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*Evaluation of Sources and Toxicity of
Copper and Zinc in the Boulder River Drainage
Jefferson County — 1985*

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and

Kurt Hill

April, 1986

Pollution Control Information Series

Technical Report

No. 4

Jefferson Co.

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copper and zinc in the Boulder River drainage,
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by:

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INTRODUCTION

Over the last fifteen years there have been several assessments of sources of metals to the Boulder River drainage and of the impacts of metals on the Boulder River (Braico and Botz 1974; Vincent 1975; Nelson 1976; Gardner 1977; Pedersen 1977). Generally, this earlier work indicated that fish populations declined significantly downstream of the town of Basin and below Cataract and Basin creeks and that numbers were further reduced downstream of High Ore Creek.

Knudson (1984) summarized the information collected up to that time and offered several suggestions for reclamation. He concluded that High Ore Creek was the major source of metals to the Boulder and that diffuse tailings near the Comet Mine were the primary problem. Knudson (1984) concluded that reclamation efforts would be most productive in this portion of the drainage.

Our examination of the Knudson report indicated several possible sources of error in reaching this conclusion. First, the data that was available to Knudson did not include equal numbers of samples taken from each location nor was the timing of sampling similar at each site. This inconsistency made it difficult to compare average concentrations between sites because metals concentrations vary depending on the season of sampling. Secondly, stream discharge records were not available for the dates when the metals samples were taken; hence there was no means of quantifying the amounts of metals entering the Boulder from each of the tributaries. Thirdly, the most recent data summarized by Knudson (1984) were collected nearly ten years ago. Conceivably, the sources and distribution of metals have changed over that time.

Accordingly, we initiated a monitoring program in the spring of 1985 to gain more current information on the sources of metals in the drainage. This data should help us in our consideration of options for using mitigation funds that are being provided by the Montana Highway Department to compensate for fishery habitat losses that occurred during Interstate 15 construction.

MATERIALS AND METHODS

Fourteen stations on the Boulder River and its mainstem tributaries were sampled weekly from the first week in May through the first week in July, 1985 (Fig. 1). Sampling was conducted to bracket the run-off period because previous work indicated that metals concentrations are highest during this time. Two sampling sites were established on High Ore Creek -- one near the mouth and a second several miles upstream and immediately downstream of the Comet Mine. This allowed us to assess whether metals in High Ore Creek originate primarily from the Comet tailings or if additional metals are being picked up in lower reaches of the stream channel.

Parameters measured in the field included pH (with a Corning model 620 pH meter), alkalinity (by titration with 0.020 N sulfuric acid and using bromocresol green, methyl red indicator), hardness (by titration with 0.01 N EDTA and using Hach Man Ver-2 indicator powder pillows), and stream discharge with a Marsh McDirney model 201 portable water current meter.

Grab samples were collected at each station for subsequent analyses of total recoverable copper and zinc. Metals analyses were performed by the Chemistry Laboratory Bureau, Montana Department of Health and Environmental Sciences, using atomic emission spectroscopy; certified Environmental Protection Agency procedures were employed (USEPA 1983).

Instantaneous copper and zinc loading (kg/day) were calculated for a given location and date by multiplying stream discharge by the measured metal concentrations.

Figure 1

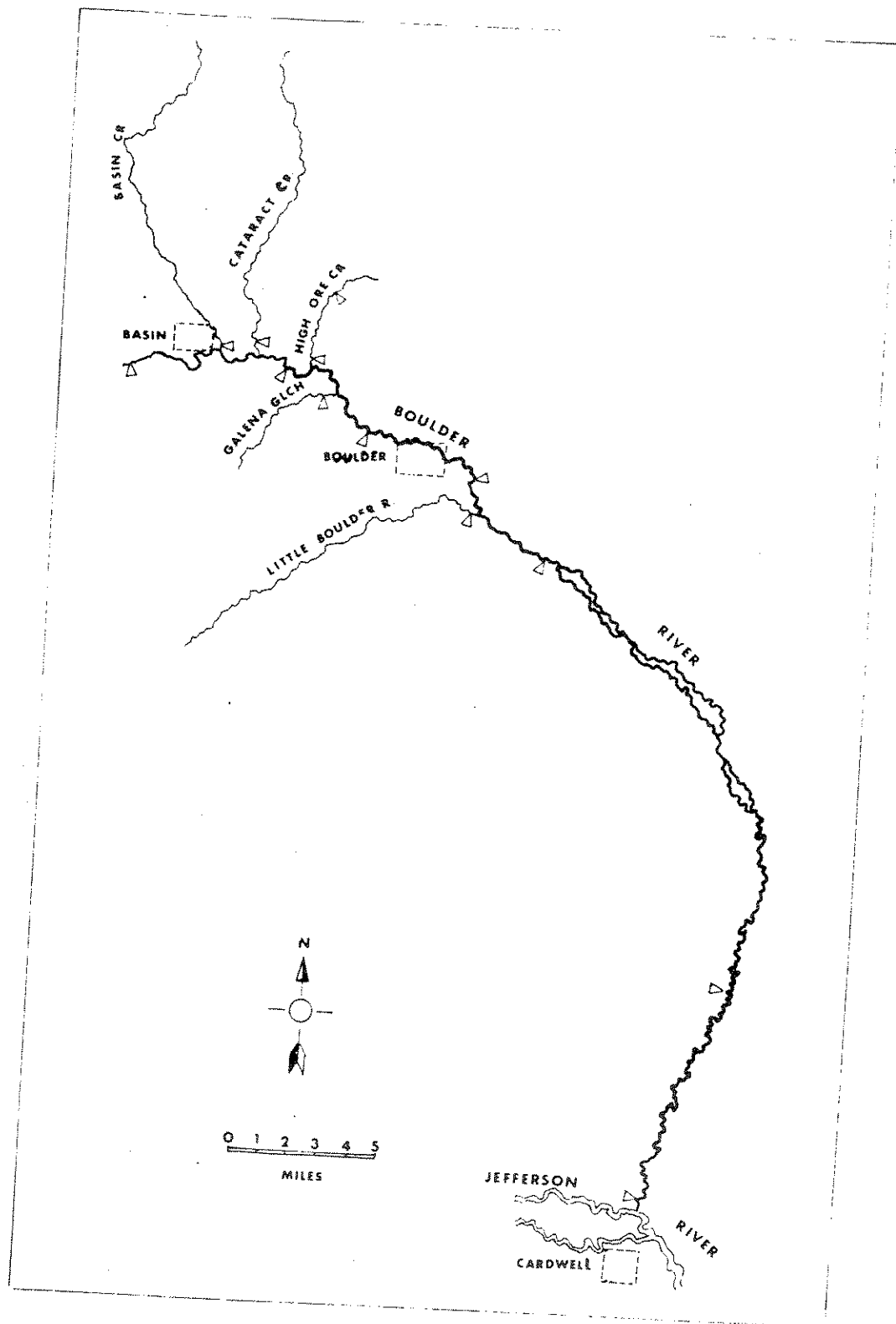


Figure 1. Map of the Boulder River drainage; arrows indicate water sampling stations.

RESULTS

Alkalinity, Hardness and pH

The five tributaries to the Boulder River that were sampled during this investigation have different water quality characteristics. Both Galena Gulch and High Ore Creek have relatively hard and alkaline water while Basin and Cataract creeks and the Little Boulder River have relatively soft waters that are low in alkalinity (Table 1). Expectedly, the less alkaline waters were also lower in pH. Both High Ore Creek and Galena Gulch Creek flow through limestone deposits whereas the remaining streams flow through the granitic materials that are characteristic of the Boulder Batholith.

