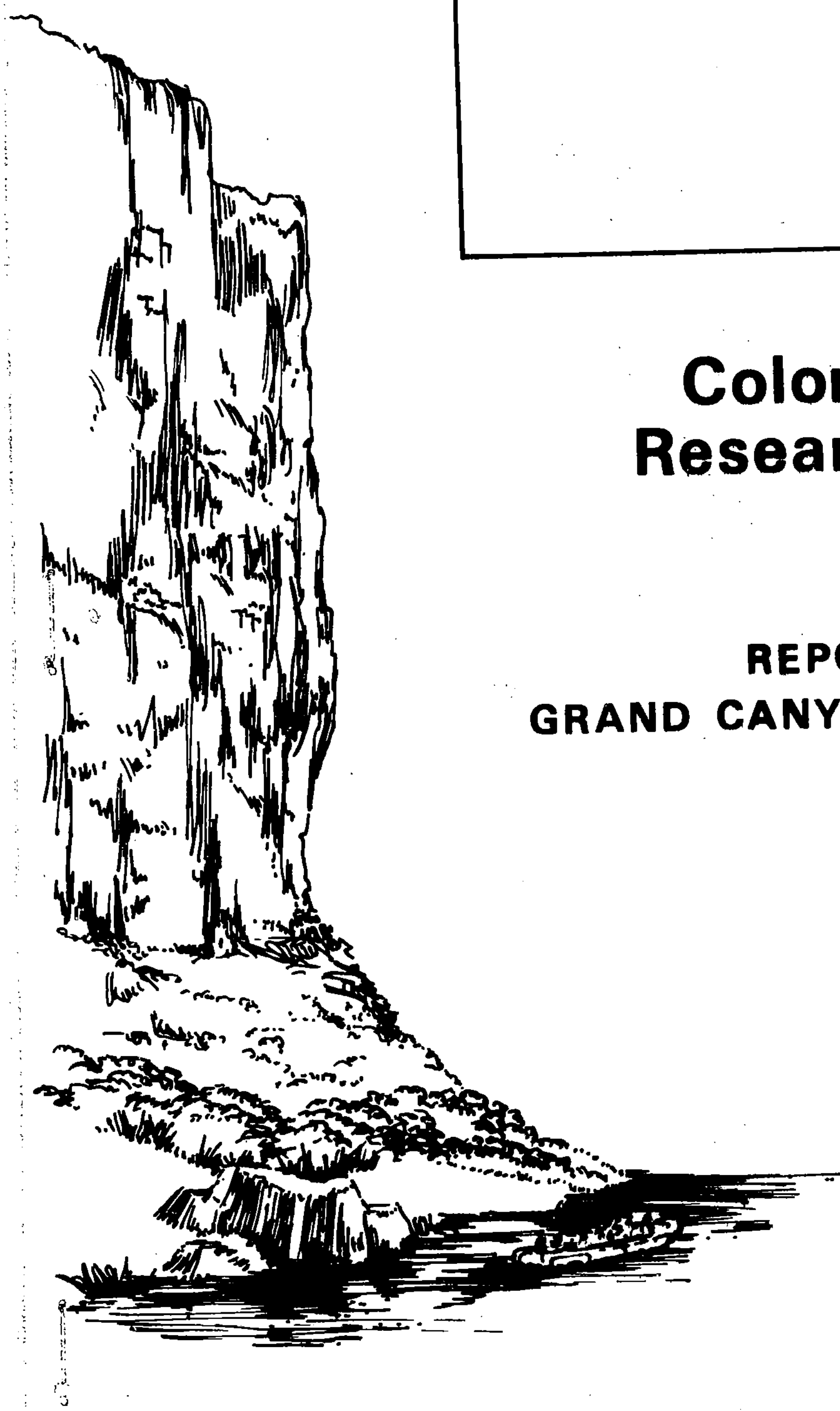

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The Colorado River Research Program was initiated by the National Park Service in 1974 to secure scientific data to provide a factual basis for the development and the implementation of a plan for appropriate visitor-use of the Colorado River from Lee's Ferry to Grand Wash Cliffs and for the effective management of the natural and cultural resources within the Inner Canyons. The intensified research program consists of a series of interdisciplinary investigations that deal with the resources of the riparian and the aquatic zones and with the visitor-uses including river-running, camping, hiking, and sight-seeing of these resources, as well as the impact of use and upstream development upon canyon resources and visitor enjoyment.

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LIMNOLOGIC STUDIES ON THE COLORADO RIVER FROM
LEES FERRY TO DIAMOND CREEK

Gerald Cole and Dennis M. Kubly

Colorado River Research Program Final Report
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LIMNOLOGIC STUDIES ON THE COLORADO RIVER AND ITS MAIN TRIBUTARIES FROM LEE'S FERRY TO DIAMOND CREEK INCLUDING ITS COURSE IN GRAND CANYON NATIONAL PARK

Submitted to

GRAND CANYON NATIONAL PARK

NATIONAL PARK SERVICE

DEPARTMENT OF THE INTERIOR

by

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ABSTRACT

Data were collected on 5 research trips from Lee's Ferry (Mile 0) to Colorado River Mile 225 during 1975-76. The river is cold (44.6-50°F) and transparent at Lee's Ferry, but attains at least 59.4°F at Mile 225 and becomes extremely turbid when the Paria and Little Colorado are flooding. The latter contributed as much as 827 grains/gal of suspended solids and reduced the mean vertical light penetration from 75% to less than 0.001% per yard in the main stream. Some indices of salinity, specific conductance, total dissolved solids (TDS), sum of meq/liter of the 7 principal ions, and ionic strength averaged 643 ppm (37.3 grains/gal), 940 µmhos/cm at 25°C, 18.8 meq/liter, and 0.0138, respectively. Computed TDS values were 0.88 x those found by evaporation. The lowest mean values occurred at Mile 0 with a 3% increase in salinity at Mile 225; some intermediate stations had the highest values because salt concentrations from the Little Colorado were diluted later by downstream tributaries. Factors useful for converting conductance of Colorado water to TDS, sum of meq/liter and ionic strength are: 0.68, 0.02, and 1.46 x 10^{-5}, respectively.

Ionic abundances in terms of meq were

$$SO_4^{=} > CO_3^{=} Cl^{-} \text{ and } Na^{+} > Ca^{++} > Mg^{++} > K^{+}.$$

Rarely calcium slightly surpassed or was subequal to sodium. The latter was especially abundant below the Little Colorado. Potassium amounted to 3.9 ppm (0.23 grains/gal); silica averaged 8.4 ppm (0.49 grains/gal); inorganic P ranged from 0.01 - 0.235 ppm (0.0006-0.014 grains/gal); and inorganic N (not including NH_4-N) was 0.1 to 0.6 ppm (0.006 - 0.035 grains/gal). Ca-Mg hardness averaged 255 ppm as $CaCO_3$ (14.8 grains/gal). The first 19 miles of flow was always undersaturated with calcite, but past that point the river was usually in equilibrium or slightly oversaturated.

Most tributaries dilute the main flow. On the basis of 500 ppm (29 grains/gal) as the upper acceptable limit for continued human consumption, the entire stretch of river does not carry potable water; the sodium-adsorption ratio is low, however, and the water is adequate for agriculture and industry. It is recommended that discharge be kept at high levels for the Colorado and its tributaries to maintain water quality.

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INTRODUCTION

Limnologic data on the Colorado River and selected tributaries in Marble Canyon and Grand Canyon were collected on five raft trips in 1975-76. The trips, chronologically arranged, were: 22 April to 5 May; 3-12 June; 11-21 August; 12-24 November; and 1-12 March, 1976.

The goals for gathering the limnologic data were: to assay the physico-chemical nature of the Colorado River from Lee's Ferry, designated Mile 0, to Mile 225 just above the mouth of Diamond Creek; to determine the nature of the major tributaries entering the river including Diamond Creek at Mile 225.8; to determine changes occurring during the 225-mile course of the Colorado River with particular attention to modifications, if any, brought about by tributary influents; to determine the seasonal changes in both the mainstream and the tributaries due to such factors as snowmelt and rainfall in their watersheds; and to search for relationships that will shorten future physical and chemical analyses of the Colorado River in the Grand Canyon. In addition, samples of aquatic invertebrates were taken whenever possible.

The tributaries selected for study were: the Paria River at Mile 0.3; Vasey's Paradise, Mile 32; the Little Colorado River, Mile 61.5; Bright Angel Creek, Mile 88; Shinumo Creek, Mile 108.5; Elves' Chasm, Mile 116.5; Tapeats Creek, Mile 133.6; Deer Creek, Mile 136.2; Kanab Creek, Mile 143.5; Havasu Creek, Mile 156.7; and Diamond Creek at Mile 225.8.

Sampling of the influents was done at their mouths, yet above the main river. Procedures were designed to eliminate mixing effects of the Colorado River on samples of tributary waters.

METHODS

The following physico-chemical parameters were measured, usually, on all five trips and at all sampling stations: water temperature, transparency, turbidity, specific conductance, suspended particulate material, total dissolved solids (filtrable residue), pH, total alkalinity, chloride, sulfate, silica, dissolved orthophosphate, and nitrate-nitrite nitrogen. Those tests that involved unstable entities, e.g., alkalinity, pH, phosphate, and nitrogen, were conducted at the sampling stations immediately. Others, requiring either more sophisticated equipment or concerned with more stable chemical features (e.g., dissolved solids, suspended particulate matter, and sulfate) were conducted on samples returned to the laboratory at Tempe. Compared with the others, the data from the November trip are incomplete.

Sampling stations included eleven tributaries and at least five sites on the main stream. The latter varied somewhat in location because of time and river conditions, but the sites were selected in such a manner that they provided representative information concerning the Colorado River from Mile 0 to near the mouth of Diamond Creek, about 225 miles downstream. Tables 1 through 26 show these locations in river miles from Lee's Ferry, where samples were always taken.

Surface water temperatures were measured with an ordinary stem thermometer. Turbidity and transparency were evaluated employing a battery-operated Hach photometer; distilled water was used as the blank with a light path of 2.54 cm. Turbidity is reported in Jackson units (JTU) although some measurements were made in terms of a silica standard. Vertical transparency was determined on the June, August and March trips by using a 20-cm Secchi disc. Other data, relating to the transparency of small samples and the Secchi disc transparency, were calculated and are presented in Tables 5 through 8.

The suspended particulate matter carried by the river and its tributaries was estimated by withdrawing water with a 50-ml syringe and passing it through a Millipore filter (pore size, 0.45 microns). The volumes of water filtered varied from 25 to 2000 ml. Filters had been tared previously, and were reweighed in the laboratory after drying one hour at 103°C. A Mettler H-10 electric balance was used for all weight estimates.

Specific conductance was measured on fresh samples with a Beckman Conductivity Meter (Model RA-2A). All results were referred to micromhos/cm at 25°C by employing a factor of 2.5% per degree Celsius.

Hydrogen-ion concentrations, expressed conventionally as pH, were found by using the appropriate indicators and a Helige Color Comparator, equipped with glass color discs.

Dissolved oxygen (DO) was evaluated at only a few locations (Table 1); Hach powdered reagents were used for a micro-titration based on the Winkler iodometric method.

Total alkalinity (TA) was determined titrametrically with 0.02N H_2SO_4 using phenolphthalein and bromcresol green-methyl red indicators. The titer was assumed to be due to the carbonate-bicarbonate buffer system; the values for HCO_3^- and $CO_3^=$ mg or meq/liter are based on that assumption. On a weight basis, alkalinity was expressed as mg/liter $CaCO_3$, bicarbonate as total alkalinity x 1.219, and carbonate ion as TA x 0.599. It is understood, of course, that some of the titrable base may have been owed to other than salts of carbonic acid.

Chloride ion was appraised on 100-ml aliquots by mercuric-nitrate titration to the end-point of a buffered diphenylcarbazone powder. Sulfate was turbimetrically established by adding the Hach Chemical Company's SulfaVer Powder III to 25-ml samples to form a suspension of barium sulfate; dilutions were usually necessary. The resultant turbidity was determined in the Hach colorimeter with the "4445" filter in place.

The ammonium molybdate method was employed in the phosphate test, using stannous chloride as the reducing agent. Silica was colorimetrically assayed by using the heteropoly-blue, sulfite reduction method. Nitrate-N plus nitrite-N were measured photometrically at the sampling site using, first, NitraVer IV, and NitraVer III and VI (Hach) during the August and the March floats.

The cations (calcium, magnesium, sodium and potassium) were analyzed by Atomic Absorption Spectroscopy using a Perkin-Elmer Model 403; this work was performed in the laboratory of Milton R. Sommerfeld by personnel also concerned with the survey. Their data, in mg/liter, were used for the following calculations: TDS computed; meq/liter of all cations; sums of all milliequivalents; ionic strengths (μ) which had direct bearing on indices of calcite saturation, degrees of calcite saturation, free CO_2 and pH_s; calcium-magnesium hardness; and the following ratios--Ca/Mg, Ca/Na, μ/TDS, total meq/conductance, monovalent cations/divalent cations.

The sum of calcium and magnesium hardness as mg/liter of $CaCO_3$ was drawn from the Ca^{++} and Mg^{++} values by multiplying them by the reciprocals of 0.4 and 0.243, respectively.

Calcite equilibrium phenomena in the Colorado River and in the tributaries entering it between Lee's Ferry and Diamond Creek (including the latter) were calculated. This necessitated computing ionic strengths, and the activity coefficients of carbonate, bicarbonate and calcium ions. Ionic strength was calculated conventionally as half the sums of the products of molar concentrations and the square of the valency for seven major ions, Ca^{++}, Mg^{++}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-} and $SO_4^{=}$. The activity coefficients of calcium and bicarbonate were drawn from Hem (1961, Fig. 1) and Back (1961, Fig. 2). The activity coefficients of $CO_3^{=}$ were found in the Hem figure cited above. The molality of $CO_3^{=}$ was derived from the equation of Garrels and Christ (1965, pp. 83-84):

$$m\ CO_3^{=} = \frac{m\ HCO_3^{-} \times \text{activity}\ HCO_3^{-} \times K_2}{pH \times \text{activity}\ CO_3^{=}}$$

The pH is expressed as hydrogen ion concentration in the above equation and K_2 (as a function of temperature) is from Harned and Scholes (1941).

With the molality of carbonate ion known, the degree of saturation (Ω) was calculated using the following equation:

$$\Omega = \frac{(\text{activity } Ca^{++})(m\ Ca^{++}) \times (\text{activity } CO_3^{=})(m\ CO_3^{=})}{K_{sp}}$$

K_{sp}, the solubility product of $CaCO_3$, was obtained from Garrels and Christ (1965, Table 3.2).

A pH of saturation ($pH_{\underline{s}}$) was calculated using the equation:

$$pH_{\underline{s}} = \log \frac{K_{sp}}{K_2} - \log (\text{meq } Ca^{++}) - \log (\text{meq } HCO_3^{-}) + 6.3$$

The calcium and bicarbonate strengths were corrected for activity in the above.

Some calculations were made of the degree of saturation of $CaSO_4$. The paper of Hullet and Allen (1902) and the Handbook of Chemistry and Physics, 56th ed. provided solubility data. Activity coefficients of SO_4 were considered identical to those of carbonate.

The effect of the Colorado River in diluting ions from tributary inflows was explored, using the equation

$$C_3 = \frac{C_1Q_1 + C_2Q_2}{Q_1 + Q_2}$$

In this, C_1 refers to the concentration of an ion in the tributary, C_2 denotes the initial concentration in the Colorado River before mixing, and C_3 is the final concentration in the Colorado River. The volumes of the tributary and the Colorado are Q_1 and Q_2, respectively.

The index of saturation is expressed as the difference between pH_{obs} and $pH_{\underline{s}}$, negative suggesting undersaturation, and a positive result implying oversaturation, with precipitation a requisite for the return of equilibrium.

Free CO_2 or H_2CO_3 was estimated with the equation:

$$H_2CO_3 = \frac{(m\ HCO_3^-)(\text{activity}\ HCO_3^-)(H^+)}{K_1}$$

K_1 came from the data of Harned and Davis (1943).

PHYSICAL FEATURES

Temperature

There was always a net increase in surface temperature downstream (Tables 1 through 4). This was a complex function of distance and days from Lake Powell and the input from tributaries, each of which was usually warmer than the main stream it entered. The August and November trips took place after the annual heating period; the March trip occurred prior to it. Only the April-May and the June floats were during the annual heating time. In 1975, the total warming from Mile 0 to Diamond Creek amounted to no more than 4° in April-May, 5° in June, and 5.2° in August; the mean rate was, therefore, only about 0.02° per mile, ignoring the temporal factor. From Lee's Ferry at 0930 on April 22 to Mile 213 at 1730 hrs on August 21, the temperature ranged from 7° to 15.2°. Meanwhile, there had been only a 3-degree rise in the water at the Lee's Ferry station.

During March, 1976, the net increase from Mile 0 to Mile 225 was but 0.9°C, a net rate of 0.004° per mile. At that time the waters entering from Bright Angel, Shinumo, Elves' Chasm and Kanab Creek were colder than surface waters of the Colorado River.

The range of recorded temperatures at Lee's Ferry prior to 13 March 1963, when the river flow first became completely regulated by Glen Canyon Dam, was 29.5°, dropping to the freezing point on many winter days. Our lowest temperature, 7°C, might represent the present typical annual low. There may be, however, some years when the water at Mile 0 surpasses our recorded high of 10°C, according to data in yearly USGS Water-Supply Papers entitled "Quality of Surface Waters of the United States. . . ."

