# A GEOCHEMICAL-INVESTIGATION OF THE ORIGIN OF ALUMINUM HYDROXIDE PRECIPITATE IN THE RED RIVER, TAOS COUNTY, NEW MEXICO

May 25, 1989

## Executive Summary


The Red River, between the town of Red River and the Questa Ranger Station, was investigated in October and November of 1988 to determine the location and magnitude of sources of aluminum precipitate occurring in the river.

The aluminum which appears in the river originates in sulfidized, hydrothermal-scar areas which occur in tributary drainage basins, principally to the north of the river. Pyrite in the scar areas breaks down in the presence of air and water to form sulfuric acid. The acid leaches aluminum from the rocks. Sulfuric acid and aluminum are transported to the river in ephemeral streams, groundwater flow and episodic flood runoff.

Tributary stream waters have aluminum concentrations up to approximately 800 mg/l at pH 2.5. Acidic springs along the river contain up to 300 mg/l aluminum at pH values from 3.5 to 5.0. The Red River normally has a pH of approximately 8.0 and less than 1 mg/l dissolved aluminum. Spring water entering the river depresses the pH of the river to as low as 6.8 (on the date of the survey, November 29, 1988).

The solubility of aluminum increases exponentially with decreasing pH, from a minimum at pH 6.5. Solubility also rises at high pH (>6.5). The low solubility of aluminum in the river causes precipitation of aluminum hydroxide (gibbsite). Concentrations of aluminum are comparatively low (11.5 mg/l maximum on the date of the survey) but sufficient to create the observed cloudiness in the river.


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Storm runoff creates floods which briefly cause large increases in suspended loads (including aluminum) and sulfate and a decrease in pH in the Red River.

The milky appearance of the water in Red River has been observed during periods over the past several decades and probably has been more or less prevalent for several thousands of years. A cyclic precipitation pattern probably results in long-term variation in the turbidity in the river. The average discharge of Red River from 1979 through 1987 was more than double that during the preceding nine year period. This indicates a probable above-normal groundwater flow from the hydrothermal-scar areas. The above-normal groundwater flow may continue for some years after the end of the wet cycle. The river flow has been below normal since early in 1988. The higher-than-normal turbidity in Red River during 1988 and 1989 may largely be the result of this climatological sequence.

The greatest concentration of aluminous springs occurs near the Questa Ranger Station in an area not influenced by Molycorp's operations.

On the basis of limited data, it is estimated that the Capulin Creek and Goathill Gulch drainages contributed 26 percent of the total aluminum gain to the river on the date of the survey. It is speculated that a majority of the aluminum gain from these two canyons is from the large, intense, natural scar in the area of the canyons. There is a possibility that there will be an increase in the amount of aluminum discharged to Red River as a result of the mine dumps at the head of Goathill and Capulin Canyons. It is more likely that the aluminum discharge from the mine dumps has reached or passed its maximum rate. If the dumps were responsible for as much as 50 percent of the aluminum gain from the Goathill/Capulin area, this would represent only 13 percent of the aluminum observed in the river on the date of the survey.



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Acidic drainage from Sulfur Gulch which formerly flowed into the Red River is captured by the mine workings. This has the effect of offsetting a substantial amount of any acidic drainage which may be generated by the mine dumps.

The dumps downstream of the Molycorp mill and above Columbine Creek were not found to be important sources of aluminum. It is estimated that during the period of the investigation, two percent or less of the gain in aluminum in the river was derived from these dumps.

Over time there is a high variability in the quantity of aluminum discharged by the river. The data reflected by the November 29, 1988 survey may, therefore, not accurately reflect average conditions. Additional surveys are recommended to substantiate such.

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# A GEOCHEMICAL INVESTIGATION OF THE ORIGIN OF ALUMINUM HYDROXIDE PRECIPITATE IN THE RED RIVER, TAOS COUNTY, NEW MEXICO

May 25, 1989

## Purpose

This report has been prepared at the request of Molycorp, Inc. The purpose is to provide a quantitative assessment of the origin and sources of aluminous precipitate which occurs in the Red River between the town of Red River and the Questa Ranger Station.

## Background

A cloudy, white precipitate, tentatively identified as gibbsite [$Al(OH)_3$] occurs in the Red River from the town of Red River to below the Questa Ranger Station, mainly at times of low water flow. The affected reach includes the area of Molycorp's Questa Operations, particularly the Sulfur Gulch, Goathill Gulch and Capulin Canyon drainages.

The precipitate has historically been considered to be the product of leaching of aluminum from "hydrothermal scar" areas by acidic ground and surface water, followed by re-precipitation in the river. The scar areas are at least several thousands of years old, and the precipitate is known to have existed for at least several decades (A. Greslin, pers. comm., 1988). The cloudiness in the river, however, has perhaps been more noticeable and/or has received increased attention in recent years. For this reason, in part, this investigation has been commissioned to evaluate the affect, if any, that the mine dumps at the Molycorp Questa Operations have on the occurrence of aluminum precipitate in the Red River. The possible association of the dumps and aluminum mobilization is both suggested by and confused by the fact that the dumps, in part, consist of and in part overlie hydrothermal scar-type material.



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Several studies of the Red River have been made in recent years (Federal Water Pollution Control Administration, 1966; U.S. Environmental Protection Agency, 1971; Smolka and Tague, 1987, 1989). Thorne Ecological Institute (1972) Investigated the Red River for Molycorp. They noted that natural springs and hydrothermal scars were affecting the water quality of the river. The present investigation is considerably more detailed with respect to chemical aspects of the river, and defines and limits the sources of aluminum and other factors to a much greater degree than previous studies. Nevertheless, it is based on limited data. Seasonal variability in the chemistry of the river is substantial, and this report is based principally on data from one date. Additional data are needed to evaluate several influences on the chemistry of the Red River including seasonal variability and stream-water inhomogeneity over short distances and short times, and to identify long-term changes caused by climatic change and evolution of the mine dumps. Should the waters of the upper streams of Goathill Gulch and Capulin Canyon be diverted to the tailings line, continued sampling of the river would be necessary to measure the effect of such.

## Method of Investigation

Three principal objectives were identified as being fundamental to evaluating the origin and controls of aluminum hydroxide precipitate in the Red River: 1. define the chemical controls of aluminum dissolution, transport and precipitation in the ground and surface water environment; 2. determine the magnitude and distribution of aluminum sources to the Red River; and 3. evaluate the relative importance of the mine dumps and natural scars as sources of aluminum. The following tasks were outlined to achieve these objectives:

- A literature study was made of the chemical systematics of aluminum in the weathering environment.



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- Detailed surveys of the affected river area were performed to quantify the location and magnitude of aluminum sources.

- An accretion profile of the Red River was calculated to provide a baseline for the geochemical survey.
- Limited geological field investigations were carried out in the scar areas and dumps.

The field studies were briefer than originally planned, owing to winter snow cover and time limitations. It is not believed that the general conclusions of the investigation would be modified significantly by additional field work, however.

Geological Setting

The Questa mine area is very complex geologically, as is typical of sulfide ore deposits. However, for the purposes of this report, a few basic observations are significant.

Rocks in the district can be divided into three groups. The oldest is a complex of Precambrian quartzite, amphibolite and granite. Tertiary volcanic rocks, dominantly andesite, were erupted over the Precambrian rocks. Eruption of the lavas and silicic tuffs led to caldera collapse. The youngest group, Tertiary granitic rocks, were intruded into the Precambrian and volcanic rocks late in the history of the caldera. Hydrothermal solutions, related to the younger granites, altered and sulfidized the county rocks, especially the volcanics. The principal ore deposits of the district are within altered volcanic rocks.

Exposures in the mine area are dominantly andesite north of the Red River and Precambrian granite south of the river. Tertiary granite intrudes both of these. Rocks in the mine area are extensively fractured and faulted.

Hydrothermally Altered Areas. Volcanic rocks in the mine area and over much of the area around the town of Red River are extensively altered. Significant zones of alteration extend as far west as the ranger station near Questa. The alteration is characterized by replacement of feldspars and ferromagnesian minerals by clays, sericite, secondary feldspars, chlorite, epidote and pyrite. The areal extent of alteration has not been mapped in detail. However, Schilling (1956) mapped the alteration on a reconnaissance basis prior to extensive mine development by Molycorp. Plate 1 shows the general extent of altered areas, as adapted from his work and aerial photo interpretation.

Weathering of the altered areas has produced prominent "hydrothermal scars" in Hanson Creek Canyon, Goathill Gulch and many of the other canyons along the Red River. The scars originate from deep erosion in sulfidized areas. Pyrite in these rocks dissolves and oxidizes to form sulfuric acid. Most of the acid is formed at or near the surface because of a depletion of oxygen at depth. The acid causes further degradation of the rocks to clay end-products. Metallic elements including aluminum are leached and removed. The result is a "scar" area which is deeply eroded and lacking in plant cover. Little infiltration of precipitation appears to occur below the steep slopes of the scars, as the clay-rich surface is highly impermeable. Consequently, most precipitation is removed through surface run off. Mud-flow deposits, caused by summer flash floods are extensive below the base of the scars and extend to the Red River. The flow deposits are also very clay-rich and impermeable, further limiting infiltration of precipitation.

Mine Dumps. The principal dumps are located in the heads of Capulin Canyon and Goathill Gulch (185 acres combined) and to the north of the Red River between the Molycorp mill and Columbine Creek (413 acres). The dumps consist of overburden which was stripped from the open-pit mine area. The rock types are mainly andesite and granite, as is the area in general. A



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considerable part of the dump material in the Goathill Gulch and Capulin Canyon areas is altered, sulfidized, hydrothermal-scar material. However, the proportion of sulfidized material and the sulfide content have not been determined.

Highly aluminous, acidic streams emanate from the base of the Goathill and Capulin dumps. The flow of these streams has been estimated at 60 gpm, combined. The degree to which the acidity of the stream water is caused by the dumps is difficult to determine. According to Schilling's mapping (1956) the dumps are built on altered, sulfidized material, which, itself, is capable of generating acidic water.

By analogy to Hanson Creek, it can be expected that the greater part of natural flow from scar areas comes from the base of cliffs at the head of the scars. The lower areas are too impermeable to permit significant gain.

The dumps are located at the heads of their respective canyons, overlying the natural upper spring areas. Separating the effects of dumps and natural scars probably cannot be done without drilling and pump testing, which were not practical at the scale of this study.

The dump area downstream from the mill site apparently generates comparatively little acidic water, although it also is partly underlain by altered bedrock. The degree of alteration and sulfidization of the underlying rock is not known. But the relatively small areal extent of altered bed rock in this area may be a partial explanation of the low aluminum and sulfate gain.

Prior to extensive mine development, the scar area in Sulfur Gulch was a significant source of acid drainage to the Red River. This drainage was shut off from the river when the open pit mine was constructed, beginning in 1965. The volume of water originally flowing in Sulfur Gulch was probably comparable to that in Hansen Creek or Goathill Gulch, or about 25 to 35 gpm.



