on the orthophosphorus content in the samples collected at the Coeur d' Alene River at Lane and at Coeur d' Alene Lake (off Driftwood Point). The South Fork of the Coeur d' Alene River sample collected at Smeltersville contained 96 µg P/l. This concentration of phosphorus, in the presence of all other essential nutrients and in the absence of toxic materials should have supported 41.3 mg dry weight/l of S. capricornutum. Miller, Maloney and Greene, 1973 reported the following classification index, based on the 14 day maximum yield (mg dry weight/l) of S. capricornutum obtained in 49 autoclaved and filtered lake water samples.

ALGAL PRODUCTIVITY CLASSIFICATION	DAY 14 MAXIMUM YIELD
Low Productivity	0.00 to 0.10
Moderate Productivity	0.11 to 0.80
Moderately High Productivity	0.81 to 6.00
High Productivity	>6.00

The theoretical (96 x 0.43) 41.3 mg dry weight/l maximum yield calculated for the South Fork of the Coeur d' Alene River at Smeltersville indicates that this water could have a high phytoplankton growth potential if its zinc content of 7500 µg Zn/l was reduced below the algistatic level. An abundance of periphytic algal growth was observed in the river during the November, 1972, sampling. This suggests that periphyton may have a greater tolerance to high concentrations of zinc than phytoplankton.

Figure 6


SPOKANE RIVER at POST FALLS, IDAHO
Sample taken: November, 1972
Pretreatment: Autoclaved-Filtered
Test Alga: Selenastrum capricornutum Prinz
CHEMICAL ANALYSIS
Ortho P 0.008 mg/l
Dis. P 0.021 mg/l
Inorg. N 0.001 mg/l
Dis. Zinc 0.10 mg/l
SPIKE
MAXIMUM YIELD
Control 0.07 mg/l
1.00 mg/l N 0.03 mg/l
0.02 mg/l P 0.04 mg/l
N+P 0.03 mg/l
DRY WT. — Mg/L
100
10
1
.01
1
3
5
7.8
10
12
14

The autoclaved and filtered (November, 1972) water sample collected from the Spokane River at Post Falls contained 8 µg P/l, 1 µg total soluble inorganic nitrogen/l and 107 µg Zn/l. The nitrogen and phosphorus nutrient content of this water is essentially the same as that found in the autoclaved and filtered Coeur d' Alene Lake (off Driftwood Point) water sample. Water collected at both sampling sites exhibited similar algal growth response to the addition of nitrogen and phosphorus (Figures 5 and 6). The average dissolved zinc (112 µg/l) in these water samples would mask the effect of additional phosphorus loading, up to 25 times (200 µg P/l) greater than that presently found, upon the growth of planktonic algae. Dissolved zinc concentrations of 96 µg/l within waters containing up to 186 µg P/l have been shown to be algistatic (Greene and Miller, 1973). This suggests that zinc toxicity may be the predominate growth limiting factor for planktonic algae in the Spokane River between Post Falls and Nine Mile Bridge.

The Spokane River samples collected at Riverside State Park and Seven Mile Road bridge reflect the nutrient loading of the City of Spokane's sewage treatment plant (STP). The Spokane STP is the major contributor of phosphorus to the Spokane River. Cunningham and Pine (1969) cite an increase from 265 kg orthophosphorus/day (120 lb/day) in the upstream water to 6836 kg/day (3100 lb/day) immediately downstream from the STP. This is approximately a 26-fold increase of orthophosphorus in the receiving water. In September 1972 the Spokane STP contributed 57 percent of the total phosphorus loading to the Spokane River (EPA Region X Report, Feb., 1973). The maximum 14 day algal yield obtained in the