Turbidity, Transparency and Suspended Particulate Material

Turbidity was expressed in three ways. The assays were made at the river stations and included turbidity in terms of Jackson Turbidity Units (JTU), as transmittance of light, and to a lesser extent as turbidity related to a silica standard. From transmittance values, opacity and optical density (OD) were calculated (Tables 5 through 8).

The April-May and the August runs of 1975 and the March trip of 1976 showed tremendous increases in turbidity from the beginning of the trip to the stations downstream near Diamond Creek. For example, in August the increment was from one to 334 JTU. Concomitantly, the transmittance in small samples decreased from 99 to 30 percent. Accompanying these changes in light penetration were increases in particulate, non-filtrable solids, introduced largely from tributaries, although the contributions from various rapids must not be overlooked. The trend was from less than one to 888 mg/liter of particulate matter at Mile 165 and to 870 at Mile 213 in August. June was quite different from the other sampling periods. From Lee's Ferry to Mile 219 the transmittance trend was a decrease from 99 to 98 percent, the JTU change was from one to 10, and the suspended particulate matter increased from one to only 18 mg/liter.

The highest figure found for the suspended load carried by the Colorado River was 986 mg/liter at Mile 125 during the April-May trip. That datum implies that, for every 1000 cfs of flow, 1.67 metric tons of particles were carried past a given point in a minute's time.

The paramount reason for the great increase in suspended solids during the April-May, August and March expeditions and the resultant turbidity, was the flooding Little Colorado River. During the June trip of 1975 it was not in flood and, although contributing almost 2.5 g of dissolved solids per liter, it was clear water showing 98% transmittance, turbidity equivalent to only 5 JTU and but 22 mg of particulate solids per liter (Table 6).

A seemingly anomalous situation is revealed by the data from August (Table 7): the Little Colorado River was relatively clear when the research party arrived at its mouth, and the transmittance had been high in all preceding tributary waters with the exception of the Paria River, which had little effect on the transparency of small samples; the tributaries entering downstream from the Little Colorado were also clear. Samples from the main river, at Mile 132, however, suddenly revealed extreme opacity (Table 7). There had been a flash flooding in the upper drainage basin of the Little Colorado River after the party had passed it. While they were camping overnight, the muddy water caught up with them and stayed with them to the end of the float.

Either the research trips did not coincide with the muddiest times of flow, or 1975 was characterized by an unusual low turbidity. More than twice the particulate load we observed has been reported for the river since 1963. Prior to Glen Canyon Dam the annual mean reported at Lee's Ferry was 5,570 mg/liter of suspended sediment and 8,050 downstream 80 miles. There were maximum records of 152 grams per liter at the gaging station between the Little Colorado's mouth and Bright Angel Creek.

Vertical Light Penetration

Although turbidity measurements were made on 63 small samples, the data from these tests do not quantify the penetration and diminution of light in the stream from which the samples were taken. A light path of 2.54 cm is quite different from the real world of the Colorado River, where light of many wave lengths impinges on the surface from many angles and is deflected as well as absorbed by materials that may change concentration in the downward light path measured in meters, not centimeters. On the June, August and March trips, Secchi disc transparencies were determined at at least five stations in the Colorado River, and from those values some approximations about light phenomena within the river can be made.

The Secchi disc values are assumed to bear a relationship to the coefficient of vertical light attenuation so that 1.7 divided by the Secchi-disc depth in meters should yield a fair approximation of the coefficient, $\underline{k}$ (Poole and Atkins, 1929). This is,

$$\underline{k} = \frac{\ln I_0 - \ln I_z}{z}$$

where I_z represents the remaining intensity of light having passed through a water column of z meters, the original intensity at zero depth being I_0.

Because the vertical decrease of light may be due to more factors than just absorption, we are speaking of the coefficient in more general terms such as diminution, attenuation, etc. Natural logarithms are used in expressing it, however, so that it is not the coefficient of extinction (where logs to the base 10 are used) although the general idea is obviously similar (Strickland, 1958).

Using the Poole-Atkins factor 1.7 leads to another useful approximation. The depth of the euphotic zone (the subsurface level where only one percent of the surface light remains) is the product of the Secchi disc depth and 2.7. The latter value comes from:

$$0.01 = \underline{e}^{-\underline{k}z}$$

where $\underline{k}$ is 1.7/z, z being Secchi-disc depth in m. This is close to the rule-of-thumb factor, 3.0, used by many limnologists to estimate the level where 99% of the incident radiation has been quenched in its downward path.

At the start (Lee's Ferry), the Secchi disc readings were 5.8, at least 6.0 and 3.1 m in June, August and March, respectively (Tables 6 through 8). From these can be inferred "absorption" coefficients ($\underline{k}$) of 0.293, 0.283 and 0.548. The corresponding transmittances, T, expressed as percentages of light passing down through each meter-thick stratum, were 74.6, 75.4, and 57.8 percent. A further step shows that 1.0% of incident light would have remained at 15.7, 16.2 and 8.4 m on the three days in question, if the river were that deep at Lee's Ferry.

Although the Little Colorado River was not flooding during the June float, at a point (River Mile 71) past its mouth (Mile 61.5) until the end of the trip at Diamond Creek the Secchi disc disappeared 1.1 m below the surface. Thus $\underline{k}$ was 1.55, T was 21.3%, and the euphotic zone extended to a depth of not quite 3m. This situation implies that, although turbidity contributed by the Little Colorado River plays a remarkable part in reducing light penetration in the main stream, it does not appear to be solely responsible.

In August and March the Paria River was carrying a greater load of suspended material than it had in June 1975 (Tables 6 through 8). The results were marked reductions of Secchi disc transparencies downstream. The August data include Secchi disc values of 4.1 at Mile 5 and only 0.55 at Mile 18. These suggest that greater mixing had come about at Mile 18 and that the Paria flows discretely for a few miles after entering the Colorado.

When the Little Colorado was reached in August, it was found to be relatively clear, carrying water originating mainly from Blue Springs. It flooded while the party was camped below and the murky water caught up with them and stayed for the rest of the trip. This reduced visibility of the Secchi disc to depths of 0.06 m at Mile 132 and 0.04 m at Mile 213. Coefficients of vertical light attenuation were then 28.33 and 42.50, respectively, implying transmission values of practically zero. The theoretical euphotic depths extended only to 0.16 and 0.11 m below the river surface.

Floodwaters from the Paria and the Little Colorado had marked effects on light penetration; the other tributaries seemed to have no discernible impact. It is especially the Little Colorado, when carrying runoff from above the Blue Spring region, that probably reduces photosynthesis to an extremely low level, and that certainly gives the Colorado River a muddy character, reminiscent of pre-dam days.

Specific Conductance

Tables 1 through 4 and 25 show conductivity data in terms of micromhos per cm referred to 25°C. These data are expressions of the electrolytes present or the general salinity of the waters. The conductivity meter used in making the assays has a logarithmic scale with numbers crowded in the upper ranges; for this reason some dial readings, although set down precisely, may be only close approximations.

There are some irregularities in the data, but the average conductance in 25 samples from the Colorado River was 940 micromhos per cm. This is also close to the mean of data collected at the final downstream station, 936. At Lee's Ferry, the mean conductivity was 921. The highest conductances were found during April-May, 1975, averaging 977; the lowest were recorded in November, when a mean of 873 micromhos/cm prevailed.

Usually the Colorado River had its conductance surpassed only by the Little Colorado River, Kanab Creek and, rarely, the Paria River. Elves' Chasm, Havasu Creek, and Diamond Creek are the only other tributaries that approach it in electrolytic activity.

Conductivity figures have value because they relate to total salinity and filtrable residue. In a given body of water it is possible to establish empirically the ratio of TDS to conductance. The resultant factor can be used to convert conductivity to TDS, thereby eliminating the need for tedious evaporation and weighing procedures. In Tables 15, 16 and 17 the TDS/conductivity ratios are shown for various waters in the Grand Canyon system. For the Colorado River proper, the mean factor to convert micromhos conductivity at 25° to mg per liter of filtrable residue is 0.68. Similarly, the sum of the seven major ions, in meq per liter, is approximated by multiplying Colorado River conductivity by 0.02 (Tables 23, 24, 26).

Extreme conductances in the past have ranged from approximately 318 to 2,430 at Lee's Ferry and up to at least 2,900 micromhos/cm at 25° in stretches below the Little Colorado. Striking annual fluctuations, effected by the spring freshets and low-water periods at other times, seem to be damped and obscured by the Glen Canyon Dam. The same can be said for all other parameters relating to total salinity.

CHEMICAL NATURE OF THE COLORADO RIVER

Total Dissolved Solids

The Colorado River is characterized by a mean filtrable residue of 643 mg/liter (Tables 1 through 4, 25). This was determined by evaporating 24 membrane-filtered water samples to constant dryness. In April-May, 1975, the TDS values were highest. The mean at Mile 0 was 623 and at the most downstream station was 644 mg/liter. With one exception, the lowest filtrable residue was found at Lee's Ferry. Often higher figures were found at intermediate stations--Miles 71, 125 and 165, for example. As might be expected on the basis of the conductivity data, only the Little Colorado River and Kanab Creek had consistently higher TDS values. The Paria River in March 1976, however, surpassed the TDS of Mile 0 about 1.5 times.

There are problems associated with the procedure of taring vessels and evaporating water for the TDS method. A reasonable check is to compare calculated TDS sums with results of the evaporation procedure. This was done for all the waters except for August, when cation data were not available; the values are set forth in Tables 1 and 2. The calculated values include summation of the seven principal ions plus silica, phosphate and nitrogen (Tables 14 through 17). All bicarbonate values were converted to carbonate, employing the factor, 0.4917. Trace elements were not included in the summation. The results were a mean of 565 mg/liter, the waters at Mile 0 containing 552 and the samples from near the end of the trip having a mean of 570. As before, some intermediate stations had the highest totals.

In April-May 1975, the lowest TDS found by evaporation was at Mile 225, agreeing with the calculated rank (Table 1). There were three other concurrences of the evaporation and calculation methods for determining the lowest and/or highest ranks. These were from eight possible comparisons, the incomplete November data precluding estimation of TDS. In contrast to this agreement of 0.5, the concurrence between conductance and TDS by evaporation was only 0.2.

Other estimates of the concentrations of dissolved substances in the waters of the Colorado River were slightly different. These involved the sum of milliequivalents (meq/liter) in Tables 9 through 13, and μ, the ionic strength (Tables 18 through 21). When there was no great input from the tributaries (as in June and August 1975), there was an ideal increase in meq/liter to the highest figure at the final station. The mean of meq/liter was lower at Lee's Ferry than at the ultimate station, although some intermediate spots had higher concentrations. The increment of ionic strength contributed by each ion was such that the first station had the lowest mean value for μ; the final station ranked only third and intermediate stations of the Colorado were highest in ionic strength.

The April-May sum of meq/liter in the Colorado River was surpassed by the Little Colorado, but the ranking of ionic strengths was reversed. This can be attributed to the higher calcium and sulfate values in the main stream, each of which contributes a significant increment in ionic strength, and the subequal magnesium values in the two water courses. (Magnesium ion contributes the greatest increment of all the major ionic components.) This shows the use of ionic strength for comparing salinity concentrations is not suitable for entirely different waters.

Ionic Proportions

The concentrations of the principal ions in the Colorado River can be found in Tables 9 through 13. Their proportions are plotted on triangular coordinate paper in Figures 2 through 5. As far as anionic proportions go there is little change from river Mile 0 to Diamond Creek, about 225 miles downstream. The water starts as a sulfato-carbonate type, or better--a "triple" water, with chlorides, sulfates and carbonates in notable amounts, to use a scheme presented by Clarke (1924). It terminates as such, although there are some slight changes along the river's course.

The stations above the Little Colorado River had relatively more sulfate than those below during the April-May (Figure 2) and the June flows (Figure 3), with a slight comparative gain of chloride and carbonate. The cations, Ca^{++}, Mg^{++}, and the sum of Na^{+} and K^{+} were nearly equal on a percentage-of-meq basis, although sodium usually surpassed the others. During the June trip, when the Little Colorado River and other major tributaries were not in flood, calcium slightly exceeded the sodium throughout the river. In August this was also true of the upper 19 miles of the river, and in November calcium barely surpassed sodium at Lee's Ferry. In every other sample sodium was predominant (Tables 9 through 13).

Livingstone (1963) presented data on the average chemical content of the world's rivers. In his summary, the major cations are shown in this sequence:

$$Ca^{++} > Mg^{++} > Na^{+} > K^{+}$$

and the anions display the following order:

$$CO_3^{=} > SO_4^{=} > Cl^{-}$$

The Colorado River water differs from these by showing the following rankings:

$$Na^{+} > Ca^{++} > Mg^{++} > K^{+}$$

and

$$SO_4^{=} > CO_3^{=} > Cl^{-}$$

The Colorado River also has a total solute content five times greater than the mean for the world's rivers, although only about 0.5 to 0.8 times the silica. Without the influences of the major tributaries in the upper reaches of the stream, the Colorado River in the Grand Canyon would probably show the cation relationships

$$Ca^{++} > Na^{+} > Mg^{++} > K^{+} \text{ or } Ca^{++} \approx Na^{+} > Mg^{++} > K^{+}$$

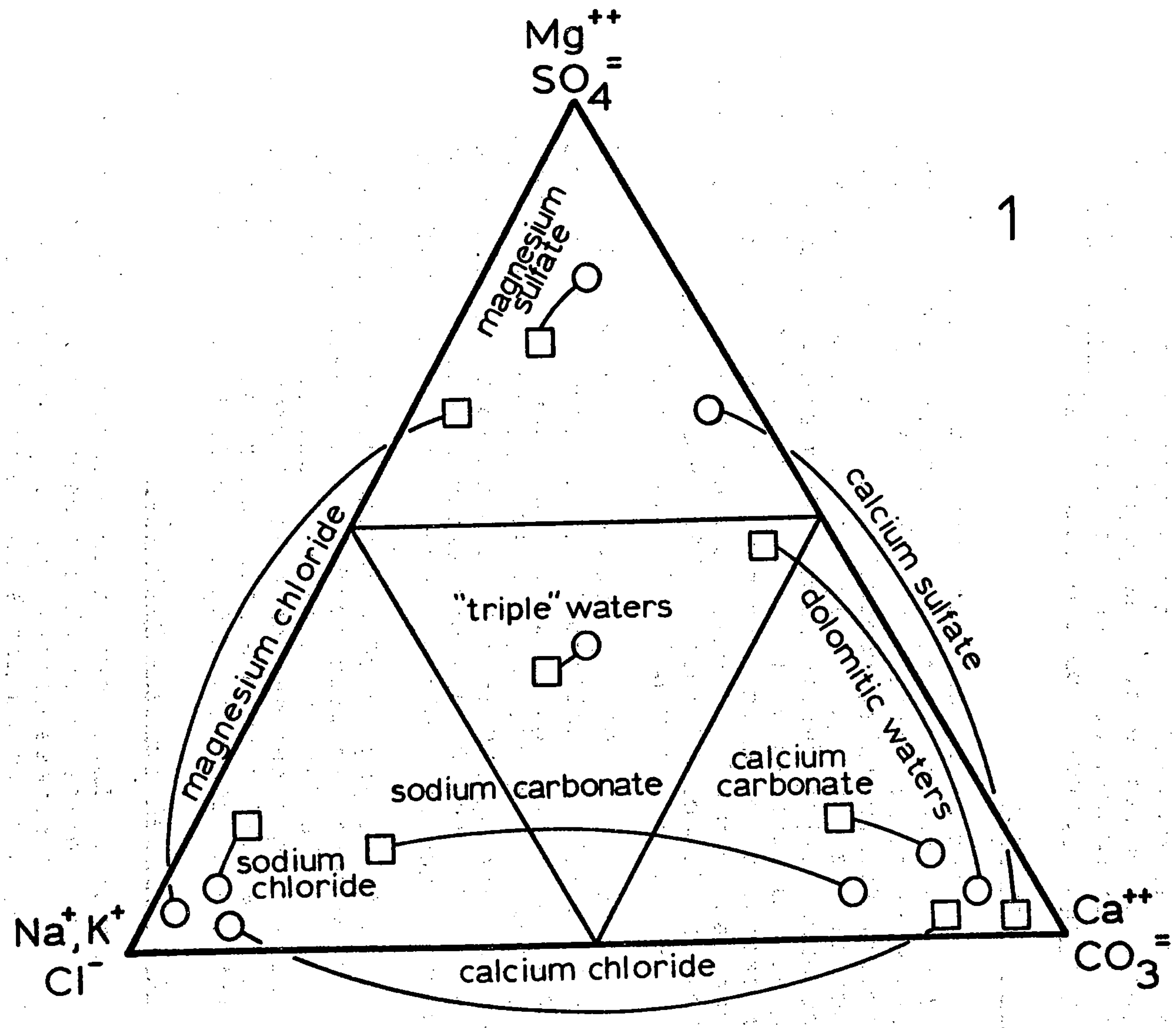

Figure 1. Triangular-coordinate plots to illustrate different types of water. Anions = circles; cations = squares. Inner triangle indicates 50% lines. Corners indicate 100% of the ion labeled there.

The water is difficult to classify; the cations approach a "triple" condition, to borrow a term from Clarke (1924). In general, the water is much like the low-salinity, humid-subtropical river-lake water of Chebotarev (1956). Surprisingly, potassium is extremely scarce in all the streams in the Colorado system examined here. One might expect it to assume more prominence, as in the category, steppe rivers and lakes, proposed by Chebotarev (1956).