Alkalinity, hardness, and pH in the mainstem of the Boulder River tended to increase from the upstream station near Basin to the mouth (Table 1). Over that distance, mean alkalinity (as CaCO_3) and hardness (as CaCO_3) both approximately tripled in concentration from near 30 mg/l to approximately 90 mg/l. The greatest increase was at the two stations nearest the mouth. Similarly, mean pH increased from approximately 7.5 to 8.0 units over the reach that was sampled. At a given site, the tendency was for all three parameters to increase during low flow periods and decrease during high flow conditions.

Stream Discharge

During the runoff season, stream flow in the Boulder River approximately doubled between the town of Basin and the USGS gauging station located immediately downstream of the town of Boulder (Fig. 2). Most of the increase in flow was

Table 1. Alkalinity, hardness and pH at several locations in the Boulder River drainage.

| Location | n | Total alkalinity mg/l as CaCO_3 | | | Hardness mg/l as CaCO_3 | | | pH | | |
|--------------------------------------|----|---|--------|-----|-------------------------------------|--------|-----|------|---------|------|
| | | mean | range | SD | mean | range | SD | mean | range | SD |
| Mainstem Boulder River | | | | | | | | | | |
| Above Basin | 10 | 35 | 24-52 | ± 9 | 32 | 22-46 | ± 9 | 7.5 | 7.1-8.2 | ±0.4 |
| Below Cataract Cr. | 10 | 33 | 22-48 | ± 9 | 29 | 16-50 | ±10 | 7.6 | 6.9-8.1 | ±0.3 |
| Above Boulder | 10 | 34 | 22-52 | ±10 | 34 | 22-56 | ±10 | 7.7 | 7.3-8.2 | ±0.3 |
| Below Boulder | 10 | 39 | 24-66 | ±13 | 38 | 26-64 | ±14 | 7.5 | 7.2-8.2 | ±0.3 |
| Elkhorn Bridge | 10 | 44 | 30-76 | ±16 | 55 | 28-144 | ±30 | 7.6 | 7.2-8.1 | ±0.3 |
| Nigger Hollow | 10 | 87 | 38-152 | ±43 | 88 | 40-156 | ±44 | 7.9 | 7.4-8.4 | ±0.3 |
| Cardwell | 10 | 89 | 42-160 | ±42 | 90 | 38-170 | ±46 | 8.0 | 7.7-8.5 | ±0.3 |
| Tributaries -- Boulder River | | | | | | | | | | |
| Basin Creek | 10 | 19 | 14-28 | ± 4 | 17 | 10-24 | ± 4 | 7.5 | 7.0-8.2 | ±0.4 |
| Cataract Creek | 10 | 29 | 18-46 | ± 9 | 30 | 16-64 | ±14 | 7.6 | 6.9-8.5 | ±0.4 |
| High Ore Creek (mouth) | 10 | 92 | 62-146 | ±24 | 134 | 74-184 | ± 4 | 7.9 | 7.5-8.5 | ±0.3 |
| High Ore Creek (below Comet mine) | 10 | 87 | 60-154 | ±26 | 133 | 27-210 | ±55 | 7.9 | 7.6-8.6 | ±0.3 |
| Galena Gulch | 10 | 97 | 60-140 | ±24 | 95 | 74-132 | ±18 | 7.8 | 7.6-8.1 | ±0.2 |
| Little Boulder | 10 | 49 | 24-82 | ±21 | 42 | 24-66 | ±15 | 7.6 | 7.1-8.1 | ±0.3 |

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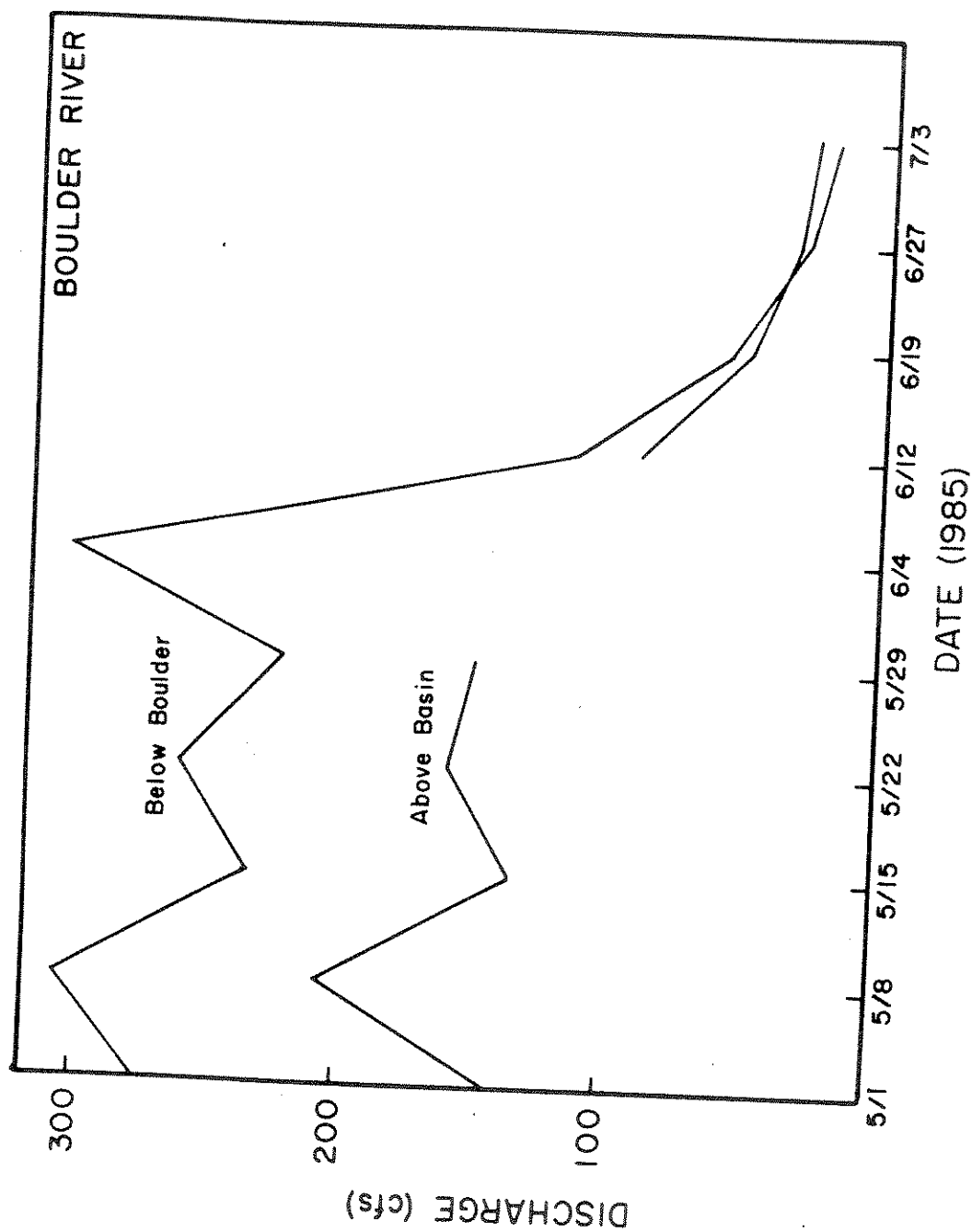


Figure 2. Stream discharge at two locations in the Boulder River: immediately upstream from the town of Basin and at the USGS gauging station downstream of Boulder.

attributable to Basin and Cataract Creeks which enter the Boulder River a short distance downstream of the town of Basin (Fig. 1). For example, on May 8, the sampling date when runoff was greatest, discharge rates of the Boulder River above Basin, Basin Creek at the mouth, and Cataract Creek at the mouth were 200, 100 and 60 cfs respectively (Fig. 3). High Ore and Galena Gulch creeks also enter the Boulder River between the towns of Basin and Boulder. However, their flows are much less significant. For example, during May the approximate percentages of flow contributed to the Boulder River below Galena Gulch were 59 from the mainstem Boulder River upstream of Basin, 24 from Basin Creek, 16 from Cataract Creek, 0.6 from High Ore Creek, and 0.4 from Galena Gulch. High Ore Creek contributed only about 1/200 of the flow volume to the Boulder River during runoff.