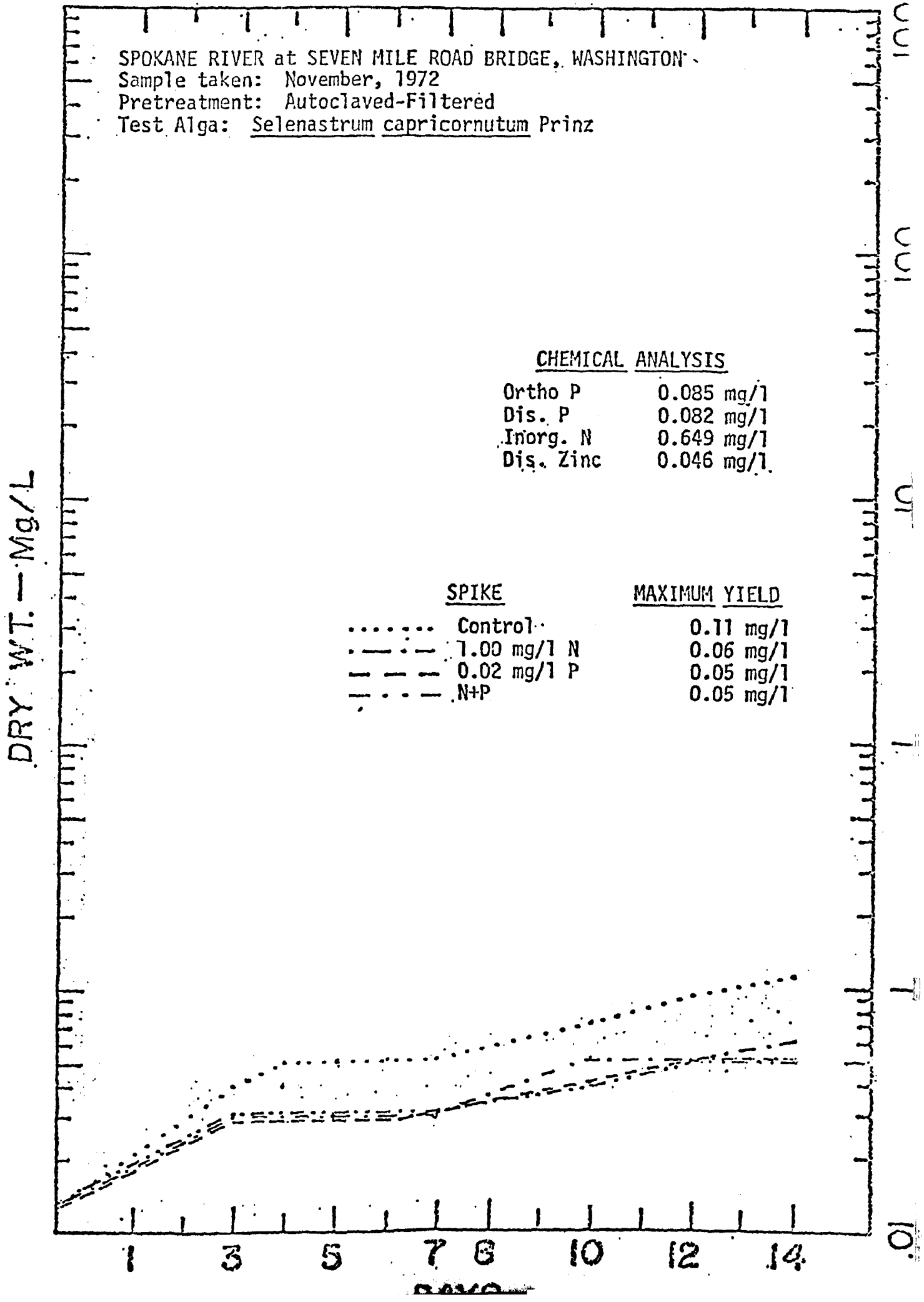
November 1972 autoclaved and filtered Spokane River at Seven Mile Road Bridge water sample was 0.11 mg dry weight/l of S. capricornutum (Figure 7). This was 0.3 percent of the theoretical yield of 36.6 mg dry weight/l that could be supported by 85 µg P/l. The predicted yield for this phosphorus level is valid when either no toxicant is present in the water or when other nutrients are not growth limiting. The November 1972 Seven Mile Road Bridge sample contained 46 µg/l of dissolved zinc. This level of zinc could limit algal growth greater than 95 percent in a water sample containing 85 µg P/l. Figure 8 shows the effect of removing the 46 µg Zn/l from the Seven Mile Road Bridge Sample (by cation exchange) upon the growth of the test algae. The algal growth yield on this treated Sample was increased to 15.4 mg dry weight/l and represented an approximate 160-fold increase in algal growth. Adding 40 and 100 µg Zn/l back to the metal stripped sample again inhibited algal growth. This reinforces the hypothesis that "upstream zinc levels mask the nutritional impact of the City of Spokane STP phosphorus loading to the Spokane River upon the growth of planktonic algae." Natural degradation and/or complexing of zinc by organic compounds reduced the concentration of zinc, which was greater than 100 µg Zn/l immediately downstream from the STP to less than 20 µg Zn/l in the November 1972 Long Lake Dam water sample. The effect of reduced zinc concentration in the water at Long Lake Dam upon the growth of S. capricornutum in the autoclaved and filtered samples collected in November 1972 is shown in Figure 9. The maximum yield obtained in this sample was 14.9 mg dry weight/l. The theoretical