Ionic Strength

The ratio of ionic strength (μ) to total dissolved solids varies from water to water, because different ions contribute different amounts to the sum. Magnesium, for example, contributes about 1.6 times as much as does an equal weight of calcium. Despite this, the empirically derived ratio from one particular aquatic system is useful for skipping the tedious work of calculating ionic strength. It yields a coefficient that can be used to obtain μ from TDS. Such ratios are shown in Tables 22 through 26. For the Colorado River the mean factor for μ/TDS is 2.145×10^{-5}.

Langelier (1936) proposed the factor 2.5×10^{-5} and Kemp (1971) modified this to account for non ionic substances, such as silica, which are part of TDS--$2.5(\text{TDS}-20) \times 10^{-5}$. Cole (1975) found the mean factor for converting TDS in mg/liter to ionic strength was 2.60×10^{-5} for 21 Arizona waters, none of which were exactly like the Colorado River in ionic proportions.

Ionic strengths of Colorado River samples, then, can be determined from conductivity readings adjusted to 25°C. The factor would be about 1.46×10^{-5}. The ionic strength becomes of special import when states of calcite equilibrium are being calculated, and activity coefficients of $CO_3^{=}$, HCO_3^{-}, and Ca^{++} must be known.

Hardness: Calcium and Magnesium

Hardness is a concept that appears in many reports on water quality. For that reason, though we did not determine hardness titrametrically, we have calculated calcium-magnesium hardness in terms of mg/liter of

$CaCO_3$. The data are presented in Tables 19 through 21 and 25 as TH (total hardness) even though the role played by manganese, iron and other heavy metals is not known. The average hardness for all five floats was 255 mg/liter expressed as $CaCO_3$. Surprisingly, the softest water was rarely at Mile 0, and usually the last station showed a diminution. Our mean is somewhat lower than the average from USGS reports made in earlier years.

If it is assumed that total alkalinity (TA) titrations, also expressed as mg/liter of $CaCO_3$, represent carbonate hardness, the difference between TH and TA is an estimate of non carbonate hardness. This is too ideal because $NaHCO_3$, for example, would contribute to alkalinity titrations, but would have nothing to do with hardness. The ratios of alkalinity to Ca/Mg hardness are shown in Tables 19 through 21. For the Colorado River, the mean is 0.59 implying (with certain restrictions) that almost 60% of the hardness is non-carbonate. According to Durfor and Becker (1964), water above 180 mg/liter is "very hard."

Calcite Equilibrium

Except for a June datum from Shinumo Creek, the only waters of the entire system that were not saturated with $CaCO_3$ were from the Colorado River (Tables 18 through 21). At least the first 19-mile flow was undersaturated at all times, and during March the water did not attain equilibrium until Mile 180 was reached. The calculated pH of saturation (pH_s) ranged from 7.74 to 8.06. The highest pH observed in the Colorado River was 8.2; therefore, no phenolphthalein alkalinity was noted.

Certain ionic ratios are instructive in attempting to discern the calcite equilibrium picture, and to detect precipitation or dissolution that might have occurred to establish equilibrium. The first of these, calcium to magnesium, is shown in Tables 18 through 21 and 25. The results are not clear, however. Except for March 1976, there were slight decreases in the ratio downstream. This suggested calcium compounds were being precipitated to a small extent, producing

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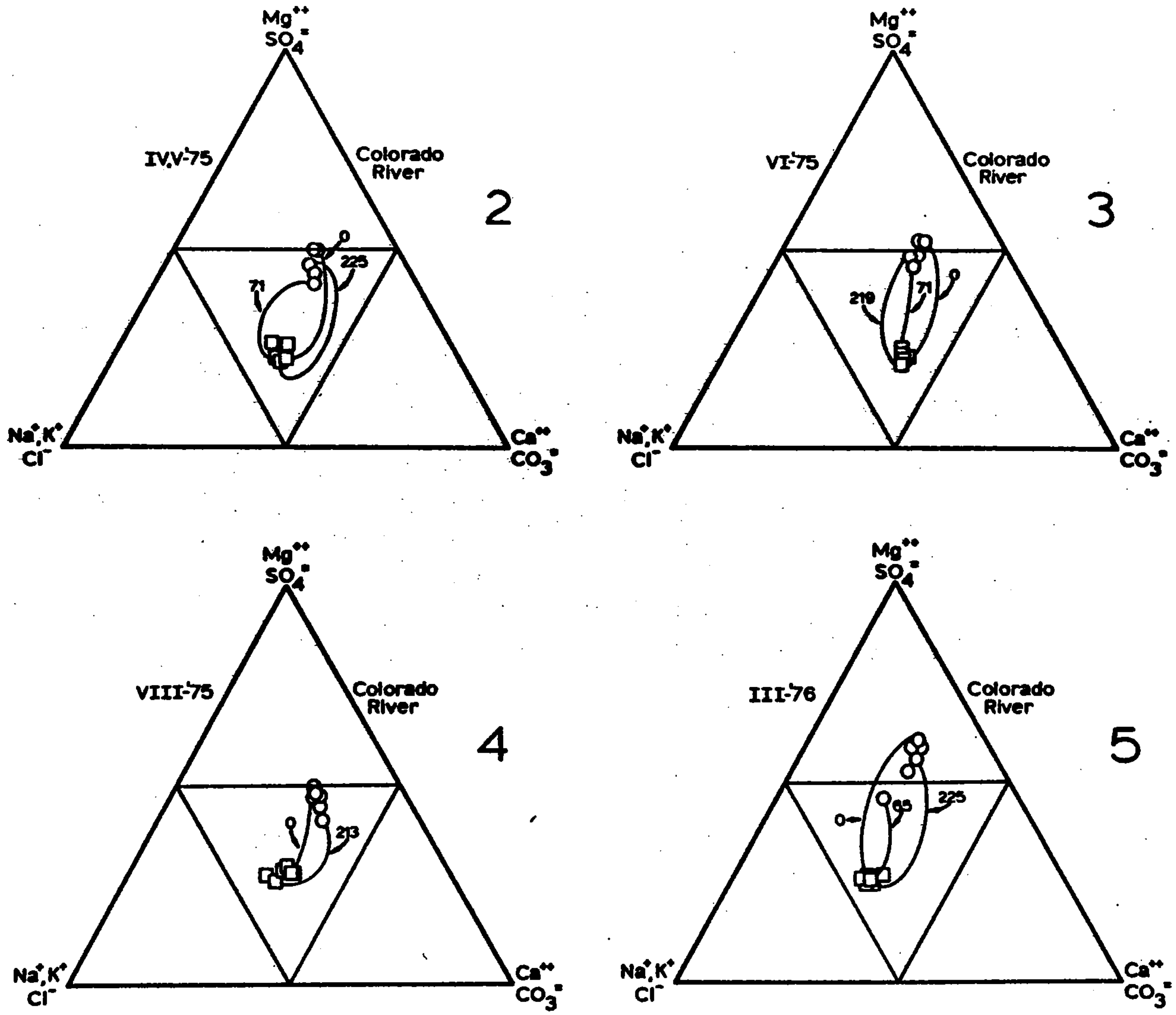

Figures 2-5. Triangular-coordinate plot of the Colorado River waters on five different trips, starting at Lee's Ferry, Mile 0. River miles indicated by numbers; not all labeled. Anions = circles; cations = squares.

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relative increases in magnesium, as the water flowed along.

Similarly, the CO_3:Cl or the CO_3:SO_4 ratios might imply something about a loss of carbonate as the more soluble chloride and sulfate compounds persist. There were, however, no clear-cut trends, and certainly the addition of chloride and sulfate from tributary inflows would obscure sequences occurring in the stream.

Another relationship, calcium to sodium, was calculated and presented (Tables 22 through 26). This ratio usually lessened below the Little Colorado River (especially on the April-May and August floats). At times there was an approach to initial values again by the time the last sampling station was reached. The ratios of monovalent cations to divalent cations (based on meq) changed little, although there were generally slight increases (Tables 22 through 26).

All of the above, suggest that the ten or so tributaries between Lee's Ferry and Diamond Creek, have effects that, although slight at a cursory glance, may be greater than is obvious. There are constant inputs of various mixtures of ions, most of which are quite different from the combinations in the Colorado River. This disturbs any natural sequence of events that might occur through time as evaporation, concentration and warming proceed. For these reasons, the ratios discussed above do not reflect calcite saturation purely and simply.

The calculations (Tables 18 through 21) for indices of saturation and degrees of saturation (Ω) produced some information, however, concerning the state of calcite equilibrium in the Colorado River. The average of all pH is above the mean theoretical pH of saturation (pH_s), suggesting that the river is usually in equilibrium or slightly saturated with calcium carbonate. This is especially true in the lower reaches.

Closely related to the state of calcite saturation are free CO_2, carbonic acid and pH. There were enough data to calculate the CO_2-H_2CO_3 values precisely for April-May, June, August and March. The free CO_2

generally decreased downstream (Table 18 through 21). As might be expected, pH values rose concomitantly.

Plant Nutrients

Silica has been a component of water-analyses reports for many years; this provides us with a comparative base to evaluate this compound in the Grand Canyon system. We are considering it a plant nutrient because it is essential to diatoms, an algal group important in the river.

Cole (1963) summarized the values for silica in waters of the American Southwest and Middle America. Later he listed some SiO_2 data from Arizona waters (Cole, 1975). In general, the small ponds along the Mogollon Rim from near Baker's Butte to, and including, the artificial Woods Canyon Lake, have very little silica--trace quantities only. These bodies of water are termed the Potato Lake Series after Whiteside (1965). Similarly, the lakes of volcanic origin around Flagstaff do not have large amounts of silica. Many other Arizona waters are fairly high in this compound, well above the mean of 13 mg/liter for the rivers of the world (Livingstone, 1963). By contrast, the Colorado River within the gorge of the Grand Canyon is relatively low (Tables 14 through 17), containing no more than half the SiO_2 of the Arizona waters reported by Cole (1975). Havasu Creek and Diamond Creek are the only waters in the Grand Canyon system that showed more than 20 mg silica per liter, a level that is not particularly high for certain waters in the state.

The phosphorus levels (Tables 14 through 17) reported from the Grand Canyon waters are based on determinations of soluble, reactive, inorganic phosphate only. Total phosphorus and organic phosphorus are unknown quantities.

In the Colorado River, the inorganic phosphorus (calculated from ortho-phosphate x 0.326) ranged from about 10 to 235 mg per m^3. If we assume that inorganic phosphorus is usually about 12% of the total P (see Wetzel, 1975, Table 12.2), we can make some estimates. Using the factor 8.0 for simplicity's sake, the total P ranges from 50 to 1,880 mg/m^3. This leaves us with high estimates. Hutchinson (1957) showed the mean of samples from several lake districts was about 21 mg/m^3, and Vollenweider (1968) categorized eutrophic waters as those containing from 30 to 100, and hypereutrophic examples as those with more than 100 mg/m^3 total P.

Nitrogen assays (Tables 14 through 17) were limited to nitrate and nitrite; ammonia and organic nitrogen compounds were not tested. For this reason, nitrogen estimates, like those of P, are too low. Vollenweider (1968) shows a classification of waters on the basis of inorganic N content. The Colorado River ranges from ultraoligotrophic (Mile 0 and 71, April) to mesotrophic and eutrophic at other times. The N/P ratios, shown in Tables 14 through 17 are typical of mesotrophic to eutrophic waters (Vollenweider, 1968).

The tests for phosphorus and nitrogen show little evidence for pollution or for lack of it. Havasu Creek waters might reflect, for example, the use of detergents and the campground upstream, but the results are most inconclusive. If there are sources of nutrient overload in the upper reaches of streams such as Havasu and Kanab Creek, the effects are biologically neutralized by the time the waters reach the main stream. Our sampling had limitations in that it was done only near the mouths of the tributaries and precluded further comment about the streams as potential sources of pollution and/or nutrient. The interesting alterations that may well occur as the creeks flow from their sources to the Colorado River can not be seen from one, nearly-terminal station.

We are left only with the impression that the Colorado River, in addition to the common salts, is rich in essential plant nutrients, and has the potential to be a productive system.

Whether or not the low temperatures and poor light penetration (at times) may limit productivity cannot be told at this time. The N/P ratios suggest that nitrogen rather than the usually scarce phosphorus, might become a critical limiting factor to the river's algae. There is abundant phosphorus, and it might be found some day that any factor limiting algal growth in the Colorado River is to be desired.

CHEMICAL NATURE OF THE TRIBUTARIES

The relative ionic composition of the tributaries entering the Colorado River within the Grand Canyon are diverse (Figures 6 through 9). Elves' Chasm is very much like the Colorado River itself, especially with respect to anions and the N/P ratio. The Paria River most closely approaches Elves' Chasm, and its waters also are much like the Colorado especially where cations are concerned. These three come closer to the category, "triple" water (Figure 1) than any other stream considered here. Further comparisons of these waters can be made from the data presented in Tables 9 through 13.

Paria River

The Paria River enters the Colorado River 0.3 miles below Lee's Ferry. Estimations of its drainage area range from 1,410 to 1,570 square miles in the Escalante Mountains and the Paria Plateau of Utah. It has been partially monitored for many years. From 1923 to 1966 recorded flow at its mouth ranged from none to 16,100 cfs; the mean was 29.9 cfs. At times its effect, therefore, on the Colorado River must be consequential. It has been called, ". . . probably . . . one of the largest sediment carriers of its size in the world; the river has a mean discharge-weighted suspended-sediment concentration of 114,000 ppm near its mouth" (Ligner *et al*., 1969).

The effect of the Paria on the Colorado is not immediate; when it is milky with suspended solids and easily differentiated from the clear Lee's Ferry water, it can be seen to remain as a discrete flow for at least five miles below its mouth, mixing more or less completely somewhere below that point.

Although the maximum conductance known for the Paria River near Lee's Ferry is 3,000 micromhos (USGS, 1969), the figure of 1,075 in April 1975 might be spurious; the ratio of filtrable residue to conductance (Table 1) was abnormal at that time when compared with results from other trips (Tables 2 through 4, 25). The conductance of 1,248 micromhos in March 1976, a figure that surpassed the Colorado River estimation, is acceptable, however.

The waters of the Paria reached the Colorado River supersaturated in calcite (Tables 18 through 21). On two occasions it exhibited phenolphthalein alkalinity, a feature noted at no station in the Colorado River. When the flow in April was fairly high and extremely turbid, chemical analyses were difficult because of the calcareous nature of the suspended solids. Particulate $CaCO_3$ was present in amounts we estimated to be from 0.3 to 0.5 g per liter. The strong acid used in alkalinity titrations tended to dissolve the colloidal (?) $CaCO_3$ and no stable endpoint was reached.

The Paria ranked first among the members of the entire system in nitrogen, and was very high in phosphorus. In silica content its waters shared a three-way tie for third place with Elves' Chasm and Kanab Creek (Tables 14 through 17).

Fluctuations were extreme in the Paria River. Its flow one evening would be, for example, quite reduced by the next morning. Moreover, its total and relative ionic composition were variable (Tables 9 through 13; Figure 6). It brings to mind the shifting physico-chemical conditions described for the Colorado River prior to the existence of Glen Canyon Dam, and underscores the danger in generalizing on the basis of analyses from one date.

The Dolomitic Tributaries

Five tributaries are very much alike in water chemistry and, although they enter the Colorado River at widely separated spots, their origins are similar. These are Vasey's Paradise, Bright Angel Creek, Shinumo Creek, Tapeats Creek and Deer Creek. Their junctions with the river range from Mile 32 for Vasey's Paradise, to Mile 136.2 for Deer Creek, but they ultimately receive their waters from the Kaibab Plateau (Huntoon, 1974). The fact that they are strong carbonate waters with more or less equal proportions of calcium and magnesium and very low quantities of sulfate, chloride, and sodium may be attributed to the nature of the Kaibab Limestone. Some chemical data from Galbraith and Brennan (1970) give a 1.4 value for the ratio of $CaCO_3$ to $MgCO_3$ in the Kaibab Limestone. Thus, the so-called limestone is actually characterized by a very significant magnesium content. It approaches a magnesian limestone. The springs that issue to create the five tributaries are largely from the Muav Limestone, although Vasey's Paradise springs from a cave 40 m up on a Redwall Limestone cliff.

The five streams had the highest Ca/Na, CO_3/Cl and CO_3/SO_4 ratios and the lowest monovalent to divalent ratios of the entire system (Tables 22 through 26). The ratio of their alkalinity titers to hardness, both expressed as $CaCO_3$, approached unity, suggesting their hardness was largely the carbonate type (Tables 18 through 21).

These streams contain dilute waters when compared with all the others in the Marble Canyon-Grand Canyon system (Tables 1 through 4, 9 through 13, 25). During our period of study, Vasey's Paradise and Deer Creek were the most concentrated, and Bright Angel was the least. There is, however, relatively little difference in their salinities and they vary seasonally to some extent; earlier reports (e.g., Johnson and Sanderson, 1968) show different positions, Bright Angel being the most concentrated water, for example.

The extremely low N/P ratios exhibited by four of the five dilute calcium-magnesium carbonate streams (Tables 14 through 17) are owed to <u>both</u> low nitrogen content and high phosphorus levels. The exception, Vasey's Paradise, yielded samples containing abundant stores of nitrogen (fourth of all the waters). Its relatively high nitrogen content put the Vasey's Paradise N/P ratio among the three highest, while the four other dilute calcium carbonate streams were last in the list for the whole river system in this respect.