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Groundwater Flow. There is little data available for determination of the groundwater flow characteristics of the canyon areas north of the Red River. Several test holes were drilled in Goathill Gulch upstream from the underground mine. Indications were that a groundwater table was present at a fairly shallow depth. However, inflow was at such a slow rate that a pump test was not conducted. The low inflow rate did indicate a very low hydraulic conductivity. Based on this observation and an evaluation of the fine-grained, clayey nature of the material, we estimate that the conductivity of the material is probably less than 10 gpd/ft$^2$. The permeability of the underlying bedrock is probably even less. The hydraulic gradient of the water table is estimated to be on the order of 15 percent. These values indicate that ground water movement is less than 200 feet per year.

A significant portion of the drainage flow from the mine dumps and from some of the active natural scar areas is by surface flow over much of the distance to the Red River. After seepage into the ground, the flow may be conducted through more permeable material near the surface.

In consideration of the foregoing, no conclusion can presently be reached as to whether or not the surface flow below the dumps is as yet fully impacting on the river. It is probable that a significant portion of the spring water below the natural scars has been in transport for many years.

Flood runoff from summer storms causes brief, large increases in both suspended and dissolved loads in the Red River. These events have received attention from the New Mexico Environmental Improvement Division (Smolka and Tague, 1987) and the U.S. Geological Survey (Garn, 1989, unpublished proposal). Observed concentrations in the Red River following a storm are shown in Table 1. A large increase in suspended

aluminum was observed which is probably attributable in large part to suspended clays, rather than aluminum hydroxide. Investigations by the Thorne Ecological Institute (1972) indicate that storm runoff has only transient effects on water quality and faunal assemblages of the Red River.

A detailed investigation of the chemistry of the storm runoff waters is beyond the scope of this report.

Table 1

Analytical data for a flood water sample from the Red River at the Questa Gauging Station, July 26, 1988.

| | |
|---|---|
| Al(susp) mg/l | 1453 |
| Al (dis) mg/l | 3 |
| $SO_4$ | 278 |
| TDS mg/l | 1112 |
| TSS mg/l | 47844 |

## Historical Data

Stream flow records have been kept for the Red River since 1913. Figure 1 gives a summary of the mean daily flow rates since 1960.

Chemical data are available for the Red River for studies in 1965, 1970, 1986 and 1988 (Federal Water Pollution Control Administration, 1966; U.S. Environmental Protection Agency, 1971; Smolka and Tague, 1987, 1989). Monthly data for the gauging station near Questa are available for 1979 to 1982. These data are insufficient to draw any extensive conclusions about the variability of river chemistry over time. However, examination of the available data for 1986 and 1988 indicate that most parameters reported were somewhat high relative to 1965 and 1970 (Table 2). The difference may be due to climatological cycles as discussed below.



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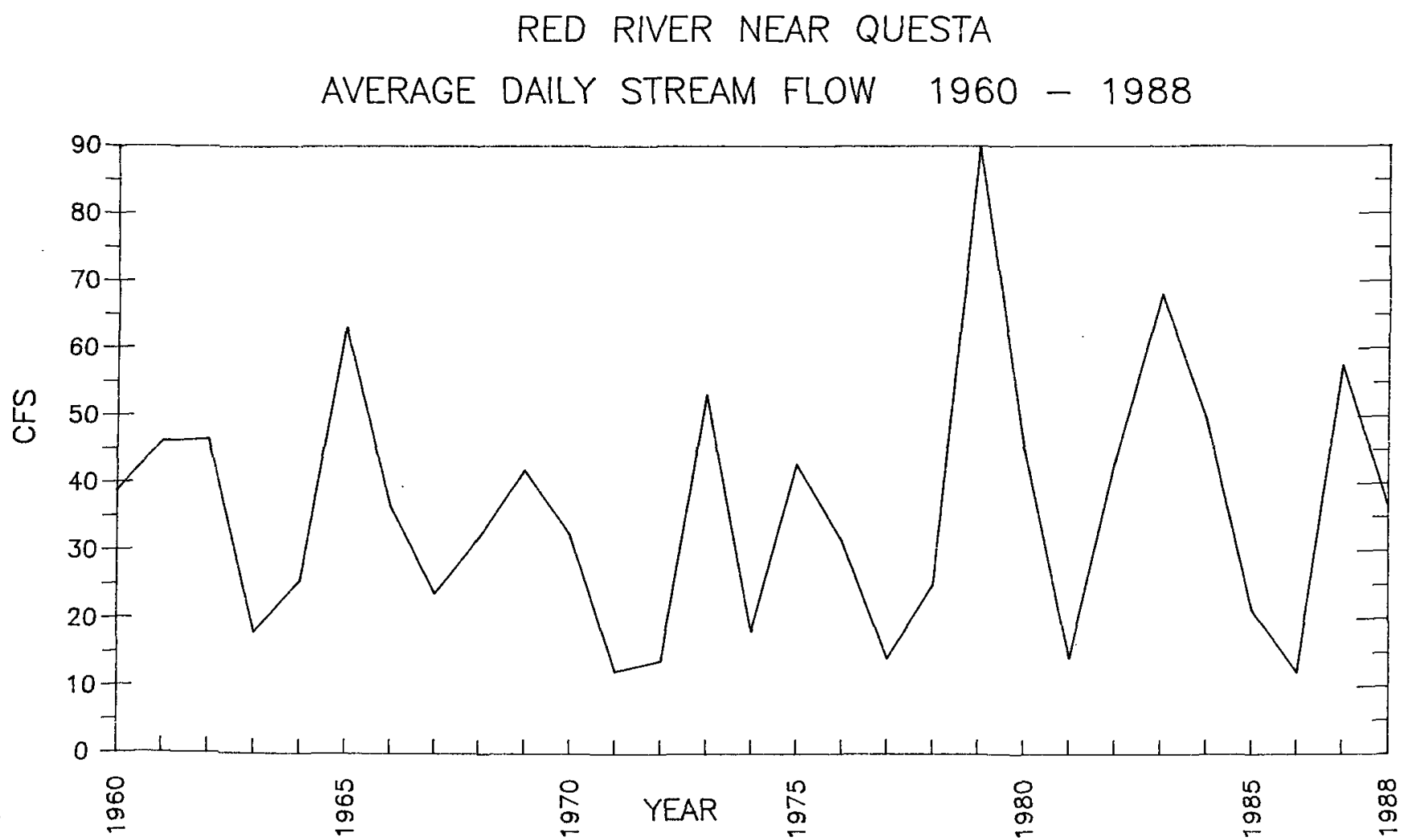
RED RIVER NEAR QUESTA
AVERAGE DAILY STREAM FLOW 1960 – 1988
CFS
90
80
70
60
50
40
30
20
10
0
1960
1965
1970
YEAR
1975
1980
1985
1988

Figure 1

Table 2

Comparison of Chemical Data for samples from four years from the Red River near the Questa Ranger Station.

| | 11-4-1965 | 11-4-1970 | 8-20-1981 | 11-29-1988 |
|---|---|---|---|---|
| Streamflow (CFS) | 26.3 | 11.9 | 40 | 17 |
| pH | 8.1 | 6.8 | 7.2 | 7.1 |
| Sulfate (mg/l) | 64 | 66 | 118 | 137 |
| TDS (mg/l) | 186 | 160 | | 263 |
| TSS (mg/l) | 25 | 2.7 | | 50 |
| alkalinity (mg/l) | 56 | 54 | 40 | 26 |
| turbidity (JTU) | 5.6 | 26.9 | 7.5 | 22 |

Cloudy appearance of the water in Red River has been observed during periods of low water over the past several decades and probably has existed for several thousands of years. The variation in the amount of cloudiness (aluminum-hydroxide precipitate) is undoubtedly influenced by fairly long-term precipitation cycles. Years of high precipitation increase the amount of groundwater flow. Groundwater moves very slowly, and the aquifer acts as a storage reservoir. Higher than normal groundwater flow, therefore, may continue for several years beyond the end of the high precipitation period. It is probable that the milky appearance of Red River is most pronounced when the groundwater flow is relatively high at a time of below average river flow.

The yearly mean flow in Red River varies with the amount of precipitation and in particular with the winter snowfall precipitation as shown in Figure 1 and Table 3.



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Table 3

Mean daily flow in cfs of the Red River at the gauging station near Questa for 1961 to 1988.

| Year | flow | Year | flow | Year | flow |
|---|---|---|---|---|---|
| 1961 | 44.80 | 1970 | 34.90 | 1979 | 87.60 |
| 1962 | 47.80 | 1971 | 11.80 | 1980 | 47.00 |
| 1963 | 19.70 | 1972 | 15.50 | 1981 | 14.00 |
| 1964 | 24.40 | 1973 | 51.70 | 1982 | 39.40 |
| 1965 | 60.60 | 1974 | 19.10 | 1983 | 71.00 |
| 1966 | 39.60 | 1975 | 41.70 | 1984 | 48.60 |
| 1967 | 40.50 | 1976 | 32.60 | 1985 | 72.30 |
| 1968 | 34.90 | 1977 | 13.40 | 1986 | 61.40 |
| 1969 | 40.50 | 1978 | 25.70 | 1987 | 60.30 |
| 9 year average | 39.20 | | 27.38 | | 55.73 |
| | | | | 1988 | 35.10 |
| | | | | 28 year average | 40.57 |

Near drought conditions prevailed from 1970 through 1978 during which the discharge of Red River was only 67% of the 28 year average. From 1979 through 1987 the discharge was 137% of the 28 year average and more than double that of the preceding nine years. In 1988, the discharge was below average and such will surely be the case in 1989.

We hypothesize that after several years of below normal precipitation, the groundwater flow from the hydrothermal scar areas decreases and generally the river has low turbidity (1973-1978). During years of above normal precipitation, there is generally sufficient flow to dilute the gibbsite precipitate and the resulting turbidity (1979-1987). Following several years of above normal precipitation there is a high groundwater flow from the scar areas, and during periods of low river flow, increased gibbsite precipitation results in high turbidity (1988-1989).



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Geochemical Overview

Relatively little research has been done regarding the chemical behavior of aluminum in natural waters. However, sufficient data are available to permit a general overview (Roberson and Hem, 1969, Hem 1970). Aluminum is generally present in natural waters in concentrations of 0.1 to 1 ppm. Higher values are reported; but those are thought to reflect the presence of minute colloidal particles which can pass through most filter media (Hem, 1970). The exception is low pH waters, including mine waters, in which aluminum concentrations can exceed 1000 ppm.

The principal control of aluminum stability in solution is acidity. In natural systems the solubility curve for gibbsite [$Al(OH)_3$] as a function of pH approximately represents the solubility controls of dissolved aluminum species. Figure 2 (Drever, 1982) shows that aluminum is highly soluble in both strongly acid and strongly alkaline solutions. In approximately neutral solutions, including most river waters, the solubility of aluminum is quite low, on the order of $10^{-7}$ to $10^{-6}$ moles/liter (0.27 to 2.7 ppm).

The presence of other ions which can combine with aluminum can affect solubility. High concentrations of fluoride and sulfate can respectively increase or decrease the solubility of aluminum. At fairly high concentrations of dissolved silica (greater than $10^{-4}$ molar) clay minerals precipitate before gibbsite and solubility of aluminum is decreased.

