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THE CHEMISTRY OF THE COLORADO RIVER AND ITS TRIBUTARIES IN MARBLE AND GRAND CANYONS

Dennis M. Kubly and Gerald A. Cole[1]

INTRODUCTION

The Colorado River Basin, with a drainage area of some 243,000 square miles in the conterminous United States encompasses a wide range of physiographic and climatic regions. By the time the river reaches Lee's Ferry in northern Arizona, it has drained approximately 107,000 square miles and has received by far the majority of water that is carried south and westward to the Gulf of California (Hely 1969). Present discharges reaching Lee's Ferry are controlled in their magnitude by regulation from Glen Canyon Dam 15 miles upstream. In contrast to the wide-scale ranges in discharge passing this point in pre-dam days, water volumes are now relatively constant. Large seasonal fluctuations have been replaced by diurnal changes in river level, reminiscent of tidal rhythms found in marine shore zones. Ionic concentration, ionic composition, temperature and sediment load, all fluctuating in response to season and discharge prior to the impoundment of Lake Powell, now show relatively little variation (USGS 1922 *et seq.*, 1941 *et seq.*)

Between Lee's Ferry (Mile 0) and the headwaters of Lake Mead, 280 miles downstream, the Colorado flows between the precipitous cliffs of Marble and Grand Canyons. River elevation falls from 3,090 feet to 870 feet, an average gradient of 7.9 feet per mile.

Many tributaries enter the Colorado in this 280-mile stretch. Some have been described in detail, but others have been hardly studied. There has been no more than cursory categorization of the springs and streams on a chemical basis, and little has been said about their relations to the main river.

It is the purpose of this short, descriptive paper to present selected data from the Colorado River and its tributaries from Mile Zero to Lake Mead, classifying the waters and discussing briefly their origins. We have assembled many data from published material, but this report will deal only with those creeks and springs that we have sampled and analyzed (Table 1). Our data were collected on six raft floats during 1975 and 1976. Chronologically, the trips were, in 1975: 22 April to 5 May, 3-12 June, 11-21 August, and 12-24 November. In 1976 there were two research trips, 1-12 March and 5 to 14 August.

THE COLORADO RIVER

Ionic proportions in the river water at Lee's Ferry were relatively constant during the period of study. They usually showed the following relationships:

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

Only during March 1976, were these proportions changed, with sodium becoming the dominant cation, although the mean values in Table 2 show sodium first. The waters are somewhat difficult to classify; cations approach a "triple" water category comparable to that proposed by Clarke (1924) for situations where the three principal anions are subequal. The Colorado River anions differ somewhat from triple water, approaching a sulfato-carbonate type. The ionic proportions differ little from month to month or as one progresses down the river (Figure 1). The small-scale fluctuations attributable to the effect of the Glen Canyon Dam, have prevailed since the completion of Lake Powell's impoundment according to subsequent chemical analyses of the water at Lee's Ferry gauging station that have been presented in USGS Water-Supply Papers since 1964.

Prior to impoundment, both chemical compositions and concentrations were correlated with river discharge (Iorns et al. 1965). High discharges were associated with comparatively dilute waters, having relatively more calcium and bicarbonate than are found at present. Low discharges produced more concentrated water than is presently found, with cations in proportions very similar to those of today, and with anions even more strongly dominated by sulfate.

Both ionic composition and concentration of the water passing Lee's Ferry today differ significantly from the average chemical features of the world's rivers presented by Livingstone (1963). He summarized the mean ionic proportions in the following sequence:

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

Calcium comprised more than 60% of the cations, and carbonate over 70% of the anions, on a milliequivalent basis.

The Colorado River has a solute content fivefold greater than the reported means for the world's rivers. At Lee's Ferry the TDS mean was 605 mg/liter which was about 0.68 the conductivity expressed as micromhos/cm @ 25°C. Its silica content, however, is below the 13 mg/liter Livingstone considered the mean; it averages roughly 8 mg/liter at Lee's Ferry.

Non-filtrable solids ranged from less than one to 54 mg/liter and the water was remarkably transparent when compared with all river stations downstream. The mean vertical transmittance of light was from 57.8 to 75.4% per meter. This clarity of the water at Lee's Ferry is a post-dam phenomenon.

Other features of the Mile-Zero water, not shown in Table 2, are: annual temperatures from 7-10°C; pH values from 7.4-7.9; free CO_2 in excess of 100% saturation; undersaturation with respect to calcite; a phosphate mean of 0.24 mg/liter; and sums of nitrate-N and nitrite-N averaging 0.27 mg/liter. These data typify the water that the springs and tributaries enter downstream.

THE TRIBUTARIES

Most tributaries joining the main stream in Marble Canyon and Grand Canyon fall in either one of two types described by Hamblin and Rigby (1969). They are, first, major streams having extensive drainage areas and characterized by extensive, deeply entrenched meanders. Such tributaries have relatively low gradients. Some are intermittent, varying seasonally from dry

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TABLE 1. Available information on water discharge from tributaries entering the Colorado River between Lee's Ferry (Mile 0) and Pierce's Ferry (Mile 279).