The five dilute dolomitic waters showed the lowest standing in silica content (Tables 14 through 17). Just above their position lay the average for samples from the Colorado River proper.

The degree of calcite saturation (Ω) was calculated for all waters when enough data were available (Tables 19 through 21). The five influents in question arrived at the Colorado River with their waters over-saturated in $CaCO_3$, except for one June day at the mouth of Shinumo Creek. Shinumo ranked last in the degree of saturation, while the overall first rating went to Deer Creek, with Vasey's Paradise second. These last two waters undergo the greatest agitation and aeration just before entering the main river. Deer Creek plunges over a 50-m waterfall a short way from its mouth, and Vasey's Paradise cascades from an opening in a cliff set back a short distance from the Colorado.

When Bright Angel Creek warmed, as it did in June and August when it reached 18° and 26°, respectively, the solubilities of calcite and CO_2 were decreased to such an extent that precipitation became a requisite for equilibrium. Then with the pH well above the pH of saturation, calcite theoretically precipitated. In contrast, when the vernal water temperatures were low (Tables 18, 21), Bright Angel Creek had the least degree of saturation of the five dilute waters.

Only Diamond Creek exhibited more consistent phenolphthalein alkalinities than did the dolomitic creeks. That may have been a function of its "soda-water" nature (Figure 9).

The Little Colorado River

The Little Colorado River drains an area of 2.69 x 10^4 square miles in Arizona and New Mexico. The flow at its mouth (Mile 61.5) is derived from the variable surface runoff in that great area and the more nearly constant discharge from at least 29 seeps and springs issuing from the Redwall Limestone from 3 to 13 miles upstream. Their mean rate of flow is 223 cfs. The largest of these sources is Blue Spring, which drains the Black Mesa hydrologic basin and discharges about 67% of the groundwater that moves through the aquifers of that basin (Cooley et al., 1969).

When flooding occurs in the upper reaches of the

Little Colorado, tremendous quantities of particulate matter are dumped into the Colorado River (Tables 5, 8). The greatest flow of the former was in April 1975, and at that time the water was the least concentrated. In March 1976, even though the suspended sediment carried was only about one-tenth that of a year earlier, Secchi disc data provide some information about the remarkably poor light penetration in the flooding Little Colorado River (Table 8). The coefficient of "absorption" (k) was 28.3, implying the vertical light transmission was less than 0.001% per meter! At a spot 3.5 miles below that mouth of the Little Colorado River the mixing appeared incomplete (k = 2.70), but at Mile 126 the coefficient was 21.25, showing the great effect that the particulate load from the Little Colorado has on the Colorado River.

When the flow from the Blue Spring outlets was undiluted by upstream input in the Little Colorado, the water was too saline for our conductivity meter to register, being somewhere above 2,050 micromhos. In the April sampling period we were able to determine a conductance of 1,246, because the Little Colorado was relatively dilute (although strikingly turbid). We estimated the June and August samples to have electrolyte strengths equivalent to more than 4,170 micromhos/cm. In November and the following March, deionized water was available and the samples were diluted. With the appropriate corrections, the conductance was estimated to be 5,800 and 4,500, respectively.

The Little Colorado is essentially a sodium chloride water (Figure 6). It carries, however, remarkable amounts of carbonate and the alkaline earth metals. When the issue from Blue Spring is diluted by upstream flooding, it reaches the Colorado River in a condition more unchanged from its source than when it flows alone to the mouth. This is seen in the April-May plot when compared with the other ordinations (Figure 6), where shifts toward the NaCl corner are seen clearly. In April-May the water was closer to the calcium carbonate corner. The distinction must be made between changes in relative composition and changes in total concentration. When the Little Colorado River is

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diluted by flooding, the water at its mouth is similar in composition to Blue Spring, but far less mineralized; the degree of calcite saturation is high, because little of this mineral has precipitated. When it is not flooded, the water arriving at its mouth is like Blue Spring in total mineral content, but the relative composition is somewhat altered, $CaCO_3$ having precipitated.

When the waters from various sources of Blue Spring arise, they probably carry about 500 mg/liter of gaseous CO_2. This statement is founded on the calculations of Cole (1975) from data that may not be accurate. He calculated 423 mg/liter, but the water sample was not fresh; it was slightly oversaturated with $CaCO_3$ ($\Omega = 1.06$) and the pH was 6.5. The water probably emerges with more free CO_2 and a greater hydrogen-ion concentration, although Johnson and Sanderson (1968) reported pH 6.5 from a spot 13 miles upstream from the mouth. By the time it reaches the Colorado River much CO_2 has been lost and $CaCO_3$ precipitated in a trend toward equilibrium. On the April-May trip the water at the mouth of the Little Colorado River showed a degree of saturation equal to 2.75. This water was turbid and diluted ($\mu = 0.01285$) by runoff from the drainage basin above the Blue Spring region. The June data revealed water at the mouth had an ionic strength of 0.05049. This was very close to the ionic strength of the Blue Spring issue, at least 0.05357 according to Cole (1975). The degree of saturation in June was 7.81. This was clear water, probably derived entirely from Blue Spring. Conditions were similar in August when the flow was much reduced.

The ratios of $CO_3^=$ to Cl^- also are instructive in explaining further the effects of flooding on the water having its provenance at Blue Spring. Cole (1975) reported a ratio of 0.687 from Blue Spring proper; in April of 1975 the carbonate/chloride ratio at the mouth of the flooding Little Colorado River was also high, 0.765. This suggests that, in addition to ionic contributions from upstream, the Blue Spring issue was diluted and swept to the Colorado River before calcium carbonate precipitation had occurred significantly. In June, August and March, the CO_3/Cl ratios were much lower (Tables 22 through 24, 26) implying carbonate had been precipitated en route to the main stream.

The discharge of March 1976 was probably greater than those of June and August, but less than that of the previous April. The result was strong sodium chloride water arriving at the Colorado (Figure 6). The ranking of flow rate is based on the assumption that the lowest sum of meq/liter represents the greatest dilution of the Blue Spring contribution, and hence the greatest flow from above the spring(s). Also, the sums of meq, TDS, and ionic strength are inversely related to the sediment carried by the Little Colorado. It appears, then, that (1) when the Little Colorado is flooding and diluted, the Blue Spring issue arrives at the Colorado River in a less concentrated state, but otherwise relatively unaltered, and (2) when the Blue Spring is the only source, the water arriving at the mouth of the Little Colorado is strongly concentrated, but its ionic proportions differ from the original effluent.

Elves' Chasm

At Mile 116.5, a minor tributary enters the Colorado River intermittently. The water is derived from a small grotto called Elves' Chasm and the discharge is estimated to be from zero to 0.5 cfs at the mouth of the Colorado River (Johnson and Sanderson, 1968). Its waters are rather concentrated and show anionic proportions much like the Colorado River and cation relations similar, but with far less sodium than the river (Figure 9). Whatever effect the water from Elves' Chasm has on the Colorado River would be masked because of their similarities. The impact must be insignificant, however, because of the tiny discharge from the grotto.

Kanab Creek

Kanab Creek enters the Colorado River at Mile 143.5. Although it drains some 2,000 square miles, its flow is continuous but not great--averaging about four cfs (Johnson and Sanderson, 1968). It is remarkably saline with a mean conductance of 1,422 micromhos/cm, a figure 1.5 times that of the Colorado River in Marble

Canyon and the Grand Canyon. It has a reputation as a remarkable sediment carrier, with a recorded 714 g of suspended sediment per liter near Fredonia (Ligner et al., 1969). The highest figure we ascertained was 0.46 g per liter in March 1976 at its mouth, some 40 miles downstream from the Fredonia gaging station. Its water temperature probably fluctuates about 20°C where it enters the Colorado River, and during the summer it is much warmer than the latter. Apparently, however, its low rate of discharge brings about minimal contributions to the Colorado River. In times of flooding there may be exceptions to the last statement.

Kanab Creek stands uniquely in this system as an excellent example of a sulfate water (Figure 8). Its calcium ion surpasses magnesium by about 10% on a meq-per-liter basis, placing it in the category of an impure gypsum water. It exhibits the highest magnesium-calcium hardness and the lowest alkalinity/hardness ratio of the main stream and all eleven tributaries (Tables 18 through 21, 25). It, therefore, has the highest non-carbonate hardness among the streams of the entire system. Except for the five dilute dolomitic streams deriving their waters from the Kaibab Plateau, Kanab Creek has the lowest ratio of monovalent to divalent cations (Tables 22 through 26). We found it low in nitrogen and phosphorus except for an assay (spurious?) of 1.10 mg/liter of orthophosphate in April. It shares third place in silica concentration with Paria and Elves' Chasm, being surpassed only by Diamond and Havasu creeks in this category (Tables 14 through 17).

Kanab Creek arrives at the Colorado River with its waters supersaturated with $CaCO_3$; the calculated pH of saturation (pH_s) was always below 7.61. The degree of saturation (Ω) averaged 4.7, with 1.0 representing equilibrium; only Havasu and Diamond creeks consistently showed a greater value for this. In the Colorado River, the degree of calcite saturation was usually higher below than it was upstream of Kanab Creek, but this could not be attributed solely to the entrance of the latter. Three other tributaries had joined meanwhile. To complicate matters, the cold temperatures of the Colorado River would only serve to increase the solubility of calcite arriving via the warm Kanab influent, and the inferior ionic strength in the main river would increase the activity of $CaCO_3$ by a factor of 1.3, thereby lowering solubility!

Calculations based on June data show that the molality of calcium would be increased in the Colorado River from 1.79×10^{-3} to 1.791×10^{-3}, if the river flowed at 10,000 cfs and the Kanab at 4 cfs. Furthermore, if the Kanab had been flowing at a rate of 400 cfs in June the calcium molality below its mouth in the Colorado would have been increased to 1.87×10^{-3}. This is the same as if the river discharge had been 5,000 cfs and the Kanab had contributed a volume equalling its mean of 4 cfs. The molality of Ca^{++} at Mile 219 was 1.785×10^{-3} (Table 10).

No stream contributed a greater concentration of sulfate to the Colorado River than did Kanab Creek. Despite this, the concentration below the Kanab was always less than the concentration above (Tables 9 through 13). Wondering if the lower temperatures and ionic strengths of the Colorado River could lead to a decrease in the solubility of $CaSO_4$, we performed some calculations to answer this. Using the solubility product 2.45×10^{-5} at 25° (from the Chemistry and Physics Handbook, 56th ed.) we found that gypsum was undersaturated in June to a degree of roughly 0.32 in the Kanab. Despite the Colorado River being about 13°C at the mouth of the Kanab and having half the ionic strength of the latter, two factors that would lessen the solubility of gypsum, the degree of saturation in the river was about 0.25 that of the Kanab. (Magnesium sulfate and sodium sulfate are many times more soluble than calcium sulfate and exploration of their states of saturation was not deemed worthwhile.) We are left with the conclusion that there is no precipitation of gypsum in the Colorado River below Kanab, and the decrease in meq/liter $SO_4^=$ from the river station above Kanab to that below must be a function of dilution from Tapeats, Deer and Havasu creeks.

Havasu Creek

Havasu Creek enters the Colorado River from the southeast at Mile 156.7. It arises in part from a series of seeps called Havasu Spring about 10 miles up a narrow canyon. The flow of Havasu Spring is somewhat stable, being in the neighborhood of 64 cfs (Johnson and Sanderson, 1968). At times the discharge must be significantly greater because the creek drains a large area of the Coconino Plateau.

Havasu Creek approached the Colorado River in salinity; its ionic strength was roughly 0.010 compared with the river's range of 0.009 to 0.016. The stream carries carbonate water with cations dominated by calcium and magnesium. It is best categorized as a poor example of dolomitic water. Its relative ionic composition is much like the dilute creeks derived from the Kaibab Plateau on the opposite side of the river. For example, it can be seen in Figure 7 that it resembles Tapeats Creek, but contains more chloride and sodium. Havasu is low in P and N, but rates second in SiO_2 (ca. 14.5 mg/liter).

Havasu Spring and its outflow serve as an excellent example of differences between calcium and magnesium compounds, the latter being far more soluble. Cole (1975) used data from Hem (1959) to show that the Ca/Mg ratio in Havasu Spring water is 1.59. Hem used the spring as an example of water with ". . . calcium a major constituent." By the time the mouth of Havasu Creek is reached there have been significant changes, marked by upstream travertine deposits. The ionic strength of the water has been reduced from 0.019 to 0.010 and the Ca/Mg ratio is lower; for the latter, our mean figure ($n = 5$) was 0.65 in water at the mouth of Havasu Creek (Tables 18 through 21, 25). Meanwhile the CO_3/Cl ratio falls from 6.8 at the spring to 4.2 (Tables 22 through 24, 26).

Only Diamond Creek surpassed Havasu Creek in degree of calcite saturation as it poured into the Colorado River; the Havasu mean Ω was 5.4, compared with 6.4 for Diamond Creek. Cole (1975) showed the Havasu Spring water has a $pH_{\underline{s}}$ of 6.79; it is about 7.5

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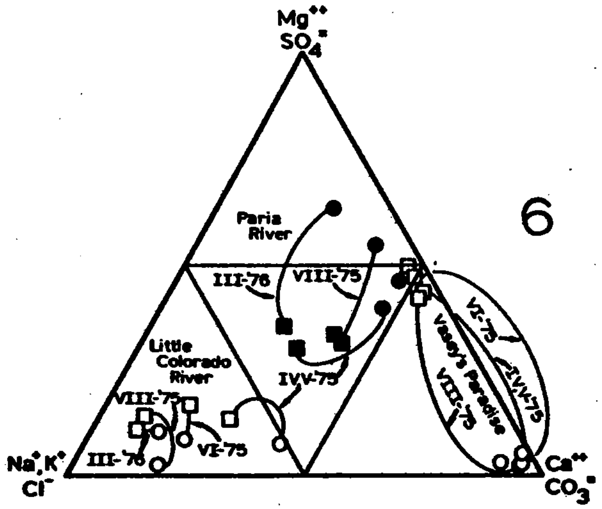
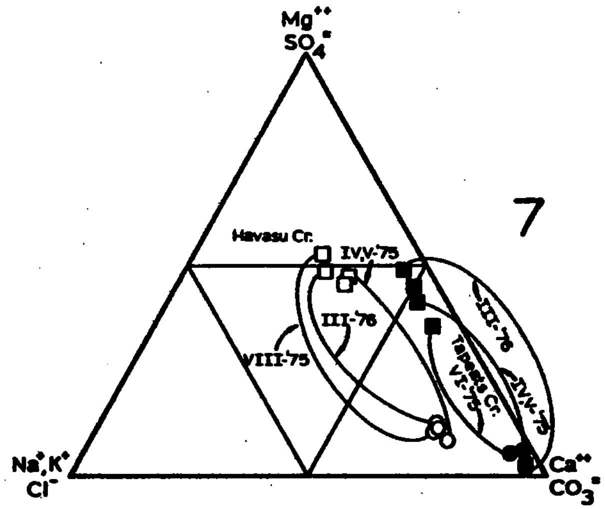


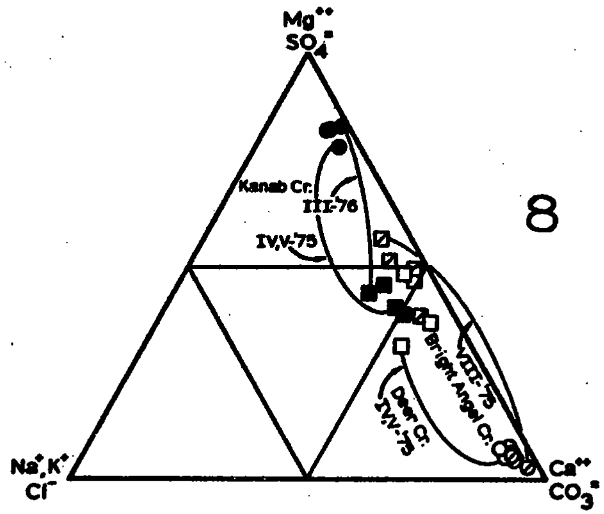
Mg++
SO4=
Na+,K+
Cl-
Ca++
CO3=
Paria River
III-76
VIII-75
IV,V-75
Little Colorado River
VIII-75
VI-75
III-76
VI-75
IV,V-75
Vasey's Paradise
VIII-75

7



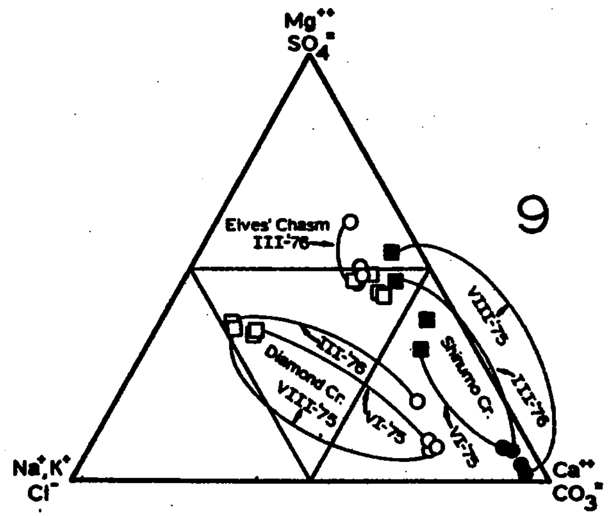
Mg++
SO4=
Na+,K+
Cl-
Ca++
CO3=
Havasu Cr.
IV,V-75
III-76
VIII-75
III-76
Tapeats Cr.
VI-75
IV,V-75

8



Mg++
SO4=
Na+,K+
Cl-
Ca++
CO3=
Kanab Cr.
III-76
IV,V-75
VIII-75
Bright Angel Cr.
Deer Cr.
IV,V-75

9



Mg++
SO4=
Na+,K+
Cl-
Ca++
CO3=
Elves' Chasm
III-76
VIII-75
III-76
Shinumo Cr.
VI-75
III-76
Diamond Cr.
VIII-75
VI-75

063451

Figure 6. Plots of the relative ionic composition of the first three tributaries entering the Colorado River on four trips. Paria River with closed symbols.