SPOKANE RIVER at SEVEN MILE ROAD BRIDGE, WASHINGTON
Sample taken: November, 1972
Pretreatment: Autoclaved-Filtered
Test Alga: Selenastrum capricornutum Prinz

CHEMICAL ANALYSIS

Ortho P	0.085 mg/l
Dis. P	0.082 mg/l
Inorg. N	0.649 mg/l
Dis. Zinc	0.046 mg/l

SPIKE	MAXIMUM YIELD
..... Control	0.11 mg/l
.—.— 1.00 mg/l N	0.06 mg/l
— — — 0.02 mg/l P	0.05 mg/l
—.—.— N+P	0.05 mg/l



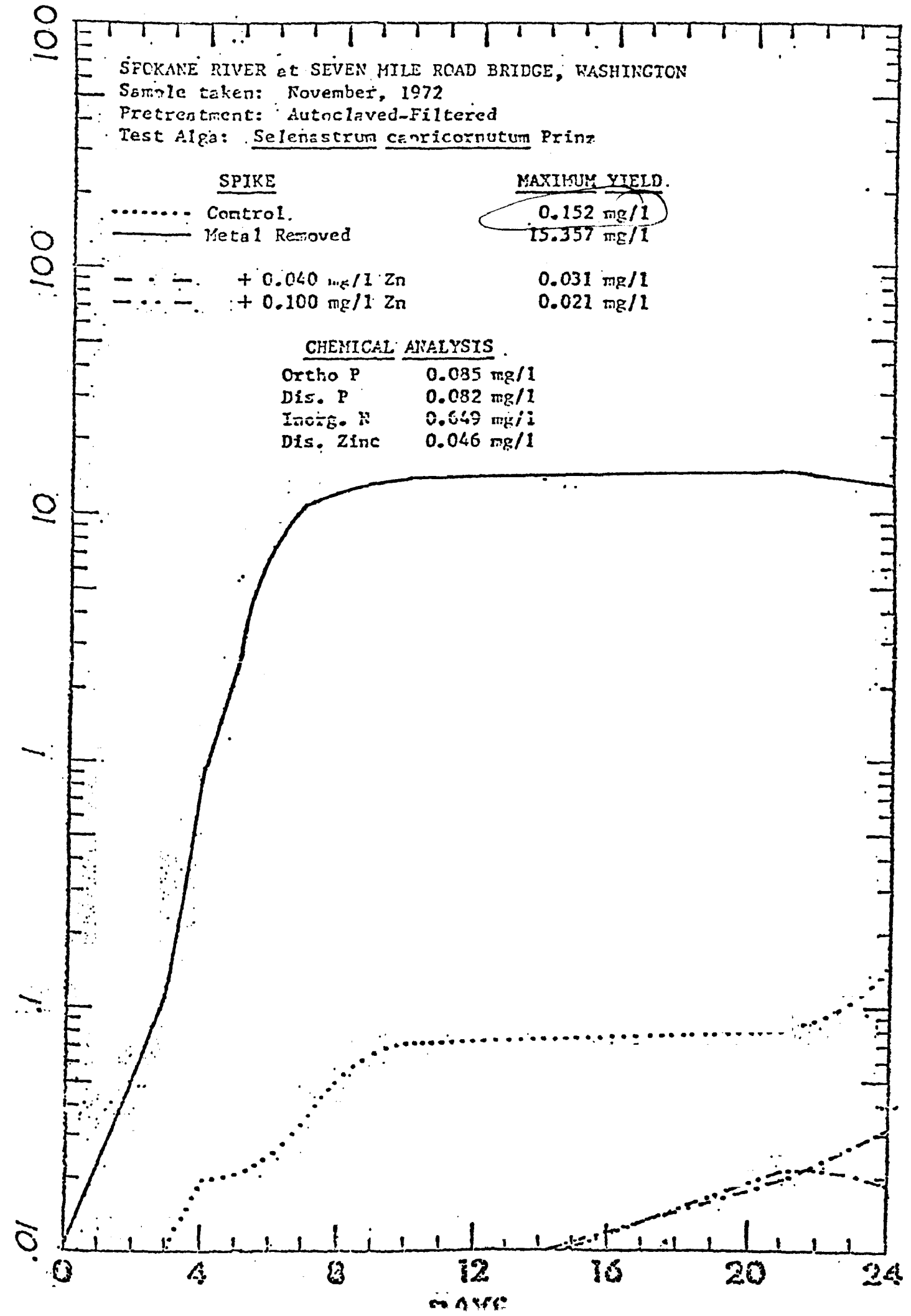
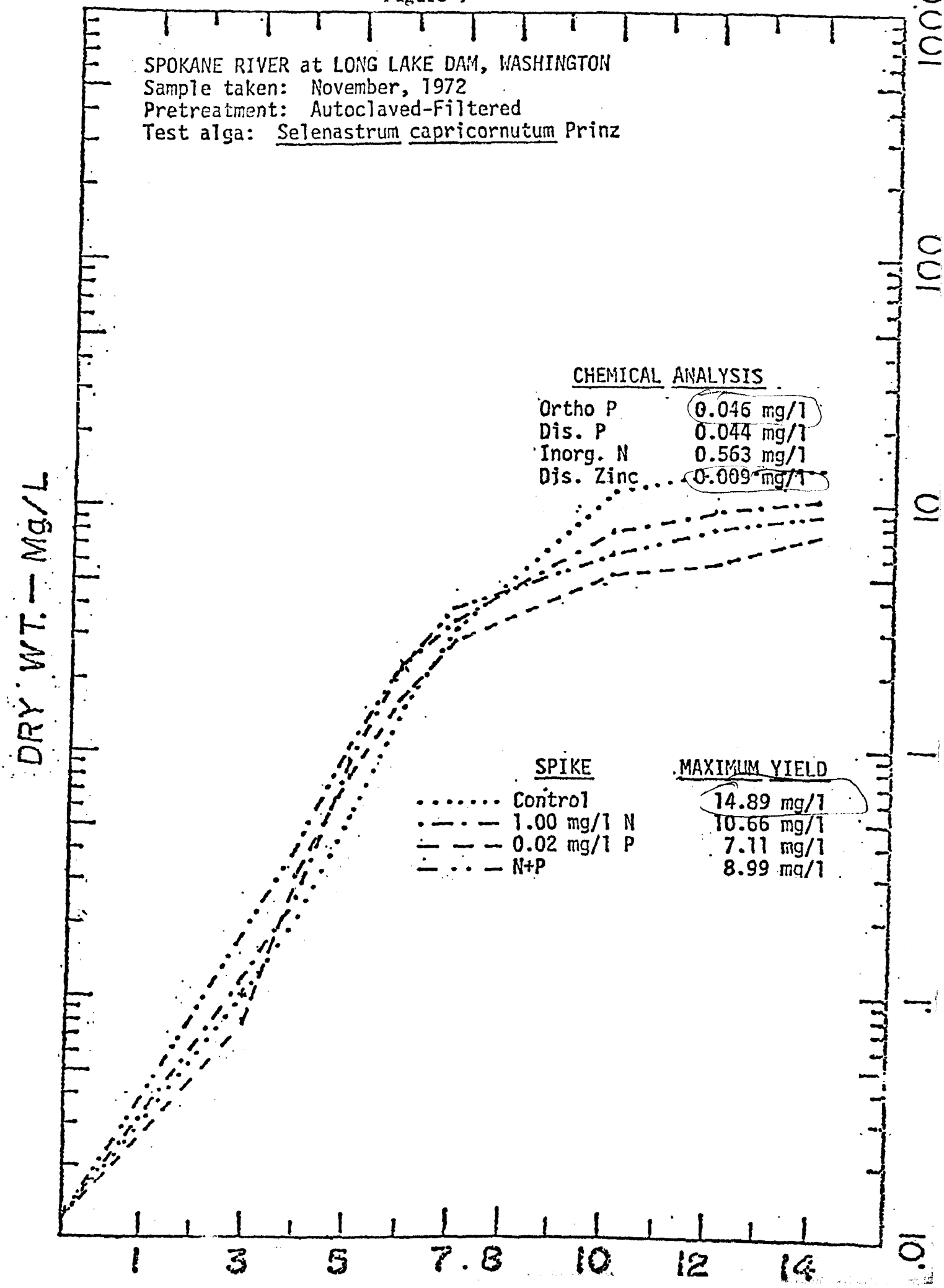