Application to the Red River. The maximum concentrations of fluoride (1.6 mg/l) and sulfate (137 mg/l) in the Red River for the period of the investigation are well below the levels at which they would affect aluminum solubilities. Few data for silica are available, but older U.S.G.S. data (Water Supply Report NM-80-1) indicate concentrations on the order of 10 mg/l ($10^{-6.7}$ molal), well below the concentration at which clay minerals would precipitate. Therefore, gibbsite is the expected precipitate in the Red River.



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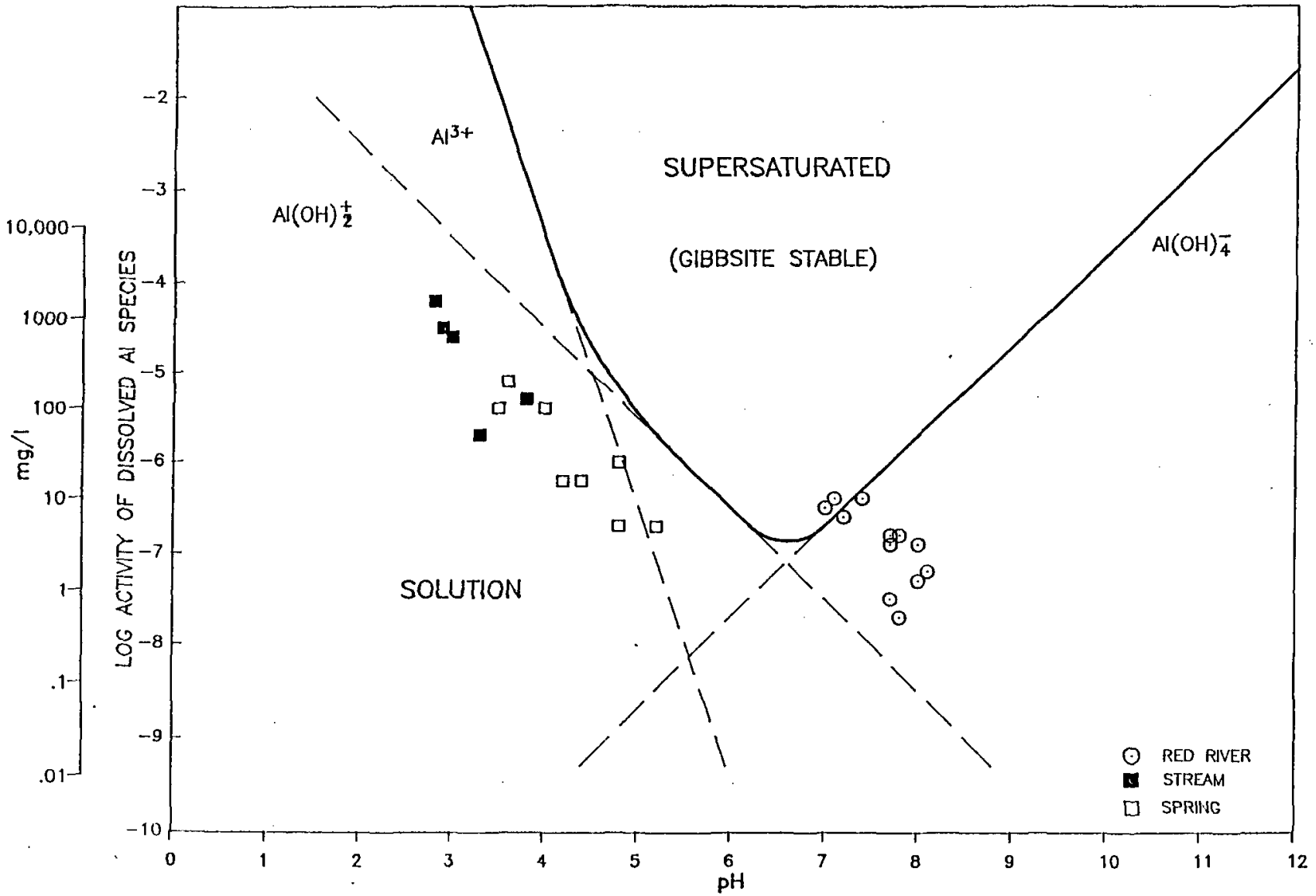


FIGURE 2. ACTIVITIES OF DISSOLVED ALUMINUM SPECIES IN EQUILIBRIUM WITH GIBBSITE [$AL(OH)_3$] AT 25°C. RED RIVER DATA ARE FROM 11/29/88. STREAM & SPRING DATA ARE FROM VARIOUS DATES.

Samples of precipitate collected above the river near the ranger station and along Hanson Creek were scanned by X-ray diffraction at the Molycorp laboratory at Louviers, Colorado. The material was found to be too poorly crystallized to yield a mineral identification. Thus, it is still somewhat conjectural that gibbsite is the mineral causing cloudiness in the river.

Total aluminum concentration (suspended + dissolved) for Red River samples and tributary springs and streams are cross-plotted with pH in Figure 2. The river data are from November 29, 1988. The spring and stream data are from various dates.

The river data show a steep trend of increasing aluminum concentration with falling pH. In general, the higher concentrations come from downstream locations, especially below Capulin Canyon. The lower concentrations cluster around an aluminum concentration of roughly 1 mg/l and tend toward a pH of 8.0.

Compositions of spring and stream waters fall on the left side of the diagram at low pH values and high aluminum concentrations. Dilution of any of these waters would cause the concentration to move on a straight line path toward the diluting water. It can be seen that most of the spring and stream waters would cross the stability boundary and precipitate gibbsite if diluted by pH 8.0/1 ppm Al water.

Solubility of aluminum decreases with increasing total ionic strength. Because the spring waters have very high concentrations of total dissolved solids, the solubility boundary may lie closer to the spring and creek samples than indicated in Figure 2.

Most of the river waters fall outside the gibbsite stability boundary, even though moderate amounts of gibbsite are visible along much of the river course. This suggests that gibbsite is unstable along most of the river. The dissolution rate is probably too low, however, to have an appreciable affect on the turbidity of the river.



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If the diluting water were consistently the composition of Columbine Creek and Pioneer Creek (about pH 8.0 and less than 0.5 mg/l Al) no precipitation would occur. Precipitation occurs only at times when the aluminum concentration increases to above 1 ppm. Above this concentration, dilution lines of spring waters cross the gibbsite boundary. This affords an explanation of why gibbsite is not visible at the town of Red River. The aluminum concentration probably seldom exceeds 1 mg/l in the town area.

Spring and stream waters also exhibit a trend of increasing aluminum with falling pH. Stream samples are mostly more acidic and more aluminous than spring samples (which were collected at the river). No acidic streams were reaching the river by surface flow at the time of the survey. Rather, these streams infiltrated gravels above the river area. Many of the springs are probably fed by infiltration of the streams. The spring water is diluted by groundwater and subsurface river water flowing in gravels adjacent to the river. Dilution raises the pH of the water and lowers the solubility of aluminum. Comparison of aluminum concentrations in the upper reaches of Capulin Canyon (655 mg/l) and Goathill Gulch (560 mg/l) with that in corresponding springs (113-225 mg/l) indicates that the streams are diluted by a factor of perhaps three to six.

The majority of the aluminum entering the Red River appears to originate at springs emerging downstream from Capulin Canyon. It is likely that aluminum concentrations at these springs are high as a result of the spring water in this area being more acidic than elsewhere (pH 3.5-4.5). This could be caused by low precipitation/infiltration rates and/or because of a low dilution in the narrow canyon.



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Red River Survey - pH

A detailed survey of the pH of the Red River in the study area was carried out from October 15 to October 21, 1988. The objective of the survey was to determine the locations of the sources of acid water accreting to the river by recording variations in the pH of the river water.

Measurements were made with a pH meter at 300-foot or smaller intervals. The location and pH of springs, where observed, was noted as well. Portions of the survey were carried out on three separate days. The weather and river level were similar on each of the survey days, and data from overlapping river survey segments indicate that no significant changes in the chemistry of the river as a whole affect the data.

The results are plotted on Plate 1. The pH of the river ranged from 6.8 to 8.1. The local average pH varied considerably from place to place, varying from about 7.3 to 8.0. It was found that a sharp dip in acidity of 0.3 or more pH units occurred at all observed acid springs. Similar dips, as shown on Plate 1, infer the location of additional springs and seeps. Measured pH values generally returned to the local background level within abut 500 feet downstream of a source.

The rebound of pH cannot be explained by dilution, as not enough water is available. Roughly 1000 times the volume of the acid water would be required, as pH 5 water contains 1000 times the $H^+$ ion content of pH 8 water. It is apparent that the acidity of the river is buffered by bicarbonate ion ($HCO_3^-$) and related species. Bicarbonate buffering is normal for river waters (Drever, 1982). Without buffering the pH of the river would be 6.0 or less at the Questa Ranger Station. Correspondingly, total alkalinity decreases downstream (Plate 1).

Spring waters were generally acidic on the north bank of the river and slightly alkaline on the south bank. More springs were observed on the north bank, probably because they were easier to identify because of their associated low pH and



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white precipitate. Also, much of the water in the southern drainage flows to the river in tributary streams rather than springs. The acid springs ranged from pH 3.5 to near neutral. Both spring and creek waters from the south side of the river were about pH 8.0.

The pH data indicate that acid springs occur at irregular intervals along the entire river segment from Red River to the ranger station. The frequency of springs is highest between the ranger station and Goathill Gulch (ten or more indicated).

Only one spring was identified in the Red River town area. However, the relatively low pH (7.5) of the river indicates that acid seepage occurs in this area. Bitter Creek was only intermittently flowing when sampled. It was somewhat acidic (pH 6.3).

Large hydrothermal scars are present from Hanson Creek to the town of Red River. However, significant acidic springs do not appear to be associated with these scars, except below Hanson Creek. Very little accretion and only one observable spring was noted in this area. The scar areas are deeply weathered to a heavy clay soil. Consequently, surface runoff predominates and apparently very little ground-water flow is present. Sulfides have largely been removed from the surface by weathering. Freshly broken boulders in the cliff area do contain disseminated pyrite on fractures. Nominal gains in sulfate and aluminum in the Red River indicate some continued dissolution of pyrite in these areas.

Red River Survey - Geochemical

A sample run was made November 29, 1988 along the Red River and major tributaries. Seventeen samples were collected over a 12-mile segment of the river. Sample locations were selected to separate and measure the affect of each of the major tributary drainages to the river. Care was taken to choose locations in which the river water and emerging spring waters should be well mixed. The run was made over a four-hour time period. PH was measured in the field.

The samples were analyzed by the assay laboratory at the Questa mine. Determinations were made for Al, $SO_4^{=}$, TDS, TSS, total alkalinity, turbidity, $F^-$ and several metallic cations. Analytical results are presented in Appendix 1 and on Plates 1 and 3.

Stream Flow. In order to make quantitative comparison, it was necessary to weight the data at individual sample locations for accretions to stream flow. Data for two U.S.G.S. stream surveys of the Red River, made at approximately the same time of year as the sample run, were used as a baseline. Stream flow at locations along the river for the date of the survey were estimated to be proportional to that of the two surveys (Table 4). Adjustments were made for the size of the drainage basins of the tributary canyons. The measured flow for November 29, 1988 at the stream gauge near the Questa Ranger Station was used as a datum.