Figure 7. Plots of the relative ionic composition of Havasu Creek and Tapeats Creek on four trips. Tapeats with solid symbols.

Figure 8. Plots of the relative ionic composition of Kanab Creek, solid symbols; Deer Creek, open symbols; and Bright Angel Creek with diagonal lines.

Figure 9. Plots of the relative ionic composition of Elves' Chasm, Diamond Creek and Shinumo Creek, the last with closed symbols.

for the water at the mouth of the creek where on two occasions the observed pH was 8.3.

Diamond Creek

At River Mile 225.8, just below the disembarkation point, Diamond Creek enters the Colorado River. Its flow is small--on the order of 2 cfs according to Johnson and Sanderson (1968) and its impact on the main stream must be minimal except during times of unusual flooding.

Diamond Creek is interesting because it is one of the rare Arizona waters that can be classified as sodium carbonate, although not an unsurpassed example of such (Figure 9). This may account for the fact that it had, consistently, high pH values (Tables 1 through 4). It has a total salinity much like the Colorado River although a bit less and, of course, with different ionic proportions. The Diamond Creek influent was always oversaturated with calcite, to the highest average degree in the entire stream system discussed here, and it had a low, Ca/Mg ratio. It had an unsurpassed alkalinity/hardness ratio (Tables 8 through 21) and, of all the waters, this one probably invalidates such a ratio as a measure of carbonate to non-carbonate hardness. Its total alkalinity, although expressed in terms of $CaCO_3$ and averaging 325 mg/liter, is owed to the carbonates of alkali metals that play no role in water hardness. Only the Little Colorado had a consistently higher ratio of monovalent to divalent cations, and a lower Ca/Na ratio. Diamond Creek, however, ranked first in SiO_2, carrying a mean of about 18 mg/liter.

EFFECTS OF THE TRIBUTARIES ON THE COLORADO RIVER

Because there is a tremendous volume of water in the Colorado River, contributions from its influents in the gorge of the Grand Canyon seem to have little effect. An exception to this is seen in the case of particulate solids and the resultant turbidity.

Five of the inflowing creeks are the $CaMg(CO_3)_2$

type, contributing small quantities of dilute water at higher temperatures than the river. There are inklings that dilution effects occur; warming is not obvious. Although the streams had high pH values and were supersaturated with calcite, there was little evidence that they affected the Colorado River. Colder river water, however, probably immediately reduced the tendency of $CaCO_3$ to precipitate, and added to the calcium content of the river.

The Paria River seemed to play a miniscule part in modifying the Colorado except for an increase in the suspended solids. The mixing was delayed somewhat, the Paria current remaining discrete for a few miles before mixing throughout the main stream.

The effects of the Paria and Elves' Chasm are masked because their ionic compositions are proportionally much like the Colorado River. Also their discharges were small, although not precisely known. The Paria's mean flow at its mouth is roughly 30 cfs, ranging from zero to 16,000 (USGS, 1947). The Elves' Chasm input is rather concentrated, but its flow at the river junction has been described as intermittent and its discharge is probably never much greater than 0.5 cfs (Johnson and Sanderson, 1968).

Chloride is probably one of the best indicators of change in water chemistry in the 225 miles of the Colorado River considered here. Its compounds are extremely soluble and it would not be lost by precipitation. Its increase could be due to tributary input or evaporation's effect. The mean rise from Lee's Ferry to the last downstream river station was 0.51 meq/liter, amounting to about 18 mg per liter. There was always an increase in the station below the Little Colorado River when compared with the water at the station above (Tables 9 through 13, Figures 2, 3, 5); this suggests that the tributary has an effect. In April-May and August, however, there were decreases from Mile 71 to the ultimate station, amounting to 0.45 meq in each instance. In June there was no change, and in March the last station showed a 0.44-meq decline compared with Mile 65. The waters of the Little Colorado, then, seemed to have no great effect on the water chemistry of the Colorado River despite the high salinity of the Blue Spring sources. The turbidity derived from the Little Colorado when it is in flood is another situation; its impact is enormous.

To explore further the effects of the Little Colorado River on the salt load of the Colorado River, some computations were made on dilution phenomena. The average chloride concentration at the first river station above the mouth of the Little Colorado was 1.64 meq/liter. This was 0.014 meq/liter lower than the chloride at Lee's Ferry and was probably not significantly different. The mean chloride content of the water in the Little Colorado River at its mouth was 27.93 meq/liter (including the low of 6.43 in April-May when flooding was marked). If we hold the two chloride measurements constant and assume a mean flow rate of 223 cfs from the Blue Spring sources, some information can be inferred about the diluting effects of the Colorado River. The results are shown in Figure 10, where the final theoretical concentrations of chloride are plotted against the Colorado's flow in cfs. The curve shows that the diluting effects increase strikingly until somewhere around 10,000 cfs. After this each extra 1,000 cfs reduces the chloride by less than one-tenth of a meq per liter. The average chloride in the Colorado River at the next station below the Little Colorado was 2.27 meq/liter. From the curve in Figure 10 the average flow of the Colorado River for the five trips was 9,700 cfs there. At 15,000 cfs the final mixture would have been reduced only to 2.03 meq of chloride.

There has been some attention devoted to the increments of salt received by the Colorado from its tributaries, and especially the Blue Spring component of the Little Colorado. Gross modifications including damming and desalting manipulations have been proposed to alleviate the salinity burden imposed on the Colorado River. At this time the plans have been abandoned, at least temporarily, they being economically, sociologically and aesthetically unacceptable. Important questions concern the actual status of the Colorado River before and after it passes the mouth of the Little Colorado River and flows toward Lake Mead and ultimately to the Imperial Dam.

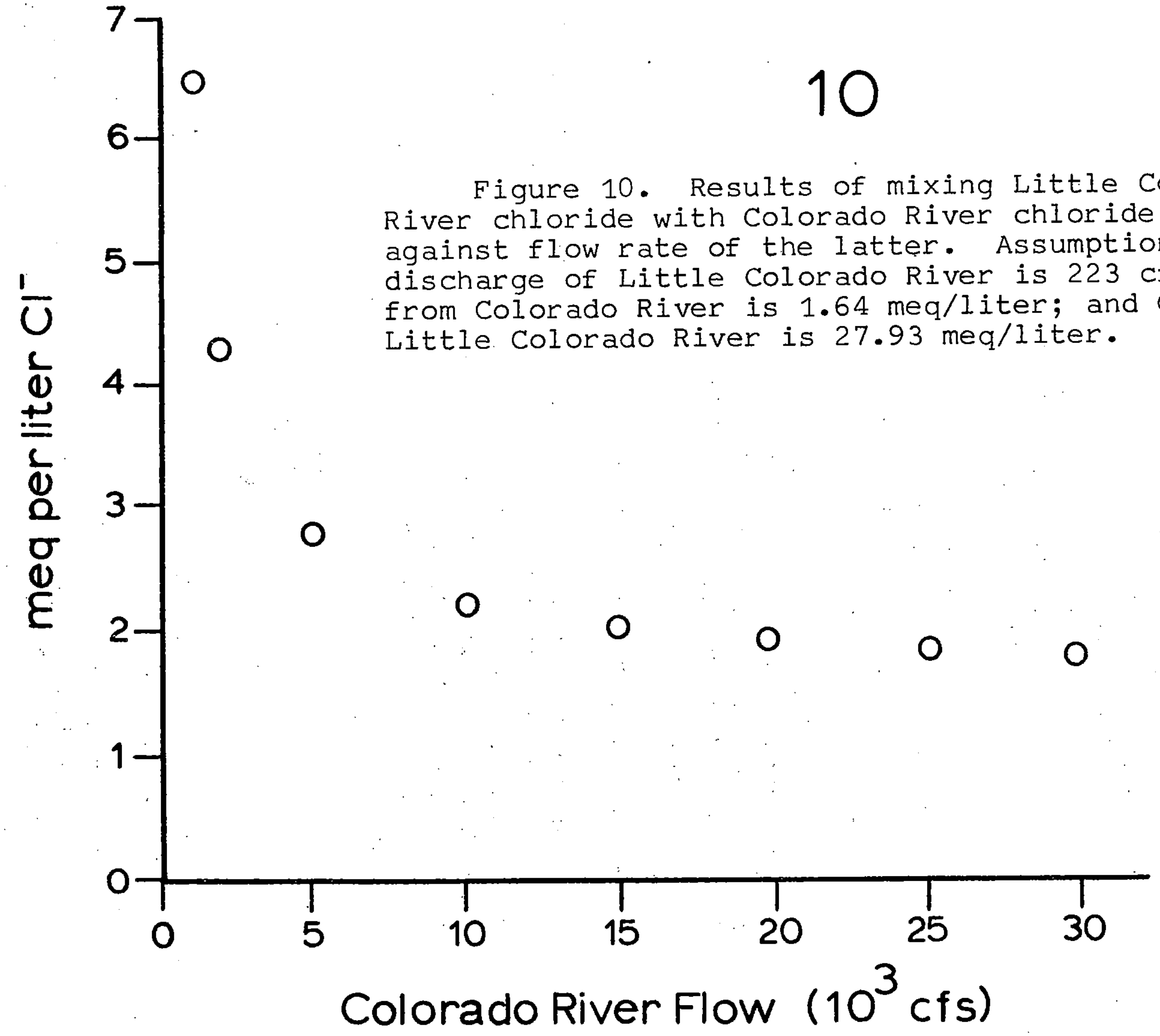


Figure 10. Results of mixing Little Colorado River chloride with Colorado River chloride plotted against flow rate of the latter. Assumptions: mean discharge of Little Colorado River is 223 cfs; Cl^- from Colorado River is 1.64 meq/liter; and Cl^- from the Little Colorado River is 27.93 meq/liter.

First, the Colorado River can be judged against various criteria. On the basis of industrial qualifications it is non-saline water throughout the 225-mile stretch in the Marble and Grand Canyon (Swenson and Baldwin, 1956). For drinking purposes, however, the water at Lee's Ferry is too saline, exceeding the 500 mg/liter dissolved solids recommended as a maximum by the U. S. Public Health Service (1962). It has been this way throughout the span of time that the river has been studied. The U.S.P.H.S. allows, however, a two-fold increase in salinity for occasional consumption and this is, of course, what applies to consumers on river trips. The increase from 623 to 644 at the ultimate collecting site represents a three-percent increase. Records from the gaging station between the Little Colorado and Bright Angel Creek show an increase of about 10% before and since the closing of the Glen Canyon Dam. This agrees somewhat with our data for collections in that segment of the stream, where we found an 8% augmentation of TDS over the mean condition at Mile 0. Our samples below Bright Angel were valuable in bringing to light dilution effects in lowering salt concentrations.

Another standard that tells something about the Colorado River is the so-called SAR, the sodium adsorption ratio. This expresses the relative activity of sodium ions in exchange reactions with soil--an index of the sodium or alkali hazards to agricultural soil. It is found from the following, using meq values,

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{++} + Mg^{++}}{2}}}$$

At all points in the section of the Colorado River we studied, the SAR is low and the increase averages 0.2 from Lee's Ferry to the last downstream site. The means were 1.87 and 2.07 at Mile 0 and the ultimate sampling site, respectively. At a conductance of 940 micromhos/cm @ 25°, any value from zero to 4.5 would be considered "low," and "medium" would range up to 10.5. On the basis of the SAR criterion, then, the Colorado

River leaves the Diamond Point region carrying acceptable water for irrigation.

The dilution brought about by the less concentrated tributaries is important in alleviating whatever bad effects are owed to the more concentrated inflows. This should be kept in mind, whenever proposals are made for reducing flows to the Colorado River.

AQUATIC INVERTEBRATE FAUNA

A list of the aquatic invertebrate species collected from the Colorado River and its major tributaries in Marble Canyon and the Grand Canyon is presented in Table 27. The list is far from complete because there were severe limitations on time, and lack of proper sampling equipment prevented thorough collecting in these waters. In addition, samples from the tributaries were always taken near their confluences with the Colorado; the fauna in upstream reaches may have been quite different. Taxonomic determinations were made to various levels, most often to the familial rank; the results were dependent upon the comparative difficulty in treating a category, our current knowledge of the group, and the familiarity of the investigator with any particular group.

Despite the shortcomings and incompleteness of the list, several valuable observations were made and some generalizations have come to light. Perhaps most striking is the difference in faunal composition between the mainstream and its associated tributaries. Significant overlap apparently occurs only in three groups: oligochaetes, chironomids and gastropods. The mainstream appears quite unproductive, with perhaps the exception of a minor stretch near Lee's Ferry. The only consistent zooplankter found in the Colorado River was the copepod, Cyclops bicuspidatus thomasi. More diversity was found in those regions at the river's edges, including backwater marshes and side pools. In such habitats were found a combination of the amphipod Gammarus lacustris, chironomid larvae, ostracods, oligochaetes and snails.

Of the tributaries, three were conspicuously impoverished both in terms of species present and numbers of organisms; these were the Paria River, Little Colorado River and Kanab Creek. A feature they share is the occasional heavy sediment load which produces unstable substrate conditions, thus eliminating many organisms that are found in the other tributaries. The Little Colorado in its lower reaches is also marked by the accumulation of calcium carbonate precipitates, perhaps further restricting the fauna. This same phenomenon is also typical of Havasu Creek as evidenced by the large travertine concretions present there. Here again, certain groups such as oligochaetes, chironomids and mayflies were either absent or present in extremely low numbers.

The faunas of Elves' Chasm, Tapeats Creek and Diamond Creek are more diverse than those of the other tributaries sampled. It is difficult to conclude any factor or factors held in common that would contribute to their higher diversity. Elves' Chasm is essentially a series of seeps and pools connected by shallow rivulets; Tapeats is a rapidly-flowing stream that seasonally supports dense beds of water cress; and Diamond Creek is a slow-flowing, shallow brook.

The invertebrates most heavily represented in the tributaries were the oligochaetes, ephemeropterans, trichopterans and dipterans. Within these groups, the baetid mayflies (Baetidae) and hydropsychid caddisflies (Hydropsychidae), along with the black-flies (Simuliidae) and midges (Chironomidae) occurred most frequently and were numerically predominant in the samples. Because of the previously mentioned limitations in sampling and taxonomic determination, it is difficult to assess the presence or absence of rare groups, or to categorize the streams by similarities in their faunas.

The value of this list (Table 27) is at least twofold. It provides limited information on invertebrate animals living within various aquatic habitats of the Grand Canyon National Park. Such information serves as a basic background for further studies, and particularly for comparisons to be made at some future date. Second, the data may have suggested a path for future research and management policies: the faunal differences between the tributaries and the main river suggest that information could be gained concerning the origin and flow of resource components utilized by consumer organisms (e.g., fish) in the Colorado River. Perhaps the mainstream consumers depend on food resources produced in the tributaries. There may be direct usage dependent upon foraging expeditions, or indirectly, invertebrate drift might be an energy source for predators in the Colorado River. Probably some valuable information could be derived from analysis of the contents of fish guts. Thus, the value of the tributaries to the main river may extend far beyond their roles as contributors of nutrients and diluters of salts.

Ultimately, the collections (on which Table 27 is based) will be deposited in the Museum of Northern Arizona, Flagstaff.

DISCUSSION AND CONCLUSIONS

The data reported here represent the first study of changes in physico-chemical parameters that occur with time and space in the 225-mile stretch of the Colorado River from Lee's Ferry to Diamond Creek. There are many older records from Lee's Ferry and from a gaging station between the mouth of the Little Colorado and Bright Angel Creek. There is, however, very little information concerning conditions below that station within the Grand Canyon. Thus, the inflows of at least eight tributaries, including Bright Angel Creek, have not been evaluated with respect to their effects on the Colorado for the 145 miles below the aforementioned gaging station.

A significant finding was that the salinity of the Colorado River is lessened somewhat by the streams entering below the Little Colorado River. The river leaves the Diamond Creek junction with a greater salt load than it had at Lee's Ferry, but not so great as might have been extrapolated from some upstream data (above Mile 88, the mouth of Bright Angel Creek). The diluting results of the river itself on the saline discharge it receives from the Little Colorado River, and the further dilution brought about by the sum of many small streams on the mixture in the Colorado River emphasizes the value of: (1) maintaining the discharge of the main river at as high a level as possible, and (2) interfering as little as is feasible with the input from the tributaries.

In many instances, <u>concentrations</u> of salts are not taken into account when the impact of saline springs, for example, are discussed. Usually the total mass of salts contributed per year is presented with no mention of the volume of water in which the material is dissolved. From the present study one could say that Havasu Creek contributes about 22,300 metric tons of salt to the Colorado River as it flows to the Imperial Dam and agricultural land to the south. It ignores the fact that the Havasu, flowing at 64 cfs and carrying a mean of 390 mg/liter TDS, dilutes the main river. Thus, if the Colorado were flowing at 10,000 cfs and carrying a mean of 644 mg/liter, the Havasu would reduce the salinity to 642.4 mg of dissolved solids per liter, improving the water quality.