Towards the end of our sampling (late June and early July) flows tended to subside more slowly in the smaller tributaries (Galena Gulch and High Ore creeks) than in the larger (Fig. 3). Hence, these tributaries contributed a larger percentage of the total flow near the end of runoff. Our sampling was discontinued too early to determine if the contribution from High Ore Creek continued to be higher throughout the remainder of the low flow season. Inasmuch as water in Galena Gulch and High Ore creeks originates primarily from snowmelt, it seems likely that flows in these creeks would also decline later in the summer.

An irrigation diversion located just upstream from the town of Boulder withdraws a substantial volume of water from the Boulder River. Because of this, stream discharge during late June and early July was almost identical upstream of the town of Basin and downstream of the town of Boulder (Fig. 2) even though several

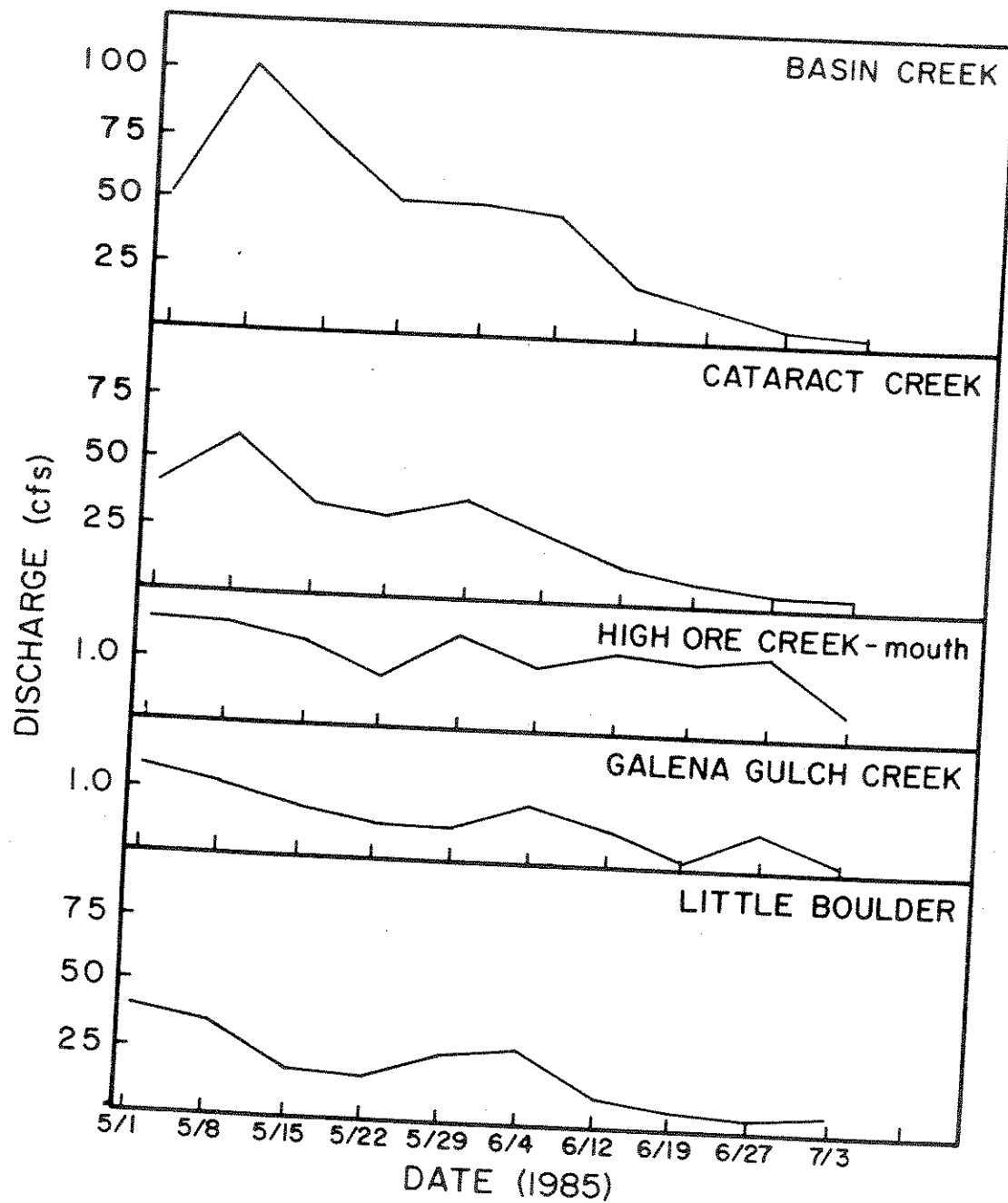


Figure 3. Stream discharge at the mouth of five tributaries of the Boulder River.

major tributaries enter over that reach. The only significant tributary that enters the Boulder River downstream of the town of Boulder is the Little Boulder River (Fig. 1). The average flow of the Little Boulder was about 25 cfs during runoff (Fig. 3).

Metals Concentrations and Loading

Data of previous investigators (Nelson 1976; Gardner 1977) suggest that zinc and copper are the most biologically limiting metals in the Boulder River drainage. Hence, our sampling was limited only to these two metals.

Zinc

At the mouths of the five tributaries that were sampled, average zinc concentrations (Figs. 4 and 5) were highest in High Ore Creek (near 2.0 mg/l) followed in order of decreasing concentration by Cataract Creek (0.2 mg/l), Basin Creek (0.1 mg/l), Galena Gulch (near or below detection) and the Little Boulder River (near or below detection). There was no apparent relationship between zinc concentrations and streamflow in the tributaries. For the most part, zinc concentrations remained relatively constant in all of the tributaries regardless of streamflow (Figs. 3, 4 and 5).

Zinc concentrations in the mainstem of the Boulder River increased from usually below detection upstream of Basin to between 0.1 and 0.2 mg/l at all stations downstream of Basin (Figs. 6 and 7). As in the tributaries, zinc concentrations tended to remain relatively stable regardless of streamflow.