The calculated incremental gains in streamflow are illustrated in Figure 3. Columbine Creek is the major tributary. Subtracting the contributions of the upper Red River, Pioneer Creek, Mallette Creek and Columbine Creek leaves approximately 3.5 cfs accretion to the river between Red River and the Ranger Station from springs and seeps at a base flow of 17 cfs on November 29, 1988. The gains to the river are near the limits of accuracy of stream gauging. Therefore, the distribution of accretion is somewhat tenuous.

Results. Analytical results are summarized in Appendix 1 and presented graphically on Plates 1 to 3.

Aluminum, sulfate, TDS, TSS and turbidity generally increased downstream from Red River to the Ranger Station. Alkalinity was variable, but overall showed a decreasing trend. In order to make quantitative comparisons of gains and losses to the river, analytical values were multiplied by the

Table 4

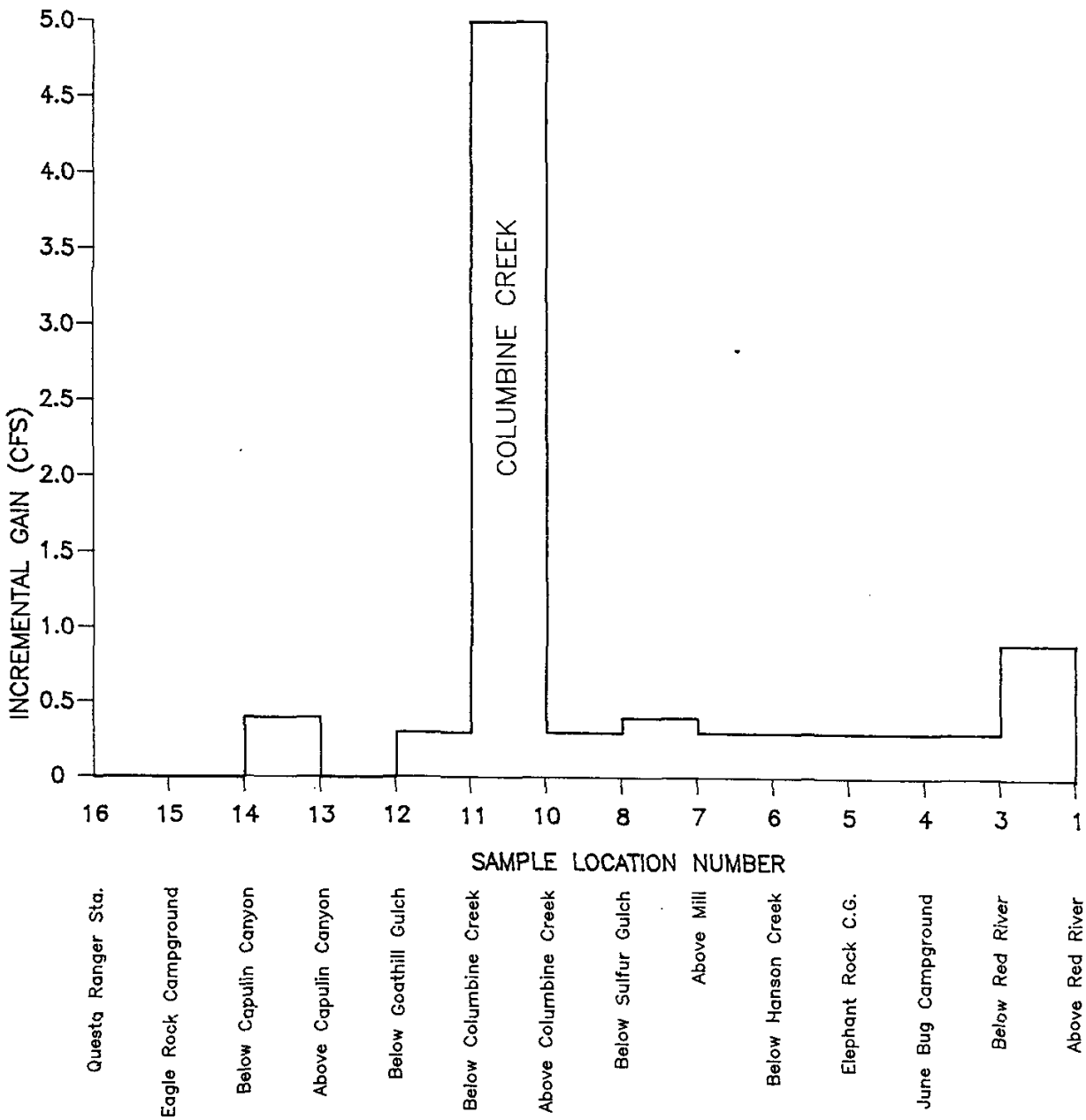
Stream flow surveys for RedRiver and proportionally calculated stream flows in cfs for 11-29-88.

| Water Sample Location | Survey Location | 11-4-65 | 10-25-88 | 11-29-88 (Calculated) |
|---|---|---|---|---|
| | Below Zwergle damsite | 11 | 11 | 7 |
| | Below Placer Creek | 9.94 | | |
| 1 | Red River (town) | | | 8.5 |
| | Below Red River | 16.3 | | |
| 5 | Elephant Rock C.G. | | 16 | 10.0 |
| 7 | Above Moly Mill | 16.2 | 20 | 10.6 |
| 10 | Above Columbine Creek | 18.2 | 19 | 11.3 |
| 11 | Below Columbine Creek | 23.6 | | 16.3 |
| 13 | Above Bear Canyon | | 29 | 16.6 |
| 16 | Ranger Station | 25.5 | 30 | 17(gauged) |
| 2 | Pioneer Creek | .81 | .78 | .4 |
| 9 | Columbine Creek | 5.29 | 6.0 | 4.5 |

FIGURE 3

# STREAM FLOW

INCREMENTAL GAINS
CALCULATED FOR 11-29-88



estimated stream flow at each sample location. The result is the mass rate of each parameter passing by the sample location, expressed as grams per second. These values are plotted on Plate 2. The magnitude of each line at any point expresses the total flow of a parameter in the river at that point. The slope of the line reflects the rate of input or removal of the parameter from the river.

The rate of constituent increase to the river can more readily be seen by plotting the incremental changes from location to location as histograms. Histograms for five stream factors are shown in Figures 4 to 8.

Incremental values for sulfate and TDS (g/sec) should always be positive, as no known mechanism for removal from the river was present at the time of the survey. At times during the year significant stream flow is lost to groundwater in the Molycorp mill and Columbine Park areas. However, it is doubtful that significant losses were occurring on the date of the survey. Apparent decreases of sulfate and TDS occurred in a few samples. These probably represent either analytical error or non-representative samples. Obtaining representative samples of well-mixed river water is difficult in areas of spring activity. Interpretation of these anomalies was made by comparison to samples up- and downstream from the affected value, and by comparison to similar sample runs made March 19, 1988 by David Shoemaker and March 14, 1989. Our estimates of the most probable values are used in the histograms. The adjustments redistribute, but do not change the total gain to the river.

Aluminum. Aluminum increased fairly steadily downstream. There were fairly sharp rises at Hanson Creek (8 percent of total gain), Goathill Gulch (8 percent) and Capulin Canyon (16 percent). However, by far the greatest part of the gain (45 percent) was from below Capulin Canyon to the ranger station. This value is possibly excessive as it may reflect aluminum precipitate which has been remobilized from the streambed.