Our use of the Secchi disc in addition to standard methods of evaluating turbidity and light penetration revealed some facts that have not been quantified before. It is quite possible that the upper reaches of the river, no longer turbid until the Little Colorado is reached (or rarely when the Paria is carrying unusual amounts of sediment) would be a productive area. The striking light penetration and the extensive benthic algal community might well support a cold-water fishery, a possibility only since the closing of the Glen Canyon Dam. This is speculation, because primary production has not been assayed, and the tremendous loss of free CO_2 from the waters below Lee's Ferry has not been evaluated in terms of physical or biological cause. The calculated CO_2 was far in excess of saturation at Lee's Ferry and its diminishing downstream, therefore, cannot be attributed solely to carbon fixation by green plants. The statements above are not to be construed as a recommendation that exotic stenothermal fish be planted in the Colorado system.

The Colorado River below the relatively new Glen Canyon Dam is much more stable than it was in the past. The striking variations in physical and chemical features that characterized it in earlier days are much reduced--fluctuations have been damped.

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APPENDIX

Tables 1 through 27

Table 1. April-May, 1975 - Collecting times, water temperatures, some physico-chemical and miscellaneous data. cond = micromhos/cm @ 25°; DO = dissolved O_2, mg/liter; TDS, mg/liter.

	hr	C°	pH	cond	DO	TDS evap	TDS calc	evap/calc
Lee's Ferry	0930	7	7.5	971	--	660	566	1.17
Paria River	0845	14	7.9	1,075	--	476	661	0.44
Mile 19	1800	8	7.8	989	10.1	668	562	1.19
Vasey's Paradise	1200	17	8.3	408	6.6	174	210	0.83
Little Colorado	1215	14	8.1	1,246	--	697	610	1.14
Mile 71	1700	8.5	8.0	970	--	692	613	1.13
Bright Angel	1800	11	8.2	266	10.8	161	155	1.04
Shinumo Creek	0830	9	8.2	342	--	191	178	1.07
Elves' Chasm	1330	13	8.2	861	--	581	495	1.17
Mile 125	1830	10	7.9	975	--	681	615	1.11
Tapeats Creek	1300	13	8.3	296	--	175	164	1.07
Deer Creek	1530	14	8.4	329	10.8	176	169	1.04
Kanab Creek	1700	14.5	8.3	1,440	--	1,099	970	1.13
Havasu Creek	1000	16	8.3	713	10.4	415	407	1.02
Mile 225	1000	11	7.9	981	--	643	555	1.16
Diamond Creek	1030	23.5	8.4	777	--	451	453	0.99

Table 2. June, 1975 - Collecting times, water temperatures, some physico-chemical and miscellaneous data. cond = micromhos/cm @ 25°; DO = dissolved O_2, mg/liter; TDS, mg/liter.

	hr	C°	pH	cond	TDS evap	TDS calc	evap/calc
Lee's Ferry	1000	10	7.8	941	616	546	1.13
Paria River	0800	18	8.1	523	355	324	1.09
Mile 19	0730	10	7.8	923	601	563	1.07
Vasey's Paradise	1200	16	8.1	281	183	151	1.21
Little Colorado	1100	24	7.9	>2,050	2,483	2,491	0.99
Mile 71	1730	12	7.9	889	668	550	1.21
Bright Angel	1130	18	8.4	244	164	150	1.09
Shinumo Creek	1330	19	8.2	290	212	107	1.98
Elves' Chasm	1600	21	8.3	839	646	474	1.36
Mile 119	0700	12	7.8	924	658	574	1.15
Tapeats Creek	1030	14	8.3	249	139	132	1.05
Deer Creek	1300	16	8.2	312	179	163	1.09
Kanab Creek	1530	25	8.1	1,300	1,115	1,039	1.07
Havasu Creek	0900	20	8.2	735	350	409	0.98
Mile 219	1800	15	7.9	933	616	577	1.07
Diamond Creek	0830	21.5	8.4	885	454	472	0.96

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Table 3. August, 1975 - Collecting times, water temperatures, some physico-chemical and miscellaneous data. cond = micromhos/cm @ 25°; DO = dissolved O_2, mg/liter; TDS, mg/liter.

	hr	C°	pH	cond	TDS evap	TDS calc	evap/calc
Lee's Ferry	0900	10	7.8	938	590	533	1.11
Paria River	1000	26	8.3	887	621	455	1.36
Mile 18	1630	10.2	7.9	940	595	479	1.24
Vasey's Paradise	1200	18	8.2	357	211	187	1.01
Mile 37.8	1700	10.2	7.9	955	618	498	1.24
Little Colorado	1500	25	7.8	>2,000	2,513	2,267	1.11
Bright Angel	1630	26	8.7	283	194	153	1.27
Shinumo Creek	1600	26.5	8.3	253	177	143	1.23
Elves' Chasm	0900	20.5	8.2	816	574	482	1.19
Mile 132	1800	13.5	8.0	928	622	552	1.13
Tapeats Creek	0900	14.5	8.3	340	178	170	1.05
Deer Creek	1030	17.5	8.3	396	210	208	1.01
Kanab Creek	1600	26	8.2	1,365	1,267	889	1.43
Havasu Creek	1030	21	8.3	773	400	370	1.08
Mile 165	0630	14	8.2	964	676	556	1.21
Mile 213	1730	15.2	8.2	926	636	568	1.12
Diamond Creek	1100	30.5	8.3	838	520	500	1.04

Table 4. March 1976 - Collecting times, water temperatures, some physico-chemical and miscellaneous data. cond = micromhos/cm @ 25°; DO = dissolved O_2, mg/liter; TDS, mg/liter.

	hr	C°	pH	cond	TDS evap	TDS calc	evap/calc
Lee's Ferry	1100	8.1	7.4	931	626	563	1.11
Paria River	1000	12.5	8.3	1,248	948	782	1.21
Mile 26.5	1730	8.1	7.5	925	630	535	1.18
Vasey's Paradise	1030	12.0	8.2	371	200	186	1.07
Little Colorado	1600	15.0	8.1	4,550	2,160	2,184	0.99
Mile 65	1800	8.7	7.6	980	654	616	1.06
Bright Angel	1330	7.5	8.3	351	200	184	1.09
Shinumo Creek	1300	7.8	8.3	380	201	199	1.01
Elves' Chasm	1500	8.0	8.3	824	609	521	1.17
Mile 126	0800	8.2	7.9	980	668	647	1.03
Tapeats Creek	1200	10.2	8.3	336	175	168	1.04
Deer Creek	1300	13.0	8.3	385	209	194	1.08
Kanab Creek	1700	7.2	8.2	1,804	1,609	1,263	1.27
Havasu Creek	1100	13.0	8.2	692	394	412	0.96
Mile 180	1800	8.7	8.0	980	653	590	1.11
Mile 225	1800	9.0	8.0	931	--	579	--
Diamond Creek	1700	14.8	8.3	819	471	460	1.02

Table 9. April-May, 1975 - Major ions in meq/liter.

	HCO_3^-	$SO_4^=$	Cl^-	Ca^{++}	Mg^{++}	Na^+	K^+	Σ
Lee's Ferry	3.00	4.68	1.66	3.54	2.01	3.41	0.10	18.81
Paria River	4.40	4.84	1.41	4.27	4.03	4.61	0.10	23.66
Mile 19	2.92	4.68	1.62	3.59	2.38	3.31	0.10	18.60
Vasey's Paradise	3.92	0.20	0.08	2.17	1.77	0.13	0.02	8.29
Little Colorado	4.92	0.62	6.43	2.64	1.15	5.39	0.11	21.26
Mile 71	3.92	4.58	2.48	3.29	2.01	3.57	0.10	19.95
Bright Angel	2.82	0.19	0.10	1.47	1.32	0.15	0.02	6.07
Shinumo Creek	3.40	0.08	0.10	1.97	1.40	0.17	0.02	7.14
Elves' Chasm	3.10	4.16	1.23	3.64	3.86	1.00	0.08	17.07
Mile 125	3.60	4.68	2.26	3.52	2.55	3.94	0.10	20.65
Tapeats Creek	2.96	0.13	0.07	1.72	1.40	0.13	0.08	6.49
Deer Creek	2.82	0.21	0.08	2.02	1.60	0.15	0.02	6.90
Kanab Creek	2.51	12.49	0.59	7.83	6.08	1.50	0.15	31.15
Havasu Creek	6.08	0.58	1.30	2.62	3.49	1.35	0.12	15.54
Mile 225	3.10	4.30	2.03	3.39	2.10	3.31	0.09	18.32
Diamond Creek	6.32	0.69	1.63	1.65	2.76	3.39	0.14	16.58

Table 10. June, 1975 - Major ions in meq/liter.

	HCO_3^-	$SO_4^=$	Cl^-	Ca^{++}	Mg^{++}	Na^+	K^+	Σ
Lee's Ferry	2.80	5.20	1.66	2.99	1.95	2.72	0.09	17.41
Paria River	2.68	2.76	0.34	1.90	1.68	1.15	0.08	10.59
Mile 19	2.80	5.08	1.64	3.42	2.16	3.02	0.10	18.22
Vasey's Paradise	2.86	0.08	0.08	1.67	1.15	0.15	0.01	6.00
Little Colorado	8.80	3.38	34.06	5.76	5.57	28.49	0.20	86.26
Mile 71	2.80	4.27	2.03	3.57	2.24	3.33	0.10	18.34
Bright Angel	2.32	0.12	0.08	1.25	0.92	0.13	0.01	4.83
Shinumo Creek	1.84	0.14	0.10	1.15	0.62	0.20	0.01	4.06
Elves' Chasm	2.84	4.16	1.13	3.54	3.62	0.91	0.08	16.28
Mile 119	2.84	4.94	1.89	3.52	2.18	3.22	0.10	18.69
Tapeats Creek	2.75	0.10	0.14	1.47	0.88	0.13	0.01	5.48
Deer Creek	2.96	0.22	0.08	1.80	1.17	0.13	0.01	6.37
Kanab Creek	1.96	14.31	0.63	7.48	6.13	1.41	0.16	32.08
Havasu Creek	5.96	0.85	1.41	2.72	3.49	1.35	0.11	15.89
Mile 219	2.88	4.87	2.03	3.57	2.22	3.26	0.10	18.93
Diamond Creek	6.44	0.83	1.82	1.77	2.98	3.50	0.16	17.50

Table 11. August, 1975 - Major ions in meq/liter.

	HCO_3^-	$SO_4^=$	Cl^-	Ca^{++}	Mg^{++}	Na^+	K^+	Σ
Lee's Ferry	2.72	4.16	1.64	2.49	1.89	2.39	0.09	15.38
Paria River	2.76	4.16	0.45	3.29	2.51	1.87	0.14	15.18
Mile 18	2.68	4.16	1.59	2.54	1.93	2.44	0.09	15.43
Vasey's Paradise	3.78	0.10	0.09	1.75	1.64	0.09	0.02	7.47
Mile 37.8	2.80	4.21	1.59	2.74	2.14	2.74	0.09	16.31
Little Colorado	6.78	0.61	34.01	3.74	5.63	30.45	0.16	81.38
Bright Angel	2.98	0.04	0.10	1.10	1.73	0.17	0.02	6.14
Shinumo Creek	2.88	0.03	0.11	1.10	1.44	0.13	0.02	5.71
Elves' Chasm	3.08	4.16	1.33	2.99	3.95	0.96	0.08	16.55
Mile 132	2.96	4.94	1.86	2.94	2.26	3.13	0.09	18.18
Tapeats Creek	3.44	0.04	0.08	1.65	1.48	0.13	0.01	6.83
Deer Creek	4.02	0.29	0.13	1.85	1.77	0.13	0.01	8.20
Kanab Creek	1.88	11.71	0.68	5.89	6.25	1.39	0.12	27.92
Havasu Creek	5.54	0.78	1.42	1.70	3.41	1.22	0.11	14.18
Mile 165	3.36	4.42	1.95	2.74	2.26	3.44	0.10	18.27
Mile 213	4.00	4.31	2.26	2.69	2.01	3.09	0.09	18.45
Diamond Creek	7.04	0.81	2.07	1.39	2.92	3.87	0.16	18.26

Table 12. November, 1975 - Major ions in meq/liter--incomplete data.

	$SO_4^{=}$	Cl^-	Ca^{++}	Mg^{++}	Na^+	K^+
Lee's Ferry	5.43	1.69	2.69	2.01	2.57	0.08
Paria River	--	--	5.39	5.55	4.39	0.13
Mile 29	--	--	2.59	1.93	2.70	0.08
Vasey's Paradise	0.04	0.77	1.80	1.69	1.30	0.01
Mile 32	5.78	1.71	--	--	--	--
Little Colorado	4.20	36.43	5.09	5.76	31.32	0.16
Bright Angel	0.04	0.48	1.65	1.77	0.17	0.02
Shinumo Creek	0.04	0.37	1.80	1.64	0.17	0.01
Elves' Chasm	5.43	1.66	3.14	4.03	1.09	0.07
Mile 120	--	--	2.74	2.14	3.18	0.09
Tapeats Creek	0.05	0.39	1.65	1.52	0.13	0.01
Deer Creek	0.29	0.51	1.95	1.85	0.13	0.01
Kanab Creek	16.80	0.87	6.94	6.41	1.52	0.14
Havasu Creek	1.04	1.69	2.20	3.78	1.44	0.10
Mile 173	--	--	2.74	2.22	3.57	0.09
Mile 225	5.95	2.50	2.64	2.18	3.35	0.09
Diamond Creek	0.94	2.09	1.35	2.84	3.65	0.12

Table 13. March, 1976 - Major ions in meq/liter.

	HCO_3^-	$SO_4^=$	Cl^-	Ca^{++}	Mg^{++}	Na^+	K^+	Σ
Lee's Ferry	2.72	6.83	1.66	2.69	2.38	3.61	0.13	20.02
Paria River	4.3	11.2	1.90	3.24	4.28	4.22	0.14	29.28
Mile 26.5	2.88	6.3	1.62	2.69	2.14	3.22	0.10	18.95
Vasey's Paradise	3.78	0.18	0.25	1.55	1.73	0.17	0.02	7.68
Little Colorado	5.06	4.20	28.70	3.74	4.28	31.32	0.16	77.47
Mile 65	3.0	7.00	2.51	2.69	2.30	4.05	0.11	21.65
Bright Angel	3.72	0.20	0.17	1.35	1.73	0.22	0.02	7.41
Shinumo Creek	3.84	0.29	0.17	1.50	1.64	0.26	0.02	7.72
Elves' Chasm	3.11	6.83	1.27	2.79	3.78	1.09	0.08	18.95
Mile 126	3.2	7.95	2.34	2.69	2.30	3.94	0.12	22.54
Tapeats Creek	3.58	0.04	0.11	1.40	1.48	0.13	0.01	6.75
Deer Creek	3.78	0.25	0.11	1.70	1.81	0.17	0.02	7.84
Kanab Creek	4.08	22.07	0.99	7.29	8.06	2.65	0.16	45.30
Havasu Creek	6.16	1.08	1.48	2.15	3.45	1.44	0.115	15.88
Mile 180	3.07	6.30	2.52	2.59	2.30	4.00	0.11	20.89
Mile 225	3.16	6.83	2.07	2.50	2.14	3.48	0.11	20.29
Diamond Creek	6.24	1.89	1.86	1.30	2.96	3.78	0.01	18.04

Table 5. April-May, 1975 - Some factors relating to transparency. Sol = non-filtrable solids; JTU = Jackson turbidity units; T = transparency, small samples; O = opacity, small samples; OD = optical density, small samples.

	Sol	JTU	T	O	OD
Lee's Ferry	2	10	0.97	1.03	0.013
Paria River	2,451	--	--	--	--
Mile 19	26	15	0.97	1.03	0.013
Vasey's Paradise	12	2	0.98	1.02	0.009
Little Colorado	14,260	--	--	--	--
Mile 71	--	--	0.09	11.11	1.05
Bright Angel	150	21	0.97	1.03	0.013
Shinumo Creek	100	32	0.93	1.08	0.032
Elves' Chasm	5	4	0.985	1.01	0.007
Mile 125	986	170	0.55	1.80	0.260
Tapeats Creek	4.5	5	1.00	1.00	0
Deer Creek	15	6	0.98	1.02	0.009
Kanab Creek	2.2	20	0.97	1.03	0.013
Havasu Creek	4.8	5	0.995	1.005	0.001
Mile 225	923	98	0.69	1.45	0.160
Diamond Creek	4.8	12	0.99	1.01	0.004

Table 6. June, 1975 - Some factors relating to water transparency. Sol = non-filtrable solids; JTU = Jackson turbidity units; T = transparency, small samples; O = opacity, small samples; OD = optical density, small samples; SD_z = Secchi disc, m; k = coefficient of vertical light attenuation; %T = % vertical transmission of light per m; P_z = calculated depth of euphotic zone, m.