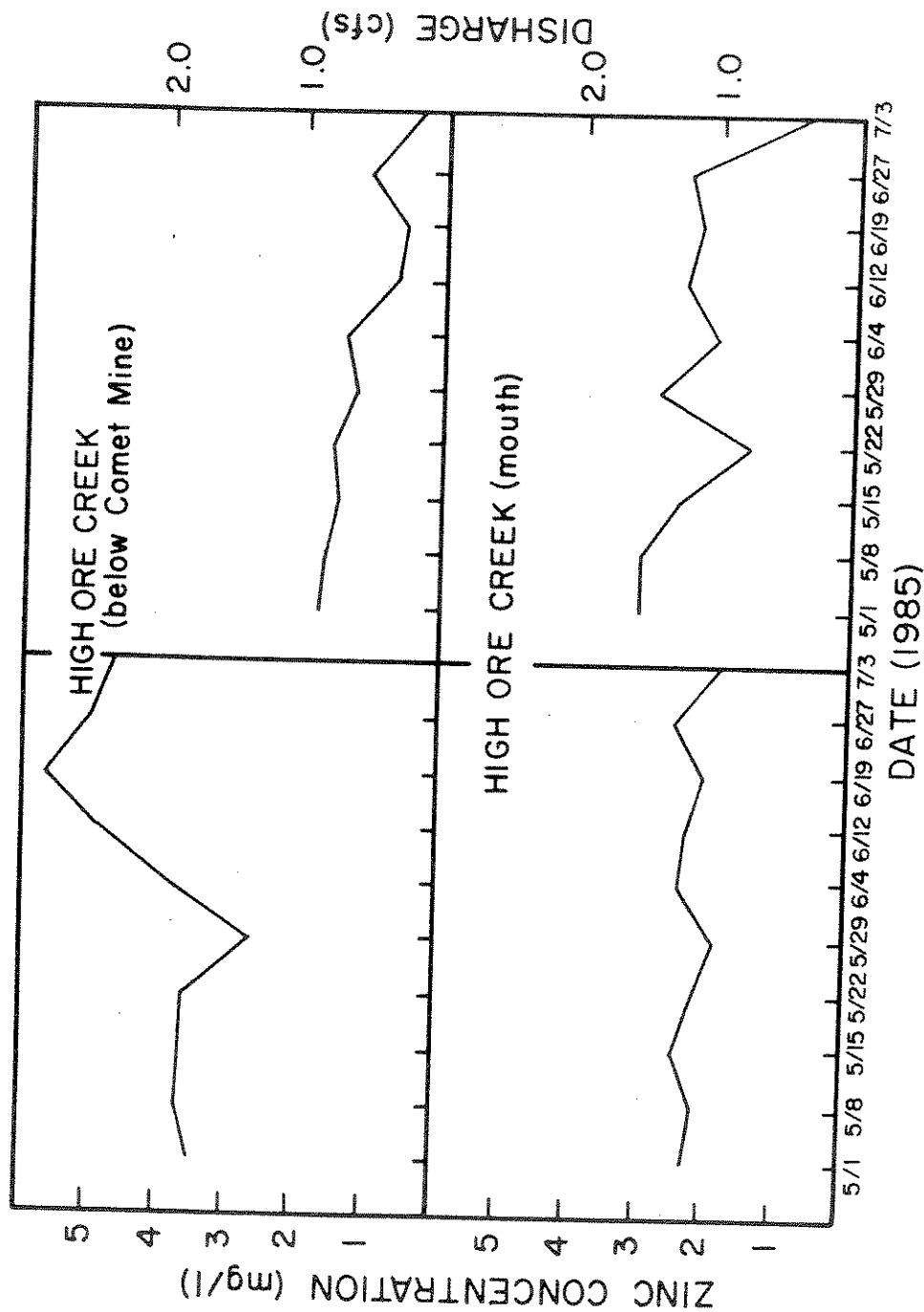


Figure 4. Zinc concentration and discharge at two locations in High Ore Creek: near the mouth and immediately downstream of the Comet Mine.

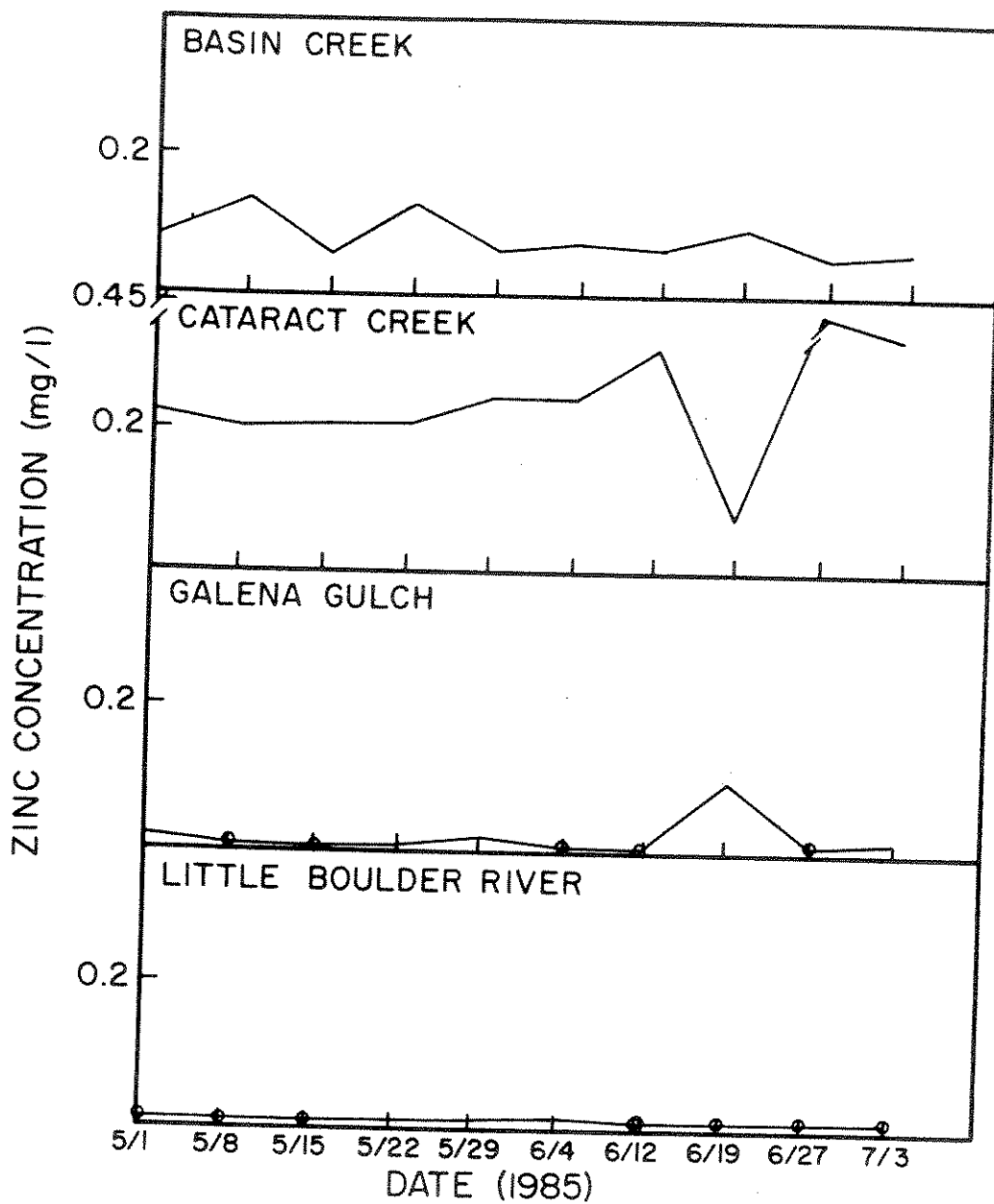


Figure 5. Zinc concentrations at the mouth of four tributaries to the Boulder River.