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FIGURE 4

# ALUMINUM

INCREMENTAL FLOW WEIGHTED
GAINS AND LOSSES TO RED RIVER
NOVEMBER 29, 1988

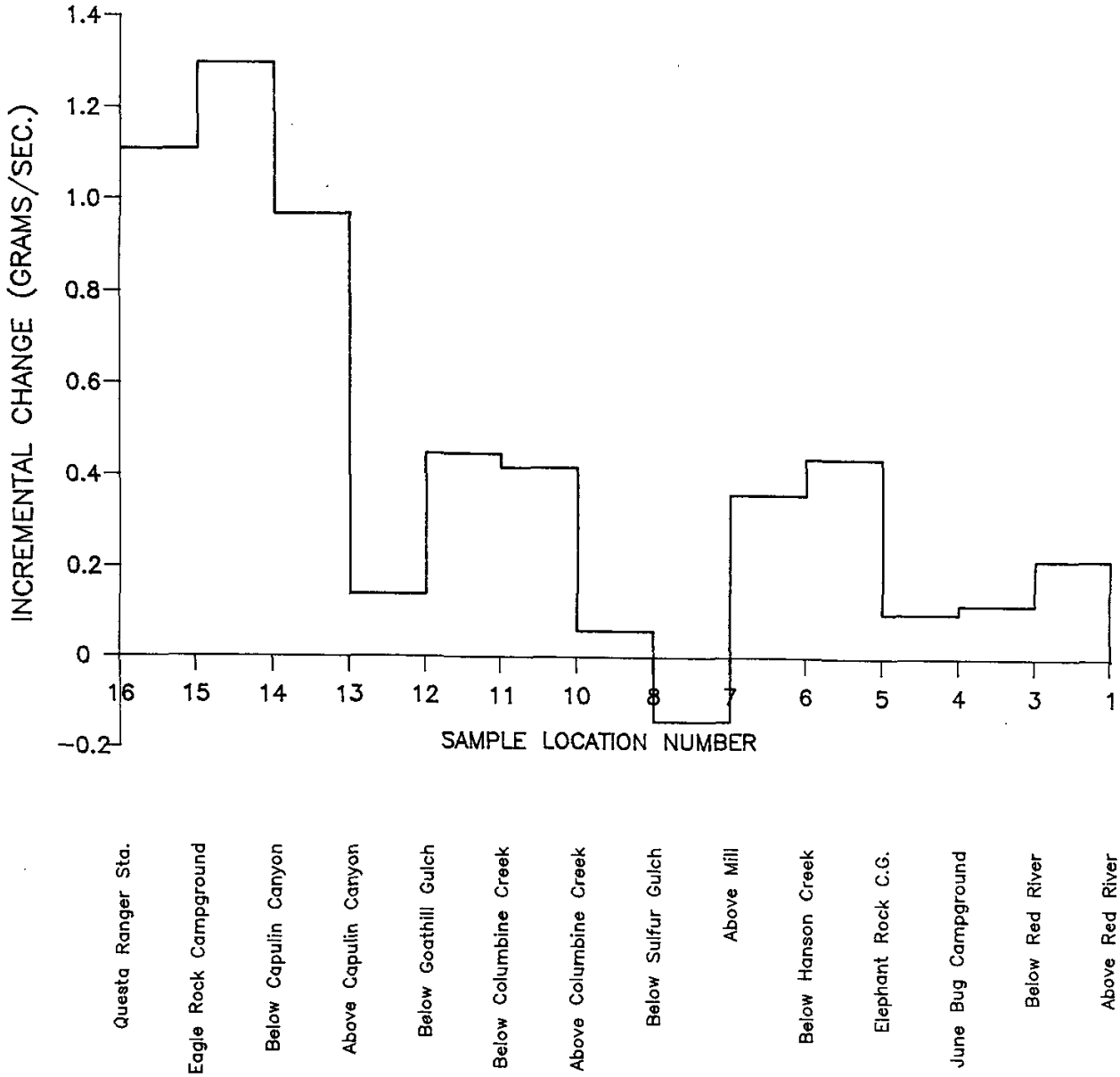


FIGURE 5

# SULFATE

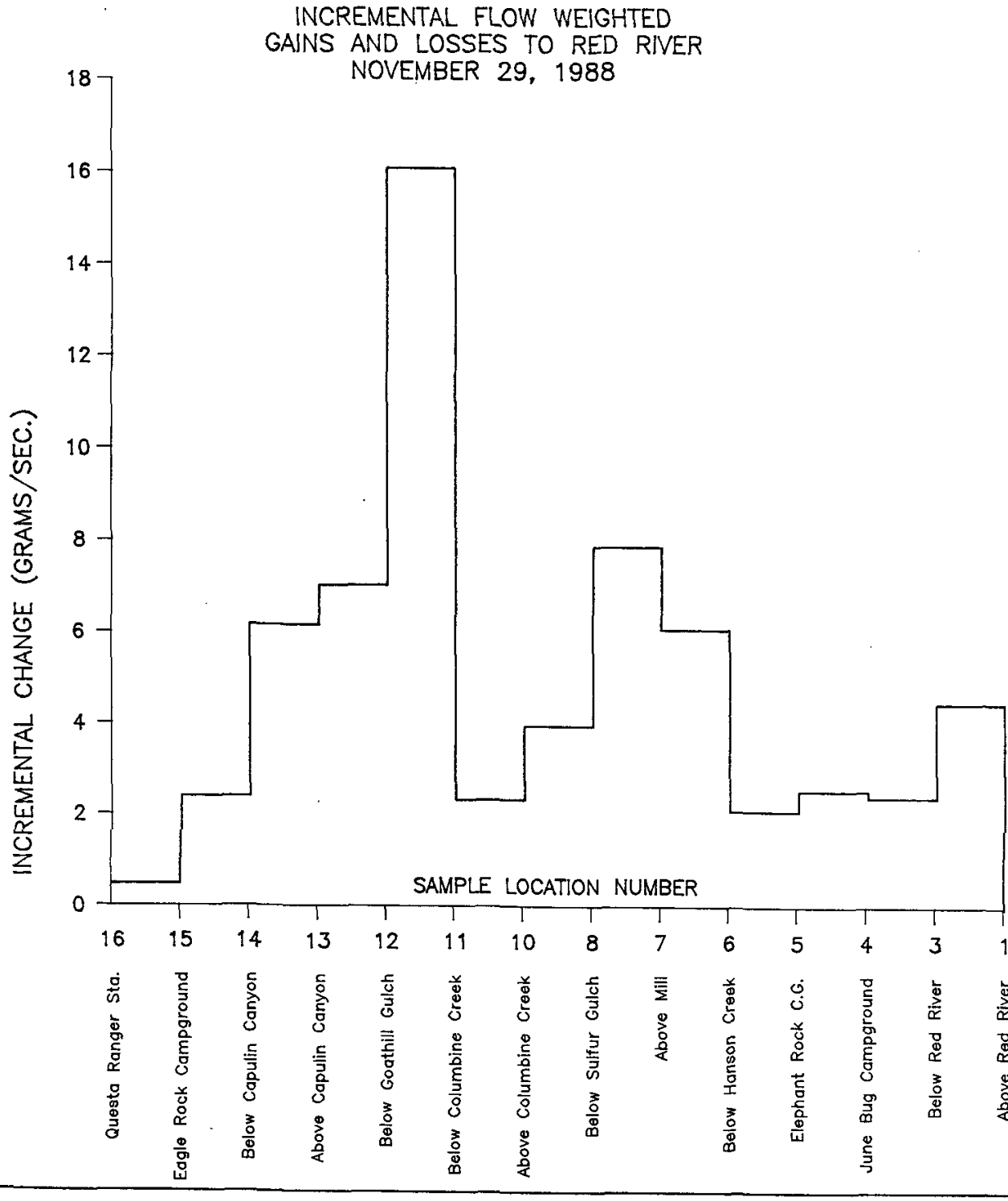


FIGURE 6

# TOTAL DISSOLVED SOLIDS

INCREMENTAL FLOW WEIGHTED
GAINS AND LOSSES TO RED RIVER
NOVEMBER 29, 1988

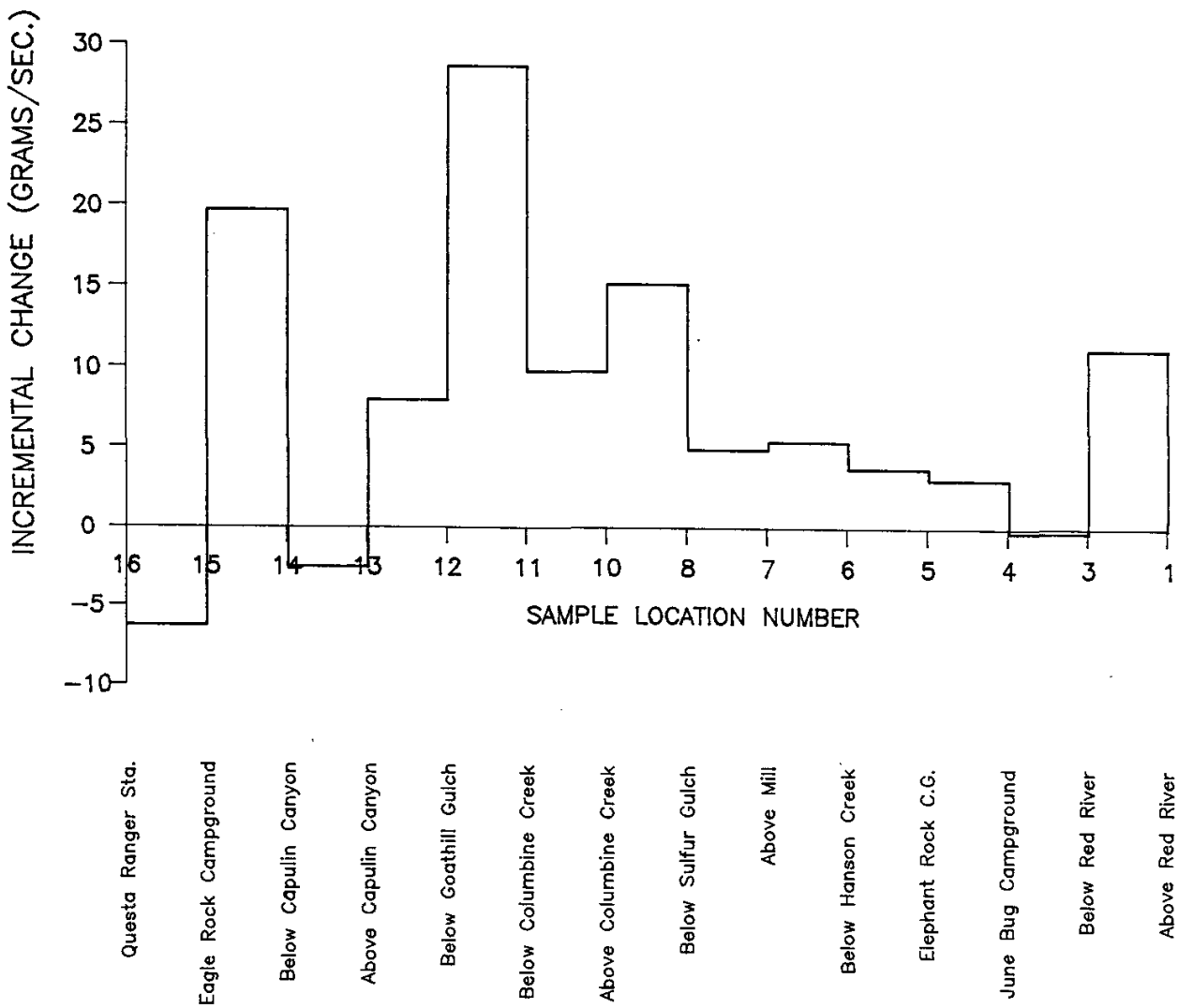


FIGURE 7

# TOTAL SUSPENDED SOLIDS

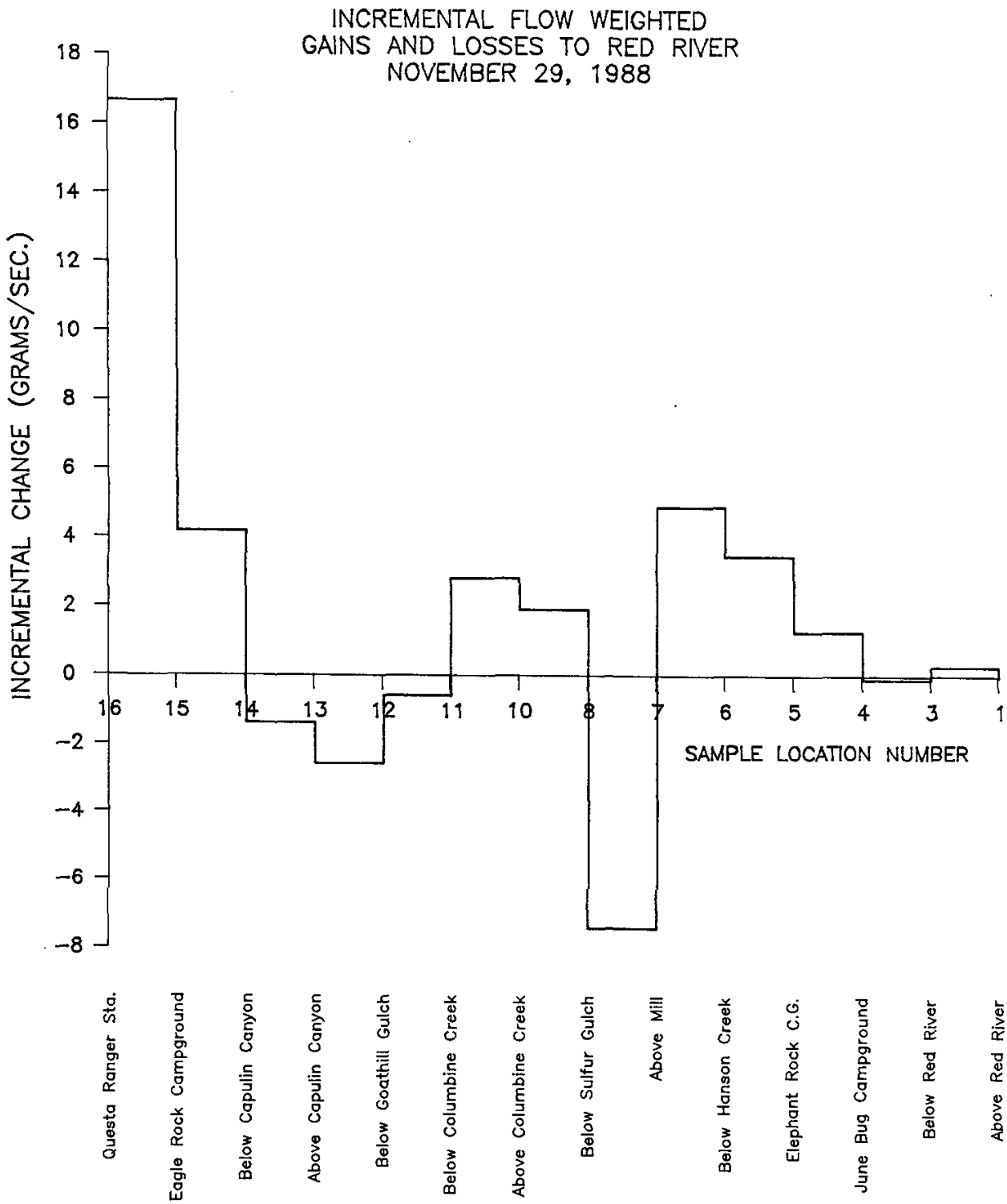
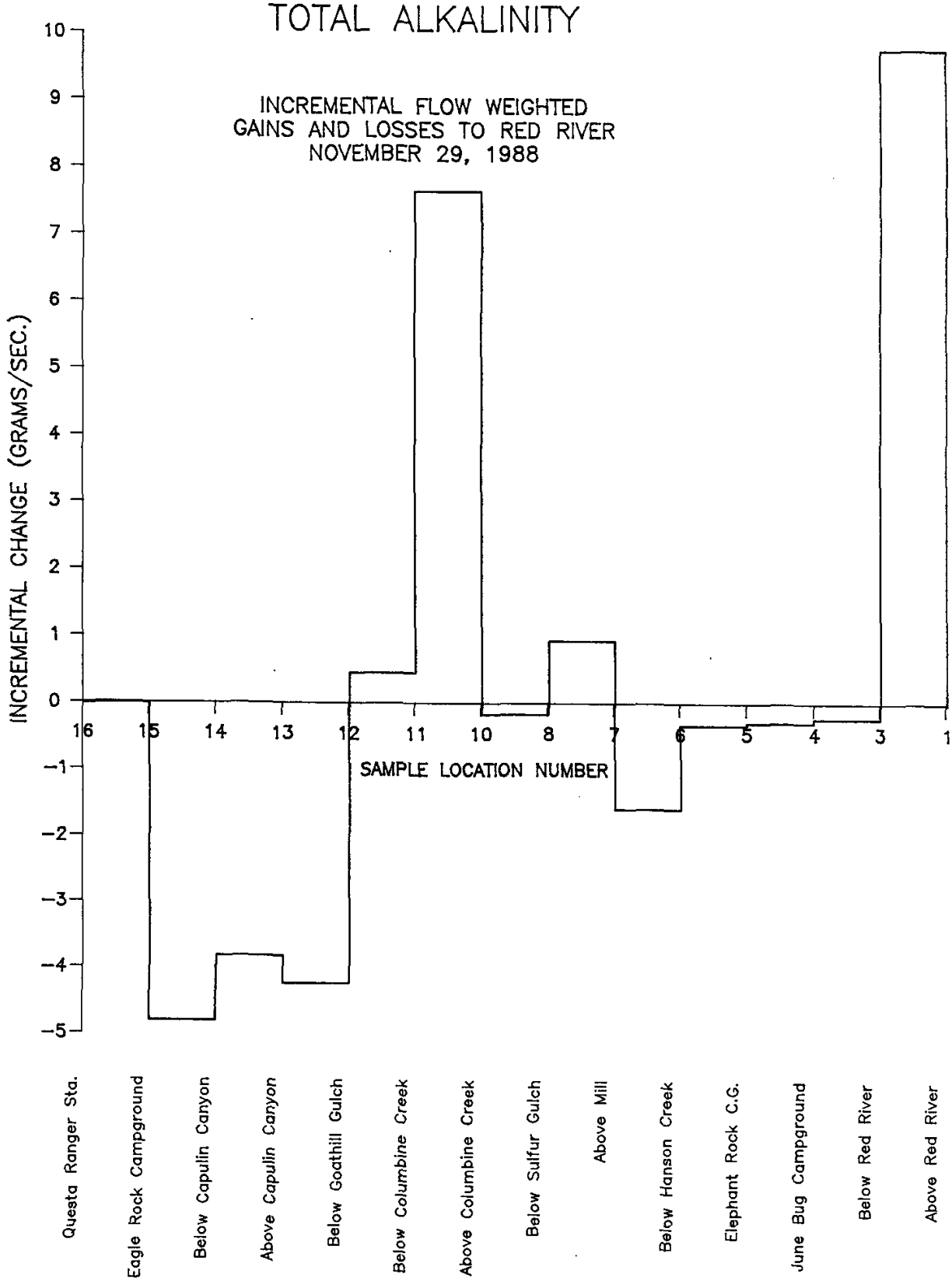


FIGURE 8

# TOTAL ALKALINITY



The indicated gains in aluminum correlate well with the location of acid springs in which aluminum precipitate was observed. Moreover, there is a particularly strong association of aluminum in river water with the pH of the springs. Only springs with pH 5.0 or lower input significant quantities of aluminum to the river. The largest gains are from downstream springs with pH as low as 3.5. The solubility relationships shown in Figure 1 indicate that aluminum is mainly transportable at pH values less than 5.0.

Sulfate. The distribution of sulfate gains to the river does not correlate proportionally with aluminum gains. Sulfate gain is informative, as it is a measure of the distribution of acid groundwater sources. The distribution of sulfate gains indicates that sources of acidic water are fairly extensive along the river. Observed pH and transportation of aluminum, however, are not always proportional to the sulfate content of the water. In particular, Goathill Gulch (sample 12) was responsible for an estimated 25 percent of the sulfate gain, but only 8 percent of the aluminum.

Total Dissolved Solids. Gains in total dissolved solids (TDS) agree somewhat with the pattern of gains in sulfate. This is to be expected, as roughly 60 percent of the gain in TDS is sulfate. Thus, TDS is also apparently controlled principally by stream accretion, except for one apparently high gain below Capulin Canyon.

Total Suspended Solids. Changes in total suspended solids (TSS) vary widely over the study area. The largest gains agree with the gains in aluminum at Hanson Creek and at the ranger station. The sharp loss below the Molycorp Mill is problematical, although it is present in both turbidity and suspended aluminum (Plate 1). Possibly, solids are settling out at Molycorp's diversion dam and other low-velocity stream reaches. Speculatively, the decrease below Capulin Canyon may also reflect lower stream velocity.



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Alkalinity. Total alkalinity (as $CO_3^{=}$) also varies considerably, although there is a general, decreasing trend of incremental changes. This is to be expected, as acid waters react with and neutralize alkaline components downstream.

Bicarbonate is the principal alkaline ion. It is principally atmospherically derived, and thus tends to replenish downstream, buffering the pH at around 8.0. The decline in alkalinity reflects the input of sulfuric acid overwhelming the natural buffer. The declines occur at roughly downstream locations from Hanson Creek, Goathill Gulch and Capulin Canyon with a one-half to one-mile lag indicating that neutralization is not instantaneous. The cause of the sharp gain at Red River has not been determined. Perhaps a man-made source of alkalinity is present in the town area.

Turbidity (Jackson Turbidity Units). Turbidity was not converted to flow-compensated values, as it is measured in light absorption units rather than concentration. However, it is useful in that the turbidity plot in Plate 1 closely follows suspended aluminum and TSS, confirming that the most important sites of clouding occur below Capulin Canyon, at Goathill Gulch, and at Hanson Creek.

Other Metals and Fluoride. Samples collected during the November 29, 1988 river survey were also analyzed for several other trace metals and fluoride.

Cadmium, barium and molybdenum concentrations were below the detection limit in all samples for the analytical methods used.

The lead concentration was below the detection limit in all samples above Capulin Creek and was reported at 0.09 mg/l downstream from Capulin Creek to the Ranger Station.

Copper concentrations remained nearly constant at .01 mg/l, suspended and .02 mg/l, dissolved from the Town of Red River to above Capulin Creek. Below Capulin Creek the copper concentration was reported at .05 mg/l, suspended and .02 mg/l, dissolved.