	Sol	JTU	T	O	OD	SD_z	k	%T	P_z
Lee's Ferry	1	1	0.99	1.01	0.004	5.8	1.293	74.6	15.7
Paria River	136	110	0.69	1.45	0.160	-	--	--	--
Mile 19	12	1	0.99	1.01	0.004	4.3	0.395	67.4	11.6
Vasey's Paradise	14	3	0.98	1.02	0.009	-	--	--	--
Little Colorado	22	5	0.98	1.02	0.009	-	--	--	--
Mile 71	14	10	0.98	1.02	0.009	1.1	1.545	21.3	3.0⁻
Bright Angel	30	8	0.98	1.02	0.009	-	--	--	--
Shinumo Creek	24	14	0.94	1.06	0.027	-	--	--	--
Elves' Chasm	5	4	0.98	1.02	0.009	-	--	--	--
Mile 119	32	9	0.97	1.03	0.013	1.1	1.545	21.3	3.0⁻
Tapeats Creek	14	10	0.97	1.03	0.013	-	--	--	--
Deer Creek	36	7	0.98	1.02	0.009	-	--	--	--
Kanab Creek	14	8	0.97	1.03	0.013	-	--	--	--
Havasu Creek	6	5	0.99	1.01	0.004	-	--	--	--
Mile 219	18	10	0.98	1.02	0.009	1.1	1.545	21.3	3.0⁻
Diamond Creek	6	9	0.99	1.01	0.004	-	--	--	--

Table 7. August, 1975 - Some factors relating to water transparency. Sol = non-filtrable solids; JTU = Jackson turbidity units; T = transparency, small samples; O = opacity, small samples; OD = optical density, small samples; SD_z = Secchi disc, m; k = coefficient of vertical light attenuation; %T = % vertical transmission of light per m; P_z = calculated depth of euphotic zone, m.

	Sol	JTU	T	O	OD	SD_z	k	%T	P_z
Lee's Ferry	< 1	1	0.99	1.01	0.004	6.0	0.283	75.4	16.2
Paria River	732	92	0.74	1.35	0.131	--	--	--	--
Mile 5	--	--	--	--	--	4.1	0.415	66.0	11.1
Mile 18	62	20	0.98	1.02	0.009	0.55	3.091	4.6	1.5
Vasey's Paradise	35	1	0.99	1.01	0.004	--	--	--	--
Mile 37.8	77	55	0.93	1.08	0.032	--	--	--	--
Little Colorado	42	55	0.88	1.14	0.055	--	--	--	--
Bright Angel	13	8	0.96	1.04	0.018	--	--	--	--
Shinumo Creek	15	30	0.92	1.09	0.036	--	--	--	--
Elves' Chasm	10	4	0.98	1.02	0.009	--	--	--	--
Mile 132	567	300	0.37	2.70	0.432	0.06	28.33	< 0.001	0.16
Tapeats Creek	7	3	0.99	1.01	0.004	--	--	--	--
Deer Creek	10	5	0.95	1.05	0.022	--	--	--	--
Kanab Creek	9	13	0.92	1.09	0.036	--	--	--	--
Havasu Creek	8	3	0.99	1.01	0.004	--	--	--	--
Mile 165	888	330	0.30	3.33	0.523	0.04	42.50	< 0.001	0.11
Mile 213	870	334	0.30	3.33	0.523	--	--	--	--
Diamond Creek	838	14	0.98	1.02	0.009	--	--	--	--

Table 8. March, 1976 - Some factors relating to water transparency. Sol = non-filtrable solids; JTU = Jackson turbidity units; T = transparency, small samples; O = opacity, small samples; OD = optical density, small samples; SD_Z = Secchi disc, m; k = coefficient of vertical light attenuation; %T = % vertical transmission of light per m; P_Z = calculated depth of euphotic zone, m.

	Sol	JTU	T	O	OD	SD_Z	k	%T	P_Z
Lee's Ferry	54	2	0.985	1.01	0.007	3.10	0.548	57.8	8.4
Paria River	1,546	850	0.17	5.88	0.769	--	--	--	--
Mile 26.5	93	5	0.98	1.02	0.009	0.90	1.888	15.3	2.4
Vasey's Paradise	22	0	1.00	1.00	0	--	--	--	--
Little Colorado	1,133	340	0.38	2.63	0.420	0.06	28.33	<0.001	0.16
Mile 65	111	9	0.98	1.02	0.009	0.63	2.698	6.9	1.70
Bright Angel	5	0	1.00	1.00	0	--	--	--	--
Shinumo Creek	4	0	1.00	1.00	0	--	--	--	--
Elves' Chasm	< 1	0	1.00	1.00	0	--	--	--	--
Mile 126	184	105	0.74	1.35	0.131	0.08	21.25	<0.001	0.22
Tapeats Creek	8	0	1.00	1.00	0	--	--	--	--
Deer Creek	9	0	1.00	1.00	0	--	--	--	--
Kanab Creek	460	325	0.38	2.63	0.420	--	--	--	--
Havasu Creek	23	0	0.995	1.01	0.001	--	--	--	--
Mile 180	68	35	0.89	1.12	0.051	0.28	6.07	0.23	0.16
Mile 225	92	55	0.865	1.16	0.063	0.13	13.077	<0.001	0.35
Diamond Creek	15	0	1.00	1.00	0	--	--	--	--

Table 14. April-May, 1975 - Plant nutrients: silica and phosphate in mg/liter; P and N in µg/liter. N = sum of NO_3-N and NO_2-N. P = orthophosphate-P.

	SiO_2	$PO_4^{\equiv}$	P	N	N/P
Lee's Ferry	10.5	0.19	61.9	100	1.6
Paria River	10.5	--	--	-	--
Mile 19	10.2	0.07	22.8	-	--
Vasey's Paradise	10.8	0.08	26.1	950	36.5
Little Colorado	9.4	--	--	-	--
Mile 71	10.2	0.19	61.9	90	1.5
Bright Angel	7.0	0.12	39.1	60	1.5
Shinumo Creek	7.5	0.10	32.6	90	2.8
Elves' Chasm	13.0	0.04	13.0	390	29.9
Mile 125	10.5	0.07	22.8	370	16.2
Tapeats Creek	9.0	0.14	45.6	10	0.2
Deer Creek	8.5	0.15	48.9	160	3.3
Kanab Creek	11.5	1.10	358.3	210	0.6
Havasu Creek	21.0	0.02	6.5	120	18.4
Mile 225	9.5	0.16	52.1	600	11.5
Diamond Creek	22.5	0.11	35.8	460	12.8

Table 15. June, 1975 - Plant nutrients: silica and phosphate in mg/liter; P and N in µg/liter. N = sum of NO_3-N and NO_2-N. P = orthophosphate-P.

	SiO_2	$PO_4^{\equiv}$	P	N	N/P
Lee's Ferry	7.0	0.03	9.8	340	34.8
Paria River	10.1	0.12	39.1	-	--
Mile 19	8.5	0.20	65.1	390	6.0
Vasey's Paradise	6.5	0.17	55.4	120	2.2
Little Colorado	11.0	0.06	19.5	180	9.2
Mile 71	10.0	0.06	19.5	400	20.5
Bright Angel	5.0	0.19	61.9	20	0.3
Shinumo Creek	5.0	0.70	228.0	60	0.3
Elves' Chasm	9.5	0.05	16.3	600	36.8
Mile 119	7.8	0.18	58.6	520	8.9
Tapeats Creek	6.0	0.22	71.7	30	0.4
Deer Creek	7.0	0.15	48.9	140	2.9
Kanab Creek	7.0	0.12	39.1	110	2.8
Havasu Creek	15.0	0.08	26.1	140	5.4
Mile 219	7.2	0.05	16.3	400	24.6
Diamond Creek	16.2	0.10	32.6	280	8.6

Table 16. August, 1975 - Plant nutrients: silica and phosphate in mg/liter; P and N in μg/liter. N = sum of NO_3-N and NO_2-N. P = orthophosphate-P.

	SiO_2	$PO_4^{\equiv}$	P	N	N/P
Lee's Ferry	7.0	0.03	9.8	300	30.7
Paria River	11.0	0.10	35.3	650	18.4
Mile 18	7.5	0.04	13.0	320	24.6
Vasey's Paradise	7.0	0.15	48.9	230	4.7
Mile 37.8	7.5	0.05	16.3	460	28.3
Little Colorado	8.0	0.08	26.1	220	8.4
Bright Angel	5.0	0.03	9.8	0	0
Shinumo Creek	5.0	0.20	65.1	0	0
Elves' Chasm	9.0	0.06	19.5	510	26.1
Mile 132	7.5	0.10	32.6	380	11.7
Tapeats Creek	6.5	0.22	71.7	100	1.4
Deer Creek	7.5	0.16	52.1	260	5.0
Kanab Creek	15.0	0.04	13.0	80	6.1
Havasu Creek	7.5	0.14	45.6	210	4.6
Mile 165	8.0	--	--	-	--
Mile 213	8.0	--	--	-	--
Diamond Creek	19.0	0.14	45.6	100	2.2

Table 17. March, 1976 - Plant nutrients: silica and phosphate in mg/liter; P and N in μg/liter. N = sum of NO_3-N and NO_2-N. P = orthophosphate-P.

	SiO_2	$PO_4^{\equiv}$	P	N	N/P
Lee's Ferry	7.0	0.72	234.7	340	1.5
Paria River	8.5	1.19	387.9	550	1.3
Mile 26.5	7.1	0.45	146.7	350	2.4
Vasey's Paradise	6.4	0.06	19.6	150	7.7
Little Colorado	11.0	0.04	13.0	260	20.0
Mile 65	7.1	0.12	39.1	380	9.7
Bright Angel	5.5	0.08	26.1	120	4.6
Shinumo Creek	5.8	0.06	19.6	100	5.1
Elves' Chasm	8.4	0.04	13.0	340	26.2
Mile 126	7.1	0.16	52.2	320	6.1
Tapeats Creek	5.5	0.08	26.1	170	6.5
Deer Creek	6.4	0.08	26.1	200	7.7
Kanab Creek	6.5	0.12	39.1	320	8.2
Havasu Creek	13.5	0.06	19.6	150	7.7
Mile 180	6.9	0.10	32.6	380	11.7
Mile 225	5.9	0.10	32.6	520	15.9
Diamond Creek	13.6	0.25	81.5	620	7.6

Table 18. April-May, 1975 - Factors relating to calcite saturation. CO_2 in mg/liter; TH = sum of Ca and Mg hardness as mg/liter $CaCO_3$; Ca/Mg ratio in meq. μ= ionic strength; Ω = degree of saturation; $pH_{\underline{s}}$ = pH of saturation; Index saturation = $pH_{obs}-pH_{\underline{s}}$.

	μ	CO_2	$pH_{\underline{s}}$	Index sat.	Ω	TH	Ca/Mg	alk/TH
Lee's Ferry	0.01440	11.7	7.93	-0.43	0.37	278	1.76	0.54
Paria River	0.01843	5.7	7.54	+0.36	2.30	415	1.06	0.53
Mile 19	0.01312	5.6	7.91	-0.11	0.78	299	1.51	0.49
Vasey's Paradise	0.00621	2.0	8.20	+0.10	3.77	197	1.23	0.99
Little Colorado	0.01285	4.1	7.65	+0.45	2.75	190	2.29	1.29
Mile 71	0.01484	4.7	7.81	+0.19	1.50	266	1.64	0.74
Bright Angel	0.00452	2.1	8.15	+0.05	1.12	140	1.11	1.01
Shinumo Creek	0.00604	2.6	8.01	+0.19	1.56	168	1.41	1.01
Elves' Chasm	0.01434	2.1	7.75	+0.45	2.80	376	0.94	0.41
Mile 125	0.01534	5.2	7.80	+0.11	1.28	286	1.38	0.63
Tapeats Creek	0.00486	1.7	8.01	+0.29	1.93	156	1.23	0.95
Deer Creek	0.00537	1.2	7.95	+0.45	2.84	181	1.26	0.78
Kanab Creek	0.02856	1.2	7.56	+0.74	5.54	697	1.29	0.18
Havasu Creek	0.01138	3.1	7.50	+0.79	6.21	306	0.75	0.99
Mile 225	0.01401	4.4	7.83	+0.07	1.17	275	1.61	0.56
Diamond Creek	0.01084	2.3	7.56	+0.88	7.52	221	0.60	1.43

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Table 19. June, 1975 - Factors relating to calcite saturation. Free CO_2 in mg/liter; TH = sum of Ca and Mg hardness expressed as mg/liter $CaCO_3$; Ca/Mg ratio in meq. μ = ionic strength. Ω = degree of saturation. $pH_{\underline{s}}$ = pH of saturation. Index of saturation = $pH_{obs}-pH_{\underline{s}}$.

	μ	CO_2	$pH_{\underline{s}}$	Index sat.	Ω	TH	Ca/Mg	alk/TH
Lee's Ferry	0.01371	5.1	7.96	-0.16	0.70	249	1.53	0.56
Paria River	0.00848	2.1	7.93	+0.17	1.47	180	1.13	0.74
Mile 19	0.01450	5.1	7.90	-0.10	0.79	279	1.58	0.50
Vasey's Paradise	0.00449	2.4	7.96	+0.14	1.46	145	1.45	0.99
Little Colorado	0.05049	9.0	7.01	+0.89	7.81	567	1.03	0.78
Mile 71	0.01418	3.9	7.83	+0.07	1.16	290	1.59	0.48
Bright Angel	0.00360	0.9	8.12	+0.28	1.91	111	1.36	1.04
Shinumo Creek	0.00301	1.2	8.22	-0.02	0.95	90	1.85	1.02
Elves' Chasm	0.01380	1.3	7.61	+0.69	4.86	358	0.98	0.40
Mile 119	0.01473	4.9	7.84	-0.04	0.93	289	1.61	0.49
Tapeats Creek	0.00380	1.3	8.13	+0.17	1.36	118	1.67	1.02
Deer Creek	0.00481	1.6	8.02	+0.28	1.50	151	1.54	0.98
Kanab Creek	0.03001	1.3	7.46	+0.64	4.39	681	1.22	0.14
Havasu Creek	0.01148	3.6	7.41	+0.79	6.15	311	0.78	0.96
Mile 219	0.01482	3.8	7.74	+0.16	1.39	291	1.61	0.49
Diamond Creek	0.01154	2.4	7.53	+0.87	7.53	238	0.59	1.35

Table 20. August, 1975 - Factors relating to calcite saturation. CO_2 in mg/liter; TH = sum of Ca and Mg hardness as mg/liter $CaCO_3$; Ca/Mg ratio in meq. μ = ionic strength. Ω = degree of saturation. pH_s = pH of saturation. Index of saturation = $pH_{obs}-pH_s$.

	μ	CO_2	pH_s	Index sat.	Ω	TH	Ca/Mg	alk/TH
Lee's Ferry	0.01305	5.2	8.06	-0.26	0.59	220	1.32	0.62
Paria River	0.01258	1.2	7.39	+0.91	5.75	291	1.31	0.47
Mile 18	0.01204	3.9	8.03	-0.13	0.73	224	1.32	0.60
Vasey's Paradise	0.00548	2.4	7.79	+0.41	2.57	170	1.10	1.11
Mile 37.8	0.01270	4.1	7.98	-0.08	0.83	245	1.28	0.57
Little Colorado	0.04569	11.4	7.62	+0.18	1.51	417	0.66	0.81
Bright Angel	0.00450	0.5	7.91	+1.60	6.18	141	0.64	1.05
Shinumo Creek	0.00414	1.3	7.90	+0.40	2.47	127	0.76	1.13
Elves' Chasm	0.01383	1.8	7.66	+0.54	3.45	348	0.76	0.44
Mile 132	0.01417	3.1	7.85	+0.15	1.29	261	1.30	0.57
Tapeats Creek	0.00504	1.9	7.93	+0.37	2.32	157	1.11	1.10
Deer Creek	0.00605	2.1	7.76	+0.54	3.48	181	1.05	1.11
Kanab Creek	0.02588	1.0	7.54	+0.66	4.88	608	0.94	0.15
Havasu Creek	0.01007	2.6	7.61	+0.69	4.82	256	0.50	1.08
Mile 165	0.01395	2.2	7.81	+0.39	2.45	251	1.21	0.67
Mile 213	0.01374	2.6	7.75	+0.45	3.09	236	0.65	0.85
Diamond Creek	0.01165	2.9	7.42	+0.88	7.59	214	0.75	1.65

Table 21. March, 1976 - Factors relating to calcite saturation. CO_2 in mg/liter; TH = sum of Ca and Mg hardness as mg/liter of $CaCO_3$; Ca/Mg ratio in meq. μ = ionic strength. Ω = degree of saturation. pH_s = pH of saturation. Index of saturation = $pH_{obs}-pH_s$.