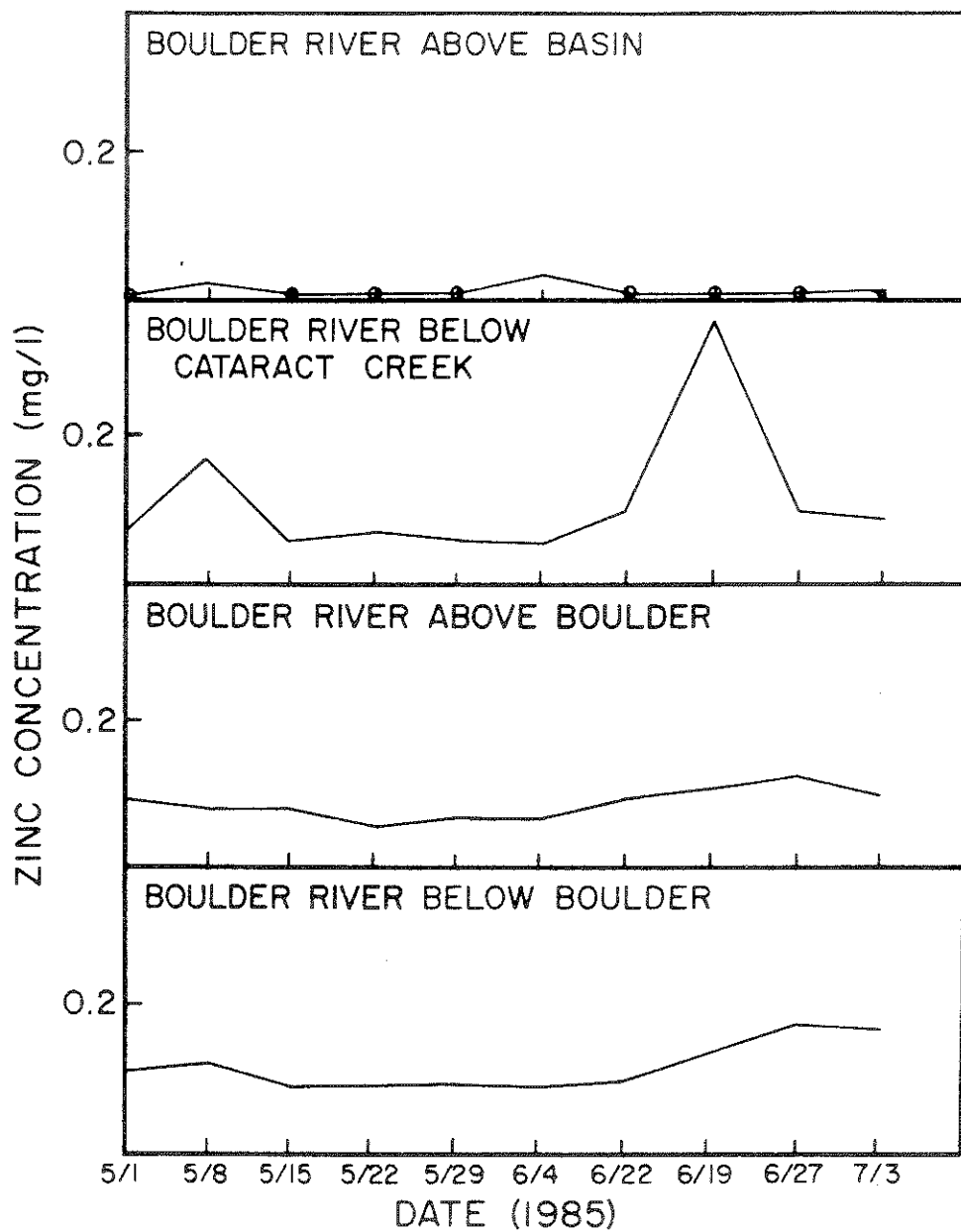


Figure 6. Zinc concentrations at four locations in the mainstem of the Boulder River.

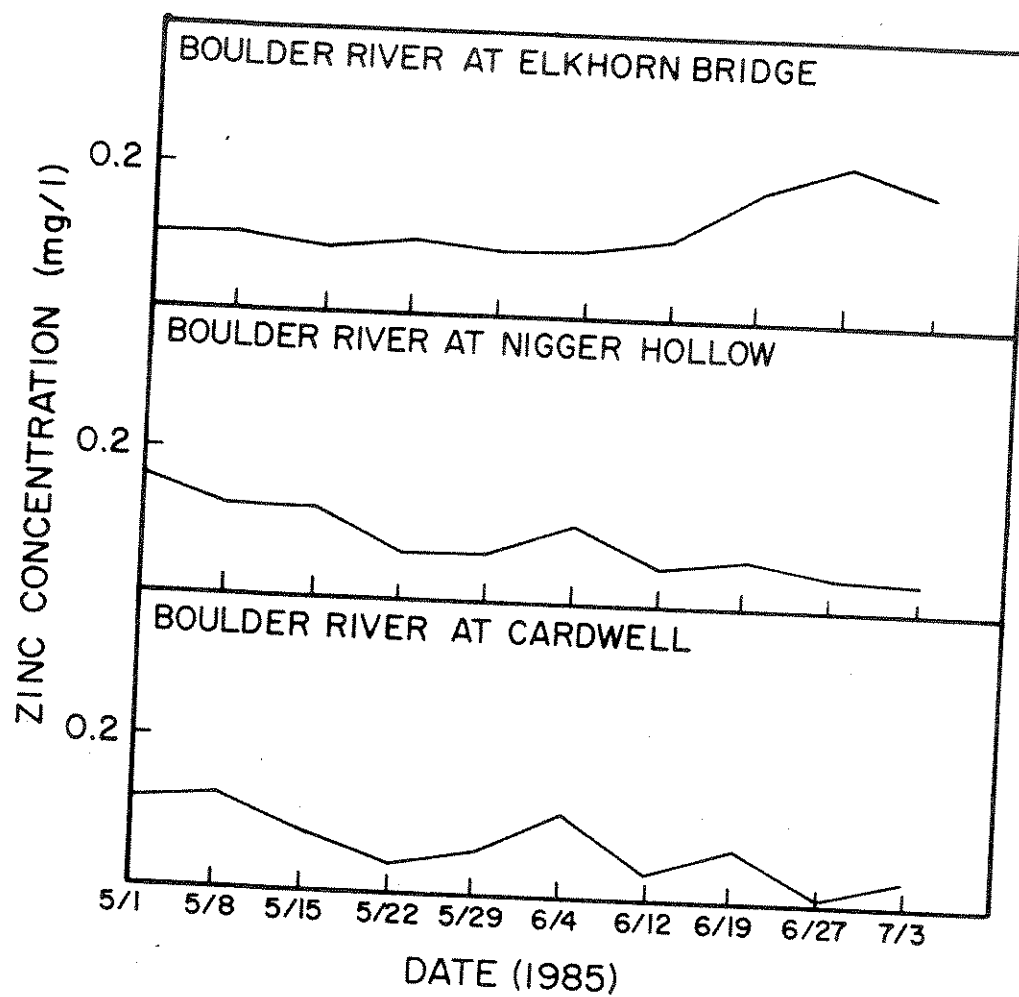


Figure 7. Zinc concentration at three locations in the mainstem of the Boulder River.

Of the tributaries, Cataract Creek was the greatest contributor of zinc followed in order of decreasing load by Basin Creek, and High Ore Creek. Both Galena Gulch Creek and the Little Boulder River contributed insignificant quantities of zinc to the mainstem.

Relative zinc loading from the three most significant tributaries (only for those dates when we had information for all three) was as follows: Cataract Creek contributed an average of 46%, Basin Creek 28%, and High Ore Creek 26%. However, the contribution from High Ore Creek became greater during the low flow portion of our sampling. At that time High Ore Creek contributed as much as 50% of the total zinc load in the river. Please bear in mind, however that the discharge of High Ore Creek had not yet tapered off to the extent that it had in the mainstem and in most of the other tributaries.

Zinc loading in High Ore Creek was virtually identical immediately downstream of the Comet Mine and at the mouth (Table 2). Apparently very little zinc enters High Ore Creek downstream of the mine -- at least during the flow conditions that we sampled. Apparently, benefits of reclaiming the Comet tailings would not be negated due to metals entering the creek lower in the drainage.

Zinc loading in the Boulder River downstream of the town of Boulder was usually greater than the sum of the quantities of zinc entering from the various upstream sources. This may indicate that additional zinc is entering the river from the floodplain; visible tailings deposits are present in the floodplain near the town of Boulder.