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Concentrations of iron, zinc, manganese and fluoride are shown on Plate 3. There was a general increase in a downstream direction in the concentration of all of these elements. The pattern of increase was similar to that of aluminum, with the larger incremental increases occurring downstream of Capulin Canyon. Such adds evidence of the high leaching activity in the mountain slopes above the lower stream reach even though there is evidently only a small ground-water flow.

Most of the iron concentration is suspended matter (1.95 mg/l at the Ranger Station compared to 0.27 mg/l dissolved). The significant fluctuation in iron concentration along the stream is attributed to oxidation and precipitation. Red staining by iron oxide is present along several reaches of Red River.

The zinc concentration at the Ranger Station is composed of .08 mg/l suspended matter and .27 mg/l dissolved matter. A similar ratio was found in samples from most other stations.

Manganese concentrations were largely dissolved matter.

Discussion

For the purposes of discussion, we have divided the length of the Red River studied into four segments.

1. Red River town to Molycorp mill area (samples 1 - 7). This reach is characterized by low accretion to the river and widespread scar and mudflow areas on the north. Pioneer Creek (sample 2), Mallette Creek and Bitter Creek are live tributary streams in this reach. Springs below Hanson Creek are the only significant source of acidic water and aluminum. Mildly acidic water enters the river in the town area, but no precipitate was observed there.

Gains of aluminum and sulfate to the Red River above the mill are small, about 22 percent and 28 percent of the total, respectively, although 45 percent of the length of the river studied falls in this reach. It is interpreted that the scar areas in this reach generate relatively little acid. There is very little spring activity in this area, indicating that infiltration and ground water flow are low. Hanson Creek is



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somewhat an exception. It flows 20 to 30 gpm at pH 3.5 over much of its length. The spring complex at the mouth of Hanson Creek added about 8 percent of the aluminum and 3 percent of the total sulfate gain of the Red River for the date of the survey.

2. Mill area to below Columbine Creek (samples 8 - 11). This area contains the upstream mine dumps. There are a few acidic springs, notably at Sulfur Gulch, but little aluminum precipitate. Columbine Creek (sample 9) is near the end of this reach. Chambers Spring on the northeast discharges a small flow of moderately alkaline water to the river. The river was relatively clear over this reach.

The reach from the mill to below Columbine Creek contributed approximately 22 percent of the sulfate gain but only 9 percent of the aluminum gain to the river. Apparently, the dumps and the small underlying altered area along this reach generate a small amount of slightly acidic water (pH>5.0), which does not transport aluminum to any significant extent. Total suspended solids, suspended aluminum and turbidity all decrease in the mill area. Possibly the Molycorp diversion dam and other low velocity areas act as settling basins for solids. Alternatively, the sample may not have been representative of well-mixed river water.

3. Above Goathill Gulch to below Capulin Canyon (samples 12 - 14). This area contains two strongly acidic drainages. Acidic (pH<5.0) springs occur along the river, and aluminum precipitate is observable and increases steadily downstream.

The greatest indicated gains in sulfate and TDS occurred at Goathill Gulch (24 percent and 28 percent, respectively). However, indicated aluminum gain is moderate at Goathill Gulch (8 percent of the total gain). TSS and turbidity dropped and alkalinity rose. Many of the springs in this area were close to or above pH 7. It appears that conditions for transport of significant amounts of aluminum to the river (that is, low pH) are not present, despite the presence of acidic creek water in



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Goathill Gulch. Possibly, the creek water is being sufficiently diluted in the subsurface that comparatively little aluminum remains in solution to reach the river.