SPOKANE RIVER at SEVEN MILE ROAD BRIDGE, WASHINGTON
Sample taken: November, 1972
Pretreatment: Autoclaved-Filtered
Test Alga: Selenastrum capricornutum Printz
SPIKE
MAXIMUM YIELD
Control.
0.152 mg/l
Metal Removed
15.357 mg/l
+ 0.040 mg/l Zn
0.031 mg/l
+ 0.100 mg/l Zn
0.021 mg/l
CHEMICAL ANALYSIS
Ortho P 0.085 mg/l
Dis. P 0.082 mg/l
Inorg. N 0.649 mg/l
Dis. Zinc 0.046 mg/l
100
10
1
.1
.01
0
4
8
12
16
20
24

Figure 9


SPOKANE RIVER at LONG LAKE DAM, WASHINGTON
Sample taken: November, 1972
Pretreatment: Autoclaved-Filtered
Test alga: Selenastrum capricornutum Prinz
CHEMICAL ANALYSIS
Ortho P 0.046 mg/l
Dis. P 0.044 mg/l
Inorg. N 0.563 mg/l
Dis. Zinc 0.009 mg/l
SPIKE
MAXIMUM YIELD
Control 14.89 mg/l
1.00 mg/l N 10.66 mg/l
0.02 mg/l P 7.11 mg/l
N+P 8.99 mg/l
DRY WT. — Mg/L
1000
100
10
1
.1
.01
1
3
5
7.8
10
12
14

yield, based on the orthophosphorus content of 46 µg P/l, is 19.8 mg dry weight/l. The lower than anticipated growth response to the addition of nitrogen and phosphorus indicates that either some essential nutrient other than phosphorus, may be limiting maximum algal growth or that a toxic substance, other than zinc, may be present in this water. However, a growth response of 14.9 mg dry weight/l of S. capricornutum in the algal assay indicates that Long Lake Dam is a highly productive body of water.

SUMMARY AND CONCLUSIONS

(1) Assessment of the nutrient enrichment problem in the Spokane River Basin is complicated by the occurrence of heavy metals (predominantly zinc) in the upper reaches of the Coeur d' Alene Lake watershed.

(2) The Coeur d' Alene Lake watershed is the main contributor of zinc to the Spokane River, contributing about 83 percent of the zinc load during September 1972 low flow conditions.

(3) Twenty µg zinc/l is algistatic for the growth of planktonic algae in waters containing less than 10 µg P/l.

(4) The city of Spokane's sewage treatment plant is the main contributor of phosphorus to the Spokane River, contributing 57 percent during September 1972 low flow conditions.

(5) The average dissolved zinc concentration of 112 µg/l in the Spokane River from Post Falls, Idaho to Riverside State Park, Washington would mask the effect of the addition of 200 µg P/l to these waters upon the growth of planktonic algae.

(6) The natural degradation of zinc from 100 µg/l to 20 µg/l downstream from the Spokane sewage treatment plant to Long Lake Dam enabled algal growth to increase proportionally to the orthophosphorus content of the water.

(7) Forty µg Zinc/l is 100 percent inhibitory (algicidal) in waters containing 20 µg P/l; 22 percent inhibitory (algistatic) in waters containing 93 µg P/l; and 9 percent inhibitory to planktonic algal growth in waters containing 186 µg P/l.

(8) Because of the high contribution of phosphorus from the City of Spokane's sewage treatment plant, it would be expected that eutrophication problems would result if the zinc content of the water was lowered considerably.