Table 2. Zinc loading in the mainstem Boulder River and in tributaries to the Boulder River during spring and early summer 1985.

| Location | Zinc loading (kg/day) ^a | | | | | | | | | |
|-----------------------------------|------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|------|
| | Date -- 1985 | | | | | | | | | |
| | 5/1 | 5/8 | 5/15 | 5/22 | 5/29 | 6/4 | 6/12 | 6/19 | 6/27 | 7/3 |
| Boulder River | | | | | | | | | | |
| Above Basin | -- | 10.13 | 1.63 | 1.95 | 1.84 | -- | 1.13 | -- | 0.44 | 0.50 |
| Below Boulder | 74.92 | 90.84 | 52.64 | 58.72 | 51.80 | 65.42 | 28.1 | 19.71 | 13.19 | 9.20 |
| Tributaries | | | | | | | | | | |
| Basin Creek | 11.1 | 36.90 | 25.46 | 17.69 | 8.23 | -- | 3.78 | 4.01 | 1.19 | 0.99 |
| Cataract Creek | 22.89 | 29.92 | 39.92 | 16.16 | 22.95 | 16.1 | 11.75 | 1.80 | 6.33 | 4.3 |
| High Ore Creek (mouth) | 8.90 | 8.70 | 7.82 | 4.31 | 6.78 | 6.01 | 7.3 | 6.06 | 7.82 | 1.97 |
| High Ore Creek (below Comet Mine) | 7.72 | 7.51 | 11.79 | 7.03 | 4.10 | 6.72 | 3.94 | 3.90 | 6.65 | 2.68 |
| Galena Gulch | 0.07 | -- | -- | 0.01 | 0.03 | -- | -- | -- | -- | -- |
| Little Boulder | -- | -- | -- | 0.20 | 0.32 | 0.51 | -- | -- | -- | -- |

^a Dashes indicate that the concentration of zinc was below the detection limit.

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Copper

Copper concentrations were below the detection limit (0.01 mg/l) the majority of the time in all of the tributaries except Cataract Creek. In Cataract Creek, copper concentrations ranged from 0.01 - 0.05 mg/l (Fig. 8). Concentrations appeared to decrease as flow decreased (Figs. 2 and 8) although there were exceptions.

Copper concentrations at the mouth of High Ore Creek were at or below the detection limit of 0.01 mg/l on eight of the ten sampling dates (Fig. 9). Concentrations were always lower than those measured in Cataract Creek for the same sampling dates.

There were no obvious copper concentration patterns in the mainstem of the Boulder River (Fig. 10) although concentrations at most of the stations tended to drop below the detection limit at most of the stations when runoff tapered off (between June 4 and June 10). The lack of a trend may be owing to the fact that concentrations were near or below the detection limit most of the time. Copper was never detected upstream of Basin whereas copper was frequently detected at all stations downstream of Basin. During runoff (early May to mid-June) there seemed to be a tendency for concentrations to become higher in the downstream direction (Fig. 10). This may reflect the presence of tailings that are being eroded during high flow conditions. We mentioned previously that tailings deposits were observed in the floodplain near the town of Boulder.

Loading calculations for copper (Table 3) clearly indicate Cataract Creek is a greater contributor of copper to the river than any of the other tributaries.

Table 3. Copper loading in the mainstem Boulder River and in tributaries to the Boulder River during spring and early summer 1985.

| Location | Copper loading (kg/day) ^a | | | | | | | | | |
|---|--------------------------------------|-------|------|-------|-------|-------|------|------|------|------|
| | Date -- 1985 | | | | | | | | | |
| | 5/1 | 5/8 | 5/15 | 5/22 | 5/29 | 6/4 | 6/12 | 6/19 | 6/27 | 7/3 |
| Boulder River | | | | | | | | | | |
| Above Basin | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| Below Boulder | 20.24 | 33.03 | 5.72 | 12.76 | 10.90 | 14.87 | 7.81 | 1.42 | -- | 1.08 |
| Tributaries | | | | | | | | | | |
| Basin Creek | 1.29 | -- | -- | -- | 1.29 | -- | -- | 0.40 | -- | -- |
| Cataract Creek | 5.09 | 5.84 | 2.51 | 2.24 | 4.65 | 2.59 | 1.09 | 0.24 | 0.28 | 0.25 |
| High Ore Creek (mouth) | 0.11 | 0.08 | -- | -- | 0.04 | -- | -- | -- | 0.03 | -- |
| High Ore Creek (below Comet Mine) | 0.09 | 0.06 | 0.06 | 0.02 | 0.03 | 0.04 | -- | -- | -- | -- |
| Galena Gulch | -- | -- | -- | 0.01 | -- | -- | -- | -- | -- | -- |
| Little Boulder | -- | 0.86 | 0.45 | -- | -- | -- | -- | -- | -- | -- |

^a Dashes indicates that the concentration of copper was below the detection limit.

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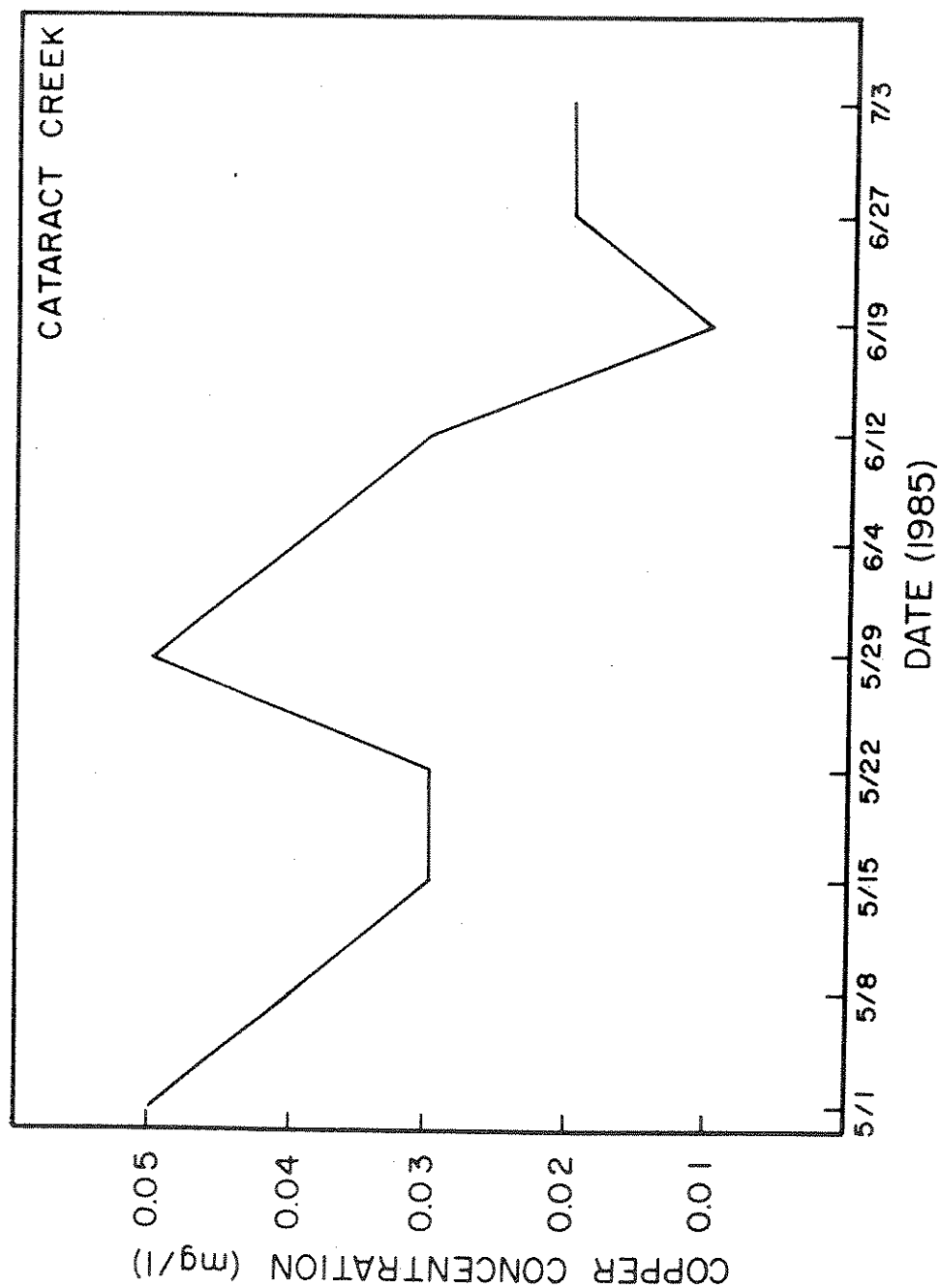


Figure 8. Copper concentrations at the mouth of Cataract Creek.