One sample from Goathill Gulch, collected March 19, 1988 was observed to be pH 3.6 with 216 mg/l Al. This somewhat contradicts the discussion above. Possibly the spring flow is too small to be a significant contributor.

Capulin Canyon is somewhat enigmatic. The reach that contains Capulin Canyon has the highest indicated aluminum gain observed (18 percent). However, the indicated sulfate gain is comparatively low. TDS and TSS show losses. Alkalinity drops greatly, indicating acid input. These data resemble the pattern found between Capulin Canyon and the ranger station more than the Goathill Gulch area.

A significant part of the indicated anomalous concentrations along this reach may be the result of sampling bias.

4. Below Capulin Canyon to Questa Ranger Station. (Samples 15-16). In this reach the pH of the river dropped to as low as 6.8, owing to the presence of many small acidic springs (pH 3.5 to 4.5). The greatest increase in cloudiness of the river was in this reach.

The downstream segment of the river extending to the ranger station is relatively short (.85 mile or 8 percent of the length of the river studied) however, by far the greatest gains in aluminum (44 percent) TSS (60 percent) and trace metals occurred in this reach. Sulfate and TDS gains were comparatively low (estimated at 4 and 20 percent, respectively). Accretion to stream flow was low here as well (Figure 3). Taken together, these observations indicate that a small flow of very low pH water carries concentrated amounts of metals to the river. Many small springs were observed in this area, mostly at pH 3.5 to 4.5. The solubility of aluminum increases 50-fold between pH 5.0 and 4.0, (Figure 1) more than compensating for the low ground-water flow.



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The increase in aluminum in the river is mainly in the suspended fraction, which is reflected in the increase in TSS. This reach is the only segment of the river on November 29, 1988 in which river waters were saturated with respect to aluminum.

The source of aluminum accretion from this segment is in all likelihood the small altered area which lies above the river on the north. Conditions here seem to favor generation of low pH waters: The altered area is rocky, fractured and not deeply weathered, which promotes infiltration of precipitation. The area is close to the river and no live streams are present. Consequently, the opportunity for dilution is diminished. Also additions of aluminum and acid in the reaches upstream have raised the river to near saturation level, so that the large additions in the lower reach must precipitate rather than being diluted in solution.

Analysis of Goathill Gulch and Capulin Canyon. Goathill Gulch and Capulin Canyon, combined, contributed an indicated 26 percent of the aluminum and 34 percent of the sulfate observed in the river at the ranger station on the date of the sample run. A major portion of this gain is attributable to natural sources. This is indicated by several observations. The area of the two canyons contains the largest and probably most sulfidized of the natural scars. The observed aluminum and sulfate gains are not unexpected, considering the size and intensity of the scar in the mine area. The scar area is roughly 950 acres, compared to 185 acres of dump material. The dumps would have to have five times the generating capacity of the scar material to be producing an equal amount of aluminum and sulfate as the scar area.



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It is possible that conditions somewhat like this existed when the dumps were first placed. The maximum rate of infiltration, acid generation and aluminum leaching probably occurred shortly after the dumps were developed, in the 1960's. With time, the openings in the dump material should tend to become filled and sealed with clay, and the dump areas can be expected to become similar in discharge characteristics to the natural scars.

Additionally, adjacent stream reaches not containing dumps were observed to be generating copious aluminum precipitate; while the largest dumps, between the mill and Columbine Creek, generate little observable aluminum and sulfate.

Flowing streams exist for some distance downstream of the mine dumps at the heads of Capulin and Goathill canyons. Generally, the water all seeps into the ground at some distance above the river. Calculations were made of the aluminum and sulfate flows in the creeks (Table 5). The flow in Goathill Canyon was measured with a V-notch weir on April 14, 1989 and a sample of water was analyzed. The flow in Capulin Canyon was measured on May 22, 1989. Analytical results have not been received for samples collected at that time. The values obtained by analysis of a sample of Capulin Canyon water collected by Mr. David Shoemaker on March 15, 1988 were used for calculation.



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Table 5

Comparison of mass loadings of aluminum and sulfate in Goathill Gulch, Capulin Canyon and the Red River.

| Discharge Parameter | Stream Flow Below Dumps: Goathill Gulch | Capulin Canyon | Accretion to: River @ GH & Capulin | @ Ranger Station |
|---|---|---|---|---|
| | 4-14-89 | 5-22-89 | 11-29-88 | 11-29-88 |
| Flow (cfs) | .08 | .051 | | 17.0 |
| pH | 3.00 | 3.00 | | 7.10 |
| Al (mg/l) | 601. | 655. | | 11.5 |
| $SO_4$ (mg/l) | 5820. | 8980. | | 137. |
| Al (g/sec) | 1.36 | .95 | 1.56 | 5.53 |
| $SO_4$ (g/sec) | 13.2 | 13.0 | 29.3 | 65.91 |

The indicated gain in sulfate in Red River in the reach extending past the Goathill and Capulin drainageways was, on November 29, 1988, essentially equal to the mass loading in the two streams below the dumps (within probable sampling error). The indicated gain of aluminum in the river was approximately 67 percent of the loading found in the upper streams. It is possible that the indicated difference in aluminum is due to attenuation of the aluminum in the groundwater flow downstream of the flowing streams or that the full impact of the stream loading has not as yet reached the river because of the low groundwater velocity. It is more likely that the aluminum in the streams is fully impacting on the river and that the apparent difference in mass loading was due to sampling bias.



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If, hypothetically, 50 percent of the aluminum and sulfate gains from the two canyons were generated by the dumps, this would be equivalent to only 13 percent of the aluminum and 17 percent of the sulfate observed at the ranger station on the date of the survey. It follows that over a considerable range of possible rates of mobilization of aluminum and sulfate from the dumps, the effect observed in the river would be small compared to the long- and short-term variability inherent in the active natural sources of aluminum and sulfate.

Most of the acidic drainage from Sulfur Gulch, which has an area comparable to that of Goathill Gulch, is diverted by the mine workings and no longer reaches the river. This diversion offsets a substantial portion and conceivably all of any increased acidic drainage that may be currently attributable to the mine dumps.

Temporal Variability of Mass Loading. There are significant variations over time in both concentration and total discharge of aluminum and sulfate in the Red River. Analysis of the available data, which is shown in Table 6, has led to development of reasonable correlations between aluminum and sulfate variations and variations in surface and groundwater flow.

The primary controls on water chemistry are the quantity and source areas of surface and groundwater discharge. Stream flow resulting from snow melt at higher elevations and south of the river is relatively dilute. Stream and groundwater flow from lower, altered areas has comparatively high concentrations of dissolved constituents. Increases in streamflow principally result from surface runoff. As the surface runoff is comparatively dilute, increased stream flow generally causes a decrease in aluminum and sulfate (and other) concentrations simultaneously with an increase in total mass loading.



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Table 6

Aluminum and Sulfate Discharge past the Questa Gauging Station for Dates from 1987 to 1989

| Date | Streamflow (cfs) | $SO^4$ (mg/l) | Al (mg/l) | $SO^4$ (g/sec) | Al (g/sec) | Comments |
|---|---|---|---|---|---|---|
| 2-27-86* | 17 | 123 | 3.4 | 59 | 1.6 | Low stable stream flow |
| 8-18-86* | 42 | 105 | 3.34 | 125 | 4.0 | Moderate stable stream flow |
| 8-19-86* | 40 | 115 | 3.26 | 130 | 3.7 | Moderate stable stream flow |
| 8-19-86* | 40 | 160 | | 182 | | Questionable analysis |
| 8-20-86* | 38 | 118 | 3.41 | 127 | 3.7 | Moderate stable stream flow |
| 11-12-87 | 21 | 178 | 5.7 | 106 | 3.4) | Low slowly declining flow-decrease |
| 11-20-87 | 19 | 152 | 3.7 | 82 | 2.0> | in $SO^4$ indicates declining gr.water |
| 11-25-87 | 18 | 139 | 3.9 | 71 | 2.0) | Al probably precipitating |
| 1-05-88 | 8-19 | 186 | 13.4 | 100 | 7.2 | Sudden flow increase-Al.remobilizing |
| 2-27-88 | 23 | 246 | 6.0 | 160 | 3.9 | Low stable flow |
| 3-14-88 | 21 | | 6.4 | | 3.8 | Low stable flow |
| 3-19-88 | 21 | 185 | 8.0 | 110 | 4.8 | Low stable flow |
| 5-16-88 | 51 | 80 | 10.6 | 116 | 15.3 | Increasing flow-Al.remobilizing |
| 6-06-88 | 74 | 54 | 3.4 | 113 | 9.2 | Steady high flow |
| 7-26-88 | 37 | 278 | 1456.0 | 292 | 1528 | Probable short thunderstorm |
| 9-13-88* | 138 | 120 | 17.0 | 470 | 67 | Thunderstorm |
| 9-20-88* | 57 | 85 | 2.0 | 137 | 3.2 | Moderate stable flow |
| 9-26-88* | 47 | 96 | 2.1 | 128 | 2.8 | Slowly declining flow |
| 10-14-88 | 39 | 110 | 5.4 | 127 | 6.0 | Slowly declining flow |
| 10-18-88 | 32 | 130 | 4.3 | 118 | 3.9 | Low stable flow |
| 10-21-88 | 32 | 126 | 3.8 | 114 | 3.5 | Low stable flow |
| 10-25-88* | 30 | 118 | 1.3 | 131 | 1.1 | Slowly declining low flow |
| 11-29-88 | 14-17 | 137 | 11.5 | 66 | 5.5 | Small sudden flow increase |
| 4-14-89 | 88 | 77 | 3.3 | 192 | 8.2 | Increasing flow |
| 4-18-89 | 99 | 68 | 1.4 | 191 | 4.6 | Increasing flow |

* From Smolka and Tague, 1989

Relative loadings of aluminum and sulfate, measured at the Questa Ranger Station vary substantially. The data indicates that aluminum decreases relative to sulfate during declining and stable stream flow conditions. Aluminum increases relative to sulfate when stream flow rapidly increases. Apparently, gibbsite precipitated during low stream flow settles to the streambed and is remobilized by the increased velocity and turbulence of rising stream flow. It appears that even small increases in stream flow are sufficient to remobilize significant amounts of the precipitate. It is probable that stream flow of 200 cfs or greater would be sufficient to fully scour the stream bed; however, the data was insufficient to confirm this.

Sulfate is fully dissolved in the river. Variability in sulfate is caused only by variation in the rate of input to the stream system. Changes in sulfate loading, therefore, are not as pronounced as aluminum changes, except during thunderstorm flood flows.

Changes in the composition and flow of groundwater accreting to the river are generally gradual over a period of time. Short- term changes in aluminum to sulfate ratios in the river as a result of change in groundwater flow are probably insignificant compared to the effects of surface tributary variation.

The data indicates that except for thundershower-type events, the highest aluminum and sulfate loadings occur during the spring snow melt period at the lower elevations. The data also strongly indicates that there may generally be a significant decrease in groundwater flow from the altered areas in the late fall and early winter months. The data was insufficient for analysis of loadings during the winter months.