	μ	CO_2	pH_s	Index sat.	Ω	TH	Ca/Mg	alk/TH
Lee's Ferry	0.00934	13.3	8.02	-0.63	0.23	254	1.13	0.53
Paria River	0.02050	2.3	7.72	+0.58	3.80	376	0.76	0.57
Mile 26.5	0.01343	11.1	8.03	-0.53	0.29	242	1.26	0.59
Vasey's Paradise	0.00407	2.8	7.97	+0.23	1.71	164	0.90	1.15
Little Colorado	0.04040	3.9	7.60	+0.50	3.16	401	0.87	0.63
Mile 65	0.01503	8.9	8.01	-0.41	0.38	250	1.17	0.60
Bright Angel	0.00528	2.4	8.17	+0.13	1.35	154	0.78	1.21
Shinumo Creek	0.00550	2.4	8.10	+0.20	1.57	157	0.91	1.22
Elves' Chasm	0.01443	1.9	8.00	+0.30	2.01	330	0.74	0.47
Mile 126	0.01570	4.8	8.01	-0.11	0.77	250	1.17	0.64
Tapeats Creek	0.00483	2.2	8.09	+0.21	1.61	144	0.95	1.24
Deer Creek	0.00584	2.1	7.92	+0.38	2.36	175	0.94	1.08
Kanab Creek	0.03568	3.0	7.59	+0.61	4.06	768	0.90	0.26
Havasu Creek	0.01099	5.4	7.66	+0.54	4.43	280	0.62	1.10
Mile 180	0.01236	3.7	8.00	0.00	1.01	245	1.13	0.63
Mile 225	0.01412	3.7	8.00	0.00	0.99	232	1.17	0.68
Diamond Creek	0.01107	3.3	7.82	+0.48	2.98	213	0.44	1.46

Table 22. April-May, 1975 - Some miscellaneous physico-chemical ratios. TDS values from evaporated filtrates, in mg/liter. Ionic ratios in meq/leter. +/++ = ratio of monovalent cations to divalent cations.

	μ/TDS x 10^5	TDS/ cond	Σ meq/cond x 10^3	Ca/Na	CO_3/Cl	CO_3/SO_4	+/++
Lee's Ferry	2.18	0.68	19.4	1.04	1.81	0.64	0.63
Paria River	3.87	0.44	22.0	1.17	3.12	0.91	0.56
Mile 19	1.96	0.67	18.8	1.25	1.80	0.62	0.57
Vasey's Paradise	2.96	0.43	20.3	16.69	49.00	19.60	0.04
Little Colorado	1.84	0.56	17.1	0.49	0.76	7.94	1.45
Mile 71	2.14	0.71	20.6	0.92	1.58	0.86	0.69
Bright Angel	2.81	0.60	22.8	9.80	28.20	14.84	0.06
Shinumo Creek	3.16	0.56	20.9	11.59	34.00	42.50	0.06
Elves' Chasm	2.47	0.67	19.8	3.64	2.52	1.35	0.14
Mile 125	2.25	0.70	21.2	0.89	1.59	0.77	0.67
Tapeats Creek	2.78	0.59	21.9	13.23	42.28	22.77	0.07
Deer Creek	3.05	0.53	21.0	13.47	35.25	13.43	0.05
Kanab Creek	2.60	0.76	21.6	5.22	4.25	0.20	0.12
Havasu Creek	2.74	0.58	21.8	1.94	4.68	10.48	0.24
Mile 225	2.18	0.65	18.7	1.02	1.53	0.72	0.62
Diamond Creek	2.40	0.58	21.3	0.49	3.88	9.16	0.80

Table 23. June, 1975 - Some miscellaneous physico-chemical ratios. TDS values from evaporated filtrates, in mg/liter. Ionic ratios in meq/liter. +/++ = ratio of monovalent cations to divalent cations.

	μ/TDS x 10^5	TDS/ cond	Σ meq/cond x 10^3	Ca/Na	CO_3/Cl	CO_3/SO_4	+/++
Lee's Ferry	2.23	0.65	18.5	1.10	1.69	0.54	0.57
Paria River	2.39	0.68	20.3	1.65	7.88	0.97	0.34
Mile 19	2.41	0.65	19.7	1.13	1.71	0.55	0.56
Vasey's Paradise	2.45	0.65	21.4	11.13	35.75	37.75	0.06
Little Colorado	2.03	--	--	0.20	0.26	2.60	2.53
Mile 71	2.12	0.75	20.6	1.07	1.38	0.66	0.59
Bright Angel	2.19	0.67	19.8	9.62	29.00	19.33	0.06
Shinumo Creek	1.42	0.73	14.0	5.75	18.40	13.14	0.12
Elves' Chasm	2.14	0.77	19.4	3.89	2.51	0.68	0.14
Mile 119	2.24	0.71	20.2	1.09	1.50	0.57	0.58
Tapeats Creek	2.73	0.56	22.0	11.31	19.41	27.50	0.06
Deer Creek	2.69	0.57	20.4	13.85	37.00	13.45	0.05
Kanab Creek	2.69	0.86	24.7	5.30	3.11	0.14	0.12
Havasu Creek	3.28	0.48	21.6	2.01	4.23	7.01	0.54
Mile 219	2.41	0.67	20.3	1.09	1.42	0.59	0.58
Diamond Creek	2.54	0.51	19.8	0.51	3.54	7.76	0.77

Table 24. August, 1975 - Some miscellaneous physico-chemical ratios. TDS values from evaporated filtrates, in mg/liter. Ionic ratios in meq/liter. +/++ = ratio of monovalent cations to divalent cations.

	μ/TDS x 10^5	TDS/ cond	Σ meq/cond x 10^3	Ca/Na	CO_3/Cl	CO_3/SO_4	+/++
Lee's Ferry	2.21	0.63	16.4	1.04	1.66	0.65	0.57
Paria River	2.03	0.70	17.1	1.76	6.13	0.66	0.35
Mile 18	2.02	0.63	16.4	1.04	1.69	0.64	0.57
Vasey's Paradise	2.60	0.59	20.1	19.40	42.00	37.80	0.27
Mile 37.8	2.05	0.65	17.1	1.00	1.76	0.66	0.58
Little Colorado	1.82	--	--	0.12	0.20	11.11	3.27
Bright Angel	2.32	0.69	21.7	6.47	29.80	74.50	0.07
Shinumo Creek	2.34	0.70	22.6	8.46	26.18	96.00	0.06
Elves' Chasm	2.41	0.70	20.3	3.11	2.36	0.74	0.15
Mile 132	2.28	0.67	19.6	0.94	1.59	0.60	0.62
Tapeats Creek	2.83	0.52	20.1	12.69	43.00	86.00	0.04
Deer Creek	2.88	0.53	20.7	14.23	30.92	13.86	0.04
Kanab Creek	2.04	0.93	20.5	4.24	2.76	0.16	0.12
Havasu Creek	2.52	0.52	18.3	1.39	3.90	7.10	0.26
Mile 165	2.06	0.70	18.9	0.80	1.70	0.78	0.69
Mile 213	2.16	0.69	19.9	0.87	1.77	0.93	0.68
Diamond Creek	2.24	0.62	21.8	0.36	3.40	8.69	0.94

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Table 25. November, 1975 - Some miscellaneous data and ratios from incomplete records. Conductance in micromhos/cm @ 25°. TDS, evaporated residue in mg/liter. TH = Ca and Mg hardness as mg/liter $CaCO_3$. +/++ = ratio of monovalent to divalent cations.

	cond	TDS	TDS/cond	Ca/Mg	Ca/Na	TH	+/++
Lee's Ferry	825	622	0.75	1.34	1.05	236	0.56
Paria River	--	--	--	0.97	1.23	548	0.41
Mile 29	--	--	--	1.34	0.96	227	0.62
Vasey's Paradise	425	426(?)	0.99(?)	1.06	13.8	174	0.04
Mile 32	870	680	0.78	--	--	--	--
Little Colorado	5,800	2,850	0.49	0.88	0.16	543	2.90
Bright Angel	385	324	0.84	0.93	9.71	171	0.06
Shinumo Creek	385	282	0.73	1.09	10.60	172	0.05
Elves' Chasm	850	678	0.78	0.78	2.88	359	0.15
Mile 120	--	--	--	1.28	0.86	244	0.67
Tapeats Creek	355	292	0.82	1.09	12.70	159	0.04
Deer Creek	425	372	0.88	1.05	15.00	190	0.04
Kanab Creek	1,395	1,216	0.87	1.08	4.57	668	0.12
Havasu Creek	850	606	0.71	0.58	1.53	299	0.26
Mile 173	--	--	--	1.23	0.78	249	0.74
Mile 225	925	669	0.72	--	--	--	--
Diamond Creek	860	616	0.72	0.47	0.37	209	0.89

Table 26. March, 1976 - Some miscellaneous physico-chemical ratios. TDS values from evaporated filtrates, in mg/liter. Ionic ratios in meq/liter. +/++ = ratio of monovalent to divalent cations.

	μ/TDS x 10^5	TDS/ cond	Σ meq/cond x 10^3	Ca/Na	CO_3/Cl	CO_3/SO_4	+/++
Lee's Ferry	1.49	0.67	21.5	0.75	1.64	0.40	0.74
Paria River	2.16	0.76	23.5	0.77	2.26	0.38	0.58
Mile 26.5	2.13	0.68	20.5	0.83	1.78	0.44	0.69
Vasey's Paradise	2.03	0.54	20.7	0.90	15.12	21.00	0.10
Little Colorado	1.87	0.47	17.0	0.12	0.18	1.20	3.93
Mile 65	2.30	0.67	22.1	0.66	1.20	0.43	0.83
Bright Angel	2.64	0.57	21.1	6.14	21.88	18.60	0.08
Shinumo Creek	2.75	0.53	20.3	5.77	22.59	13.24	0.09
Elves' Chasm	2.37	0.74	23.0	2.56	2.45	0.46	0.18
Mile 126	2.35	0.68	23.0	0.68	1.37	0.40	0.81
Tapeats Creek	2.76	0.52	20.1	10.77	32.55	89.50	0.05
Deer Creek	2.62	0.54	20.4	10.00	34.36	15.12	0.05
Kanab Creek	2.22	0.89	25.1	2.75	4.12	0.18	0.18
Havasu Creek	2.79	0.57	22.9	1.49	4.16	5.70	0.28
Mile 180	1.89	0.67	21.3	0.65	1.22	0.49	0.84
Mile 225	--	--	21.8	0.72	1.53	0.46	0.75
Diamond Creek	2.35	0.57	22.0	0.34	3.35	3.30	0.89

Table 27. Invertebrate fauna collected from the Colorado River and selected tributaries in the Grand Canyon.

INVERTEBRATE TAXA	Colorado River	Paria River	Vasey's Paradise	Little Colorado R.	Bright Angel Creek	Shinumo Creek	Elves' Chasm	Tapeats Creek	Deer Creek	Kanab Creek	Havasu Creek	Diamond Creek
COELENTERATA												
Hydra	X											
ROTIFERA	X						X					
NEMATODA			X									
OLIGOCHAETA	X		X	X	X	X	X	X	X	X		X
CLADOCERA												
Daphnia sp.	X											
Bosmina longirostris	X											
Alona sp.	X											
Chydorus sphaericus	X										X	
OSTRACODA												
Cyprinotus incongruens	X										X	
Cyprinotus pellucidus									X			
Cyprinotus salinus							X					
Paracandona euplectella	X											
Potamocypris sp.							X					

Table 27--(continued)

INVERTEBRATE TAXA	Colorado River	Paria River	Vasey's Paradise	Little Colorado R.	Bright Angel Creek	Shinumo Creek	Elves' Chasm	Tapeats Creek	Deer Creek	Kanab Creek	Havasu Creek	Diamond Creek
Ilyocypris bradyii											X	
Herpetocypris reptans							X					X
Cypridopsis vidua							X					
COPEPODA												
Diaptomus pallidus	X											
Cyclops bicuspidatus thomasi	X											
Mesocyclops edax	X											
Acanthocyclops vernalis							X					
AMPHIPODA												
Gammarus lacustris	X											
HYDRACARINA	X				X			X	X			X
COLLEMBOLA												
Isotoma sp.	X											
EPHEMEROPTERA												
Baetidae												
Baetis spp.			X		X	X	X	X	X	X	X	X
Callibaetis sp.							X					
Tricorythodes(?)												X

Table 27--(continued)

INVERTEBRATE TAXA	Colorado River	Paria River	Vasey's Paradise	Little Colorado R.	Bright Angel Creek	Shinumo Creek	Elves' Chasm	Tapeats Creek	Deer Creek	Kanab Creek	Havasu Creek	Diamond Creek
Heptageniidae												
Iron sp.								X				
ODONATA												
Anisoptera												
Aeschnidae							X	X				X
Libellulidae							X	X				X
Zygoptera												
Coenagrionidae			X				X			X		X
PLECOPTERA												
Perlodidae												
Isoperla sp.								X				
HEMIPTERA												
Corixidae												
Graptocorixa							X					
Notonectidae												
Notonecta							X					
Gerridae												
Gerris											X	
Veliidae												
Microvelia			X				X				X	X
Rhagovelia									X		X	X
MEGALOPTERA												
Corydalidae												
Corydalis					X	X	X			X		

Table 27--(continued)

INVERTEBRATE TAXA	Colorado River	Paria River	Vasey's Paradise	Little Colorado R.	Bright Angel Creek	Shinumo Creek	Elves' Chasm	Tapeats Creek	Deer Creek	Kanab Creek	Havasu Creek	Diamond Creek
COLEOPTERA												
Dytiscidae							X				X	
Thermonectes marmoratus							X					
Hydrophilidae			X									
Hydroscaphidae												
Hydroscapha natans												X
Staphylinidae	X											
Elmidae					X	X	X	X	X		X	
TRICHOPTERA												
Hydropsychidae												
Hydropsyche					X	X	X	X	X	X	X	X
Heliopsychidae												
Heliopsyche												X
Hydroptilidae			X				X					X
Psychomyiidae							X		X			X
Philoptommatidae							X					X
Rhyacophilidae								X				X
Limnephilidae							X					
LEPIDOPTERA												
Pyralidae												
Paragyractis			X		X	X		X				X
DIPTERA												
Tipulidae												
Tipula			X				X					
Antocha								X				
Psychodidae												
Maruina					X		X					X

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Table 27--(continued)

INVERTEBRATE TAXA	Colorado River	Paria River	Vasey's Paradise	Little Colorado R.	Bright Angel Creek	Shinumo Creek	Elves' Chasm	Tapeats Creek	Deer Creek	Kanab Creek	Havasu Creek	Diamond Creek
Culicidae												
Culicinae									X			
Dixidae								X				
Simuliidae			X		X	X	X	X	X	X		X
Chironomidae												
Pelopiinae												
Pentaneura						X	X			X		X
Procladius							X		X			X
Hydrobaeninae-Diamesinae	X	X	X	X	X	X	X	X	X	X	X	X
Corynoneura							X	X				
Chironominae	X		X		X	X	X	X	X	X		X
Calopsectra			X			X		X				X
Heleidae												
Culicoides	X											
Palopmyia							X					X
Stratiomyiidae												
Euparyphus			X				X					X
Empididae			X				X		X			X
GASTROPODA												
Lymnaeidae												
Lymnaea	X		X									
Physidae												
Physa	X						X				X	

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RECOMMENDATIONS FOLLOWING A LIMNOLOGIC STUDY
OF THE COLORADO RIVER AND ITS MAJOR
TRIBUTARIES IN THE GRAND CANYON

Gerald A. Cole and Dennis M. Kubly

063500

RECOMMENDATIONS

Following a year's limnologic study of the Colorado River and 11 of its tributaries from Mile Zero (Lee's Ferry) to Mile 225 just above Diamond Creek, certain conclusions have been reached. On the basis of these, some tentative recommendations can be made.

The quality of the Colorado River water can be
judged on the basis of at least four criteria: the
total salt concentration, the ionic proportions of the 41
dissolved materials, the level of nutrients that might
lead to hypereutrophication, and the degree to which
pathogenic organisms contaminate the flow. The first
three points are pertinent here.

In addition, there are factors relating to the maintenance of the entire river ecosystem as a unique environment. Superficially, aesthetic worths seem predominant here, but far-reaching values are probably involved.

With respect to water quality the Lee's Ferry
flow is too saline to meet present health standards for 41
sustained human consumption, although it is satisfac-
tory for livestock and for industrial usage. Moreover,
it is adequate for irrigation purposes. At the end of
the 225-mile stretch little has changed. It is still
satisfactory for industrial and agricultural consumption
and has, of course, not improved in terms of becoming
more potable for humans. It is rich in plant nutrients
throughout, yet there is no evidence of excessive algal 22,23
growth. There is some evidence that the water might
become nitrogen limited, if there were massive growths
of algae; phosphorus is abundant.

The key word is <u>dilution</u>. Maintaining flow rates
at least to their present level or increasing them
should command priority attention. First, the dis- 38,40
charge of the Colorado River at a high level serves to
dilute the more concentrated waters of some tributaries
--Kanab Creek, rarely the Paria River, and especially
the Little Colorado River. And, second, the flow rate
of all other tributaries should not be lessened, for
they collectively serve to dilute the main stream and
to ameliorate the salt concentration contributed by the
more saline tributaries.

Gross manipulations of tributary environments (brought about by such activities as damming, pump-storage operations and desalination) should be opposed in that they all would increase erosion, and at least the first two would lead to evaporation, concentration and weakening of desired dilution effects. Erosion in catchment basins would serve to increase the mineral content and aggravate salinity problems. Furthermore, in the American Southwest such accelerated erosion usually leads to an enormous increase in nitrate runoff. This may be important to consider, because the rich waters of the Colorado River may be somewhat nitrogen 23
deficient rather than poor in phosphorus. Undesirable features resulting from eutrophication are not yet a problem in the Grand Canyon river system, but further enrichment with plant nutrients is to be avoided, if possible.

There is some evidence that the tributaries entering the Colorado River serve as refugia for elements of the unique fish fauna that flourished in the main stream prior to the Glen Canyon Dam. Their continued existence and unaltered flows may, then, serve endangered species. In this same vein, the addition of exotic fish and perhaps other aquatic organisms, including plants and invertebrates should be undertaken with extreme caution. Just as terrestrial exotics have created problems along the banks of the Colorado River, aquatic organisms foreign to the river may alter its uniqueness.