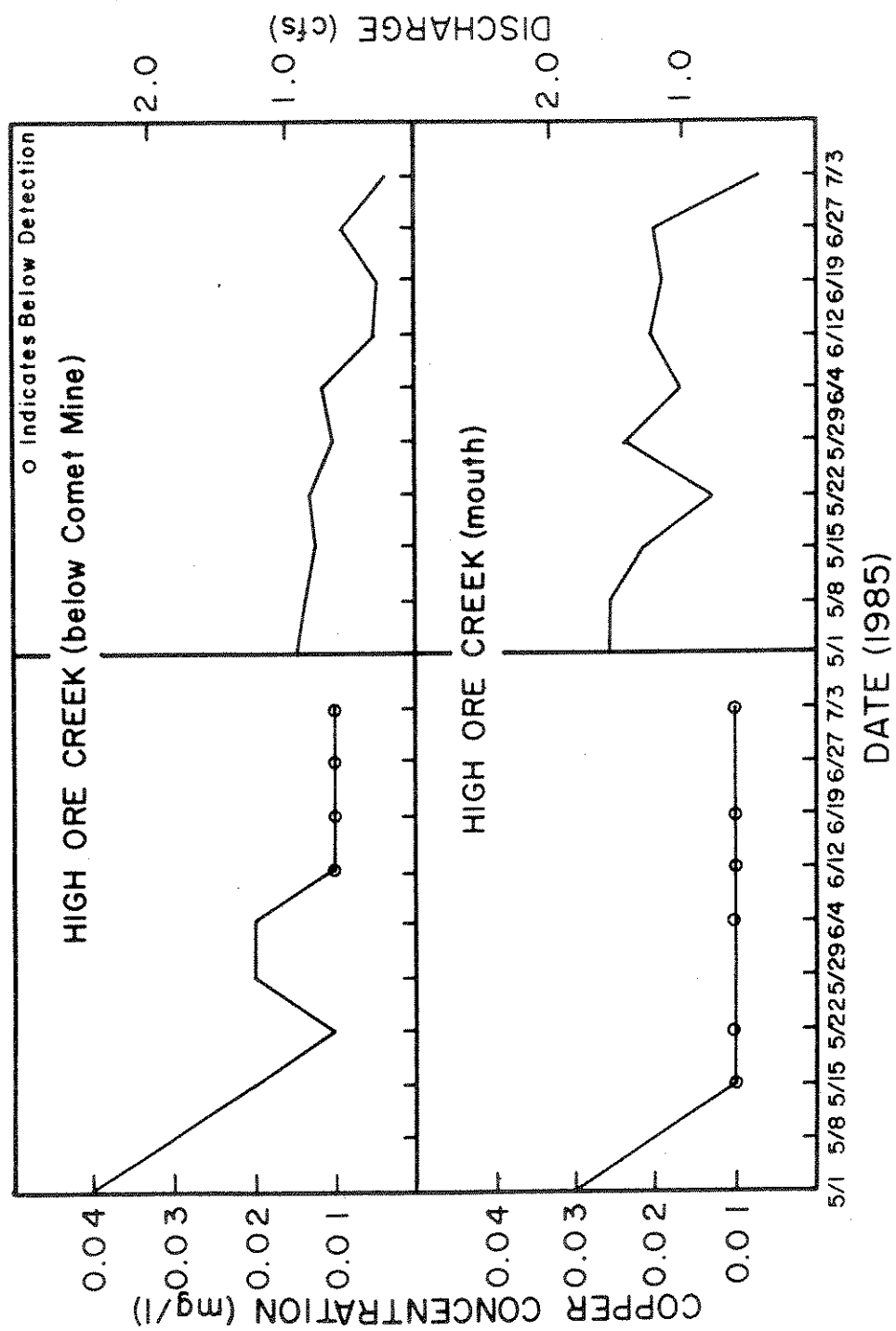


Figure 9. Copper concentrations and stream discharge at two locations in High Ore Creek.

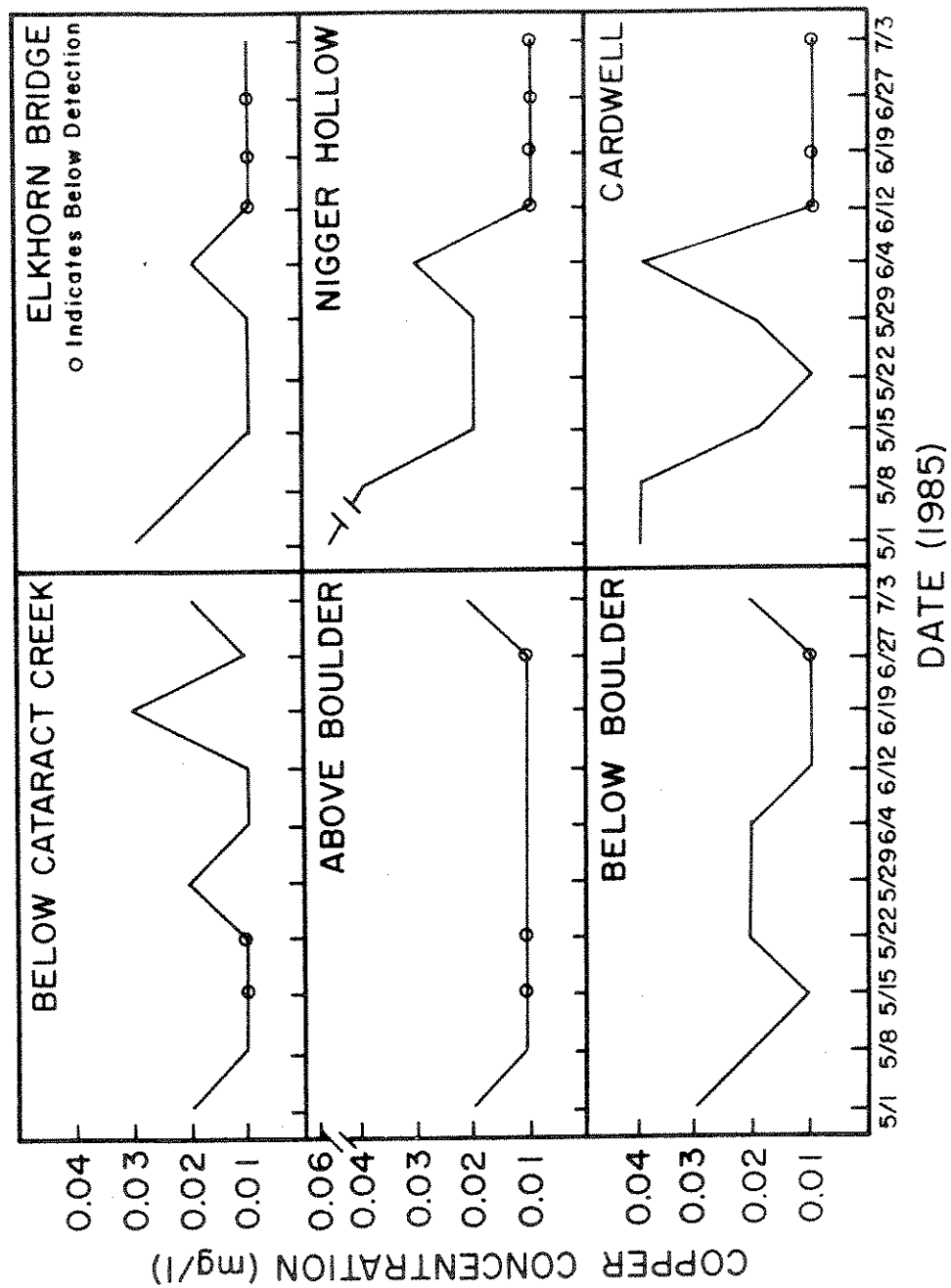


Figure 10. Copper concentrations at six locations in the mainstem of the Boulder River.