Comparison of the various sampling surveys of Red River indicates a generally good consistency of results. Generally the data indicated that concentrations progressively became greater in a downstream direction and that when concentrations were relatively high or low at one station they were also



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relatively high or low at the other stations. Occasional erratic data points occur in most of the stream surveys. Such points varied from survey to survey. It is believed that a least part of the apparent discrepancy was caused by sampling bias. In particular since most of the aluminum is in the suspended fraction, it is possible that the collected samples captured varying amounts of the precipitate depending on whether the sample was collected from relatively quiescent or highly turbulent areas or from near the surface or near the stream bottom.

In order to minimize sampling bias it is proposed that all future samples be consistently taken from the portions of stream reaches with high velocity and turbulent flow, and from about the midpoint of stream depth. For consistency the samples for each run should be collected from the identical locations to the extent practical.

Much of the analysis in this report was based on data from a stream survey conducted on November 29, 1988. On this date the average river flow past the ranger station was gauged at 17 cfs. On both the preceding and following days the average river flow was 14 cfs. The low river flow during this period indicates that accretions of flow to the river were primarily from ground water and perennial tributaries.

On the basis of our analysis, it is our opinion that groundwater flow from the hydrothermal scar areas was probably below the annual average on the survey date, owing to seasonal variability. Consequently, accretion rates of aluminum and sulfate were probably also below average.

Nevertheless, the concentration of aluminum (11.5 mg/l) was above average and the loading of aluminum (5.54 g/sec) near or slightly above the estimated annual average at the ranger station. The short-term increase in stream flow from 14 cfs to 17 cfs may have been sufficient to mobilize a significant amount of aluminum precipitated from the streambed.



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Similarly, the combination of low stream flow and low groundwater flow resulted in a sulfate concentration (13.7 mg/l) that was near average at the ranger station, but with a below (66.1 g/sec) average loading.

As stated, there appears to be a high variability in the daily discharge of aluminum and sulfate by the Red River. Therefore, our estimates of contributions to the river from various sources are somewhat tenuous. Continuation of sampling and analysis, as outlined in the recommendations, will make it possible to better define the average discharge and variation of aluminum and sulfate in the river. This will lead to more precise determination of the relative and absolute contributions from Goathill Gulch and Capulin Canyon.

Summary

In the preceding pages it has been shown that large gains in aluminum, sulfate and other stream factors occur in the Red River from the town of Red River to the Questa Ranger Station. The details of the mechanism of aluminum hydroxide accretion in the river are still uncertain. However, a tentative model can be made:

. Aluminum is leached from sulfidized country rocks and transported to the river by sulfuric acid which is created by the breakdown of pyrite.

. Aluminum is transported in the subsurface and in small streams at concentrations up to about 1000 mg/l and pH 2.5.

. Dilution of the aluminum laden water occurs by intermingling with groundwater above the river. This reduces the composition of the aluminous water to about 200 mg/l Al or less at pH 3.5 to 5.0.

. Aluminum emerges at springs along the river. Increase of pH to near neutral causes precipitation of gibbsite [$Al(OH)_3$].



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. The greatest concentration of gibbsite occurs where the pH of the acid spring water is lowest. This occurs between Capulin Canyon and the Questa Ranger Station. Apparently, the spring water is relatively undiluted in this reach.

. Natural sources can account for most of the aluminum and sulfate gains to the river. Thirteen percent of the total aluminum and 40 percent of total sulfate are estimated limits for contributions by dump material for the date of the study. This is partially offset by the diversion of the Sulfur Gulch acidic drainage, which no longer reaches the Red River. Contributions may vary seasonally.

. Long term variations in springs, controlled by precipitation cycles, are possibly responsible for observed increases in sulfate and aluminum hydroxide in the Red River in recent years. Long term, systematic sampling of the Red River is needed to establish this relationship conclusively.

Recommendations

The analysis given above indicates that the Molycorp mine dumps may be contributing an estimated 13 percent more or less of the total aluminum in the Red River for the date of the survey. If the aluminous, acidic water in the creeks were diverted, the effect on the river would probably be small. However, the current practice of impounding the creeks in Goathill Gulch and Capulin Canyon appears to be an effective measure of at least distributing over a period of time the amount of aluminum from both mine and natural sources reaching the river. The ponds redirect the creek water to the subsurface where natural dilution by groundwater reduces the aluminum concentration (but probably not total mass flow).

The results of this investigation are tentative. In large part this is because of several limitations to the present data base. One drawback is that groundwater accretion rates to the river are at the limit of precision of standard stream gauging field methods. In addition, the spacing of measurement stations in the available U.S.G.S. data is too



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great to clearly define local accretion rates. A second problem is that large changes in stream chemistry occur from sample to sample at the present data spacing. In many instances, it is not possible to determine if an apparent, abrupt change is caused by real change in the river, by sampling technique, analytical error or by inhomogeneity of the river water. A major parameter of concern is the stream flow of Capulin Canyon and Goathill Gulch. If the creek flow diminishes seasonally in proportion to the river system in general, our estimates of potential aluminum impact might by reduced significantly. Finally, lack of historical chemical data make it impossible to compare current levels of aluminum with historical trends.

Several measures can be carried out at modest expense that will lead to a more precise, quantitative determination of the effects of the mine dumps on the Red River:

1. Carry out periodic geochemical sampling of the Red River and tributaries. Sampling for two years at the intervals tabulated below should provide the necessary background data to closely determine short-and long-term trends in the Red River, Goathill Gulch and Capulin Canyon

| | |
|---|---|
| Questa Ranger Station | Weekly |
| Above Goathill Gulch | Monthly |
| (2 samples approximately 50 feet apart) | |
| Below Capulin Canyon | Monthly |
| (2 samples approximately 50 feet apart) | |
| Goathill Creek | Monthly |
| Capulin Canyon Creek | Bimonthly |
| River Survey (16 locations) | Quarterly |

The majority of the sampling can be carried out by Molycorp staff. Samples should be collected at locations selected on geologic, hydrologic, and topographic criteria. Measured parameters should include Al, $SO_4^{=}$, alkalinity and turbidity. Analysis of trace metals is probably not necessary.



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2. Gauge the stream flow at each station simultaneously with the quarterly sample run. Several series of stream flow measurements would provide for averaging of gains and loss and result in much greater accuracy than obtainable by one run. Installation of additional gauging stations has recently been proposed by the U.S. Geological Survey. Such stations would decrease the need for stream gauging during sampling runs.

3. Installation of simple V-notch weirs in Capulin Canyon and Goathill Gulch would facilitate collection of accurate data regarding the variation of flow in the creeks.



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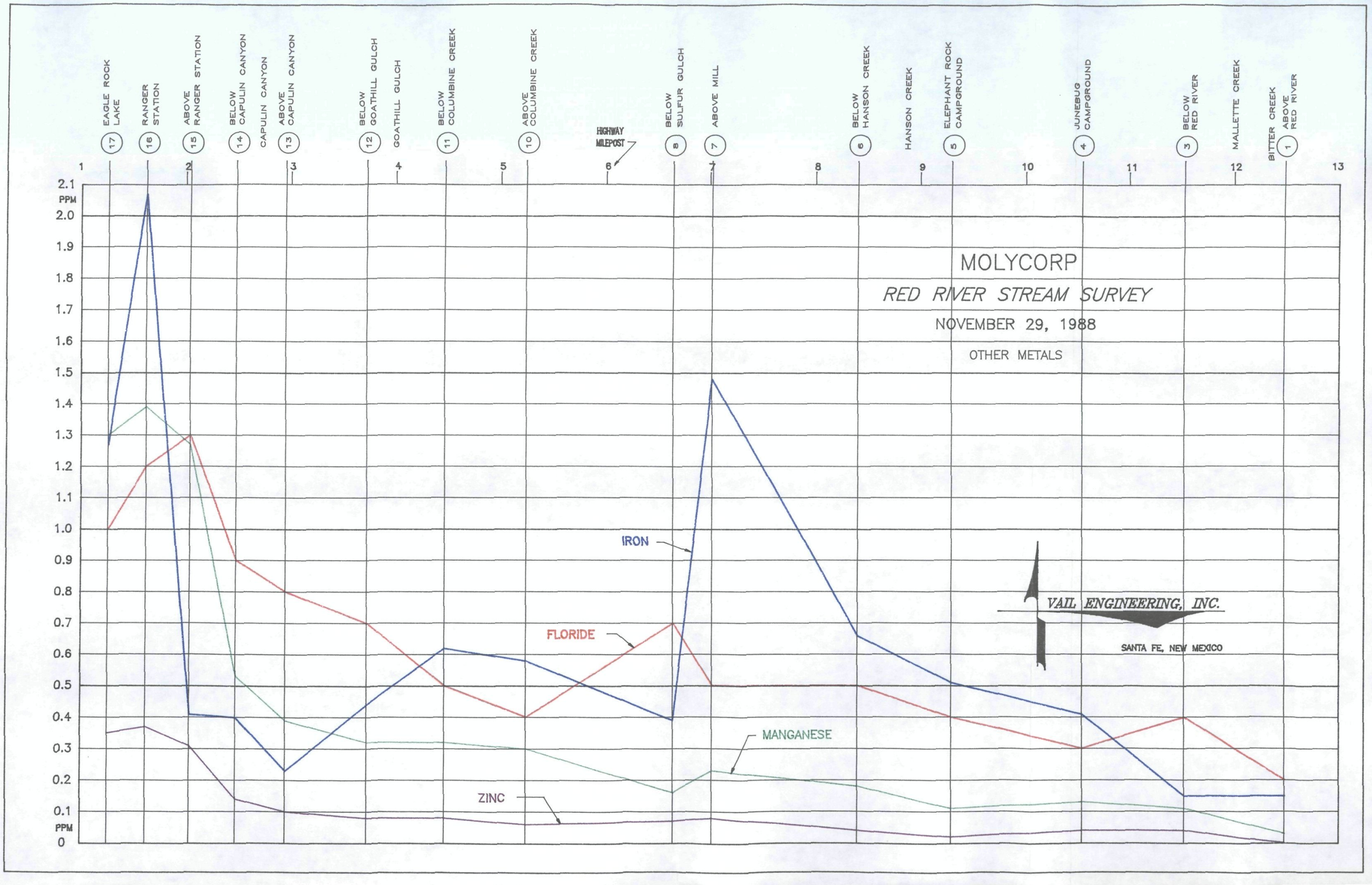
MOLYCORP
RED RIVER STREAM SURVEY
NOVEMBER 29, 1988
OTHER METALS
VAIL ENGINEERING, INC.
SANTA FE, NEW MEXICO
EAGLE ROCK LAKE
RANGER STATION
ABOVE RANGER STATION
BELOW CAPULIN CANYON
CAPULIN CANYON
ABOVE CAPULIN CANYON
BELOW GOATHILL GULCH
GOATHILL GULCH
BELOW COLUMBINE CREEK
ABOVE COLUMBINE CREEK
HIGHWAY MILEPOST
BELOW SULFUR GULCH
ABOVE MILL
BELOW HANSON CREEK
HANSON CREEK
ELEPHANT ROCK CAMPGROUND
JUNEBUG CAMPGROUND
BELOW RED RIVER
MALLETTE CREEK
BITTER CREEK
ABOVE RED RIVER
IRON
FLORIDE
MANGANESE
ZINC
PPM
file: MCRRALB