However copper loading in the mainstem, downstream of the town of Boulder, is much greater (usually several-fold) than the total from all of the upstream tributaries (Table 3). This is further evidence that the river is picking up copper upstream of the USGS gauging site -- perhaps originating from the tailings that are present in the floodplain near the town of Boulder.

DISCUSSION

Alkalinity, Hardness and pH

Alkalinity, hardness and pH are all important factors influencing the toxicity of metals to fish and other aquatic life. Metals tend to be less soluble and consequently less toxic as pH and alkalinity increase. Increasing water hardness also tends to decrease the toxicity of metals because the cations that contribute to hardness (primarily calcium and magnesium) tend to compete with metals for binding sites at the surfaces of the gills of fish (Pagenkopf 1983).

The observed gradients in pH, alkalinity and hardness from upstream to downstream and as streamflow subsides means that fish in upstream reaches are more vulnerable to metals than those in downstream reaches and that metals are a greater threat during high flow conditions than during low flow. This conclusion does not take into account differences in vulnerability that may be owing to varying water temperatures during different seasons of the year nor does it take into consideration the influence of suspended sediments on the availability of metals to aquatic organisms. Nevertheless, water chemistry is an important variable in the Boulder River with respect to toxicity and needs to be considered in interpreting metals data.

Fish in Basin and Cataract creeks are particularly vulnerable to metals toxicity because of the low pH, hardness and alkalinity of their waters (Table 1). These creeks also affect the vulnerability of fish in the Boulder River because these two tributaries together contribute almost half of the flow of the Boulder.

Toxicity

The recently revised federal criteria documents for zinc and copper suggest using a formula that adjusts the chronic toxicity threshold based on water hardness (USEPA 1985a; 1985b). For example, at hardness concentrations of 50, 100 and 200 mg/l the values recommended for protection of aquatic life are 21, 37, and 66 ug Zn/l and 6.5, 12 and 21 ug Cu/l.

The above criteria were frequently exceeded in several of the tributaries that enter the Boulder River as well as in the mainstem. Adjusting for water hardness, the average concentrations of zinc measured in High Ore, Cataract and Basin creeks exceeded the criteria by approximately 40-, 15- and 10-fold respectively. Clearly, all of these tributaries are severely impacted by zinc. In comparison, copper and zinc concentrations were almost always below detection in Galena Gulch and the Little Boulder River.

The mainstem of the Boulder River upstream of the town of Basin is relatively free of zinc; however, aquatic life in virtually the entire river downstream of Basin are probably suffering from chronic zinc toxicity. Zinc concentrations were similar at all six stations between Cataract Creek and the mouth, although concentrations were slightly higher downstream of Cataract Creek and slightly lower near the mouth. Concentrations remained near 0.1 mg/l at all six stations throughout the sampling period (Figs. 6 and 7). Because hardness increases as you move downstream in the Boulder River, zinc exerts less toxicity in the lower reaches. Hence, a concentration of 0.1 mg Zn/l represents an approximate 7-fold exceedance of the criterion below Cataract Creek but only a 3-fold excursion near the mouth.

There appeared to be a tendency for zinc concentrations to decrease as river flow decreased at the two downstream most stations. Springs entering the lower reaches of the river may dilute zinc. Higher fish populations near the mouth (Vincent 1975) suggest that conditions are more favorable in that reach. Perhaps these springs provide refugia from zinc where sensitive life stages can survive.

Other than Galena Gulch and the Little Boulder River there are virtually no good quality tributaries between the town of Basin and the mouth that are not seriously dewatered. Of the tributaries, Cataract Creek is contributing the greatest amount of zinc to the Boulder River although Basin and High Ore creeks are also significant sources.

The significance of copper in the drainage is more difficult to assess because the detection limit for copper achieved by the state laboratory (0.01 mg/l) is between 2 and 3-fold higher than the chronic toxicity criterion at some of the very low hardness values that were measured. Nevertheless, several conclusions can be drawn.

Copper concentrations present during our sampling in Basin Creek, High Ore Creek, Galena Gulch Creek and the Little Boulder River were usually below the detection limit. None of these streams appeared to be contributing significant amounts of copper to the Boulder River. By comparison, copper was always detectable in Cataract Creek at concentrations 2-10 times the chronic toxicity criterion. Of the tributaries, Cataract Creek is contributing the largest copper load to the Boulder River.

Sources of Metals

Between early May and mid-June, copper concentrations in the mainstem were actually higher in the lower reaches of the river than upstream of Boulder (Fig. 10). This may reflect the erosion during runoff of tailings deposited in the floodplain. Once runoff was completed, copper concentrations dropped below the detection limit at the three downstream most stations while copper remained within a detectable range immediately below Cataract Creek. This seems to support the hypothesis that tailings are entering the river in the downstream reaches.

The concentrations of zinc that we observed in High Ore, Basin and Cataract creeks were similar to those recorded by Nelson (1976) between April and June 1975. However, Nelson (1976) measured higher copper concentrations in High Ore Creek than we did. It is difficult to interpret the reason for these differences. Possibly, runoff was greater in 1975 than in 1985 which could have caused greater erosion of tailings. Alternatively, modifications of the High Ore Creek channel completed by a miner who is working the Comet Mine may have reduced the quantities of metals entering the Boulder River from High Ore Creek.

Knudson (1984) concluded that High Ore Creek is the largest single contributor of metals to the Boulder River. However, Knudson did not have stream discharge information available to him so that he could calculate metals loading. While High Ore Creek continues to have higher zinc concentrations than other tributaries to the Boulder River, its flows are much less than other tributaries that are also contaminated with zinc. Our data show that during 1985 both Cataract and Basin creeks contributed more zinc to the Boulder River than did High Ore

Creek. Additionally, Cataract Creek contributed a greater quantity of copper than the other tributaries. The data suggest that the Boulder River picks up both copper and zinc downstream of Boulder perhaps due to the erosion of tailings deposited in the floodplain.

Fish Populations

Trout densities during 1975 and 1976 were noticeably lower in the Boulder River downstream of High Ore Creek than downstream of Cataract and Basin Creeks (Nelson 1976). However, it should also be recognized that trout numbers in the stream reach downstream of Basin may be artificially high owing to recruitment from the reach having the highest fish populations located just a short distance upstream. The above considerations, combined with the fact that fish population numbers have not been estimated in the Boulder River for nearly a decade, suggest that it would be prudent to collect more current data on fish populations before making a decision on use of reclamation funds in the drainage. Additionally, previous interpretation of metals sources in the drainage is based on information that may be outdated. Conclusions reached in earlier reports need to be re-evaluated.

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