Tributary	River Mile	Discharge (cfs) Average	Discharge (cfs) Range
Paria River[a]	0.5	30.1	0 - 16,100
Vasey's Paradise[b]	31.7	4.0	0.2 - 10
Little Colorado R.[a]	61.5	205	0 - 24,900
Blue Springs[b]	61.5	223	217 - 232
Clear Creek[b]	84.1	1.6	0 - 3.0
Bright Angel Creek[a]	87.5	35.4	10 - 4,400
Shinumo Creek[b]	108.5	9.1	5 - 15.5
Elves Chasm[b]	116.5	0.2	0.1 - 0.3
Stone Creek[b]	131.8	0.5	0 - 1.2
Tapeats Creek[b]	133.6	100.1	51.4 - 283
Deer Creek[b]	136.2	7.2	5.4 - 8.2
Kanab Creek[a]	143.5	5.7	0 - 4,360
Havasu Creek[b]	156.7	63.8	59.3 - 74.5
Lava Warm Spring[b]	179.3	11.0	6 - 15
Diamond Creek[b]	225.8	1.9	1.5 - 2.2
Travertine Falls[b]	230.5	---	0.2
Spencer Creek[b]	246.0	2.7	1.1 - 4.4

[a] Information obtained from long-term records presented in U. S. Geological Survey Water-Supply series Surface Water Supply of the United States.

[b] Information based on sporadic records of U. S. Geological Survey as compiled in Johnson and Sanderson (1968).

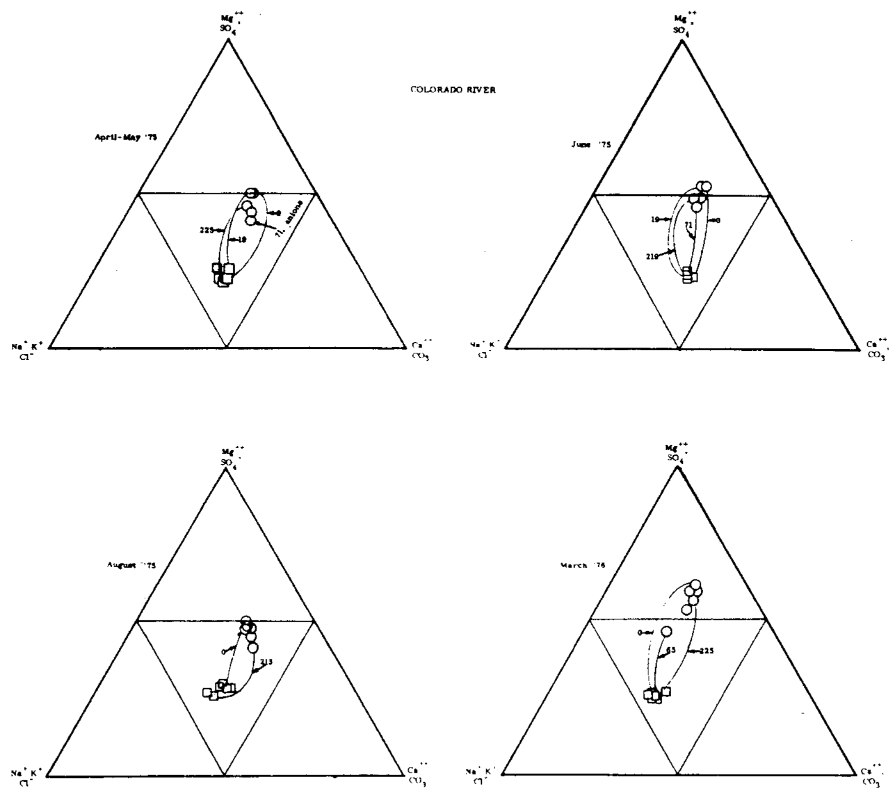

FIGURE 1. Triangular coordinate plots of the principal ions in the Colorado River on four separate raft trips; some mileages indicated. Ordinations show percentages of milliequivalents. Circles = anions; squares = cations.

TABLE 2. Means of principal ions and their sums from the Colorado River at Lee's Ferry and the dolomitic and impure dolomitic tributaries and springs. Values expressed in meq/liter.

	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^{-}	$SO_4^{=}$	Cl^{-}	Sum
Lee's Ferry	2.88	2.05	2.94	0.10	2.81	5.26	1.46	17.50
Dolomitic Waters								
Vasey's Paradise	1.79	1.57	0.14	0.02	3.59	0.13	0.13	7.37
Redwall Moss Sp.	1.98	1.80	0.11	0.01	3.76	0.17	0.18	8.01
Clear Creek	1.38	2.47	0.35	0.03	3.72	0.22	0.34	8.51
Bright Angel	1.29	1.43	0.17	0.02	2.96	0.13	0.11	6.11
Shinumo Creek	1.43	1.28	0.19	0.02	2.99	0.12	0.12	6.15
Stone Creek	1.32	2.93	0.43	0.02	4.39	0.30	0.34	9.73
Tapeats Creek	1.54	1.31	0.13	0.03	3.18	0.08	0.10	6.37
Deer Creek	1.84	1.59	0.13	0.02	3.40	0.23	0.10	7.31
Impure Dolomitic								
Havasu Spring	7.18	4.52	1.22		10.19	1.25	1.50	25.86
Havasu Creek	2.30	3.46	1.34	0.12	5.94	0.75	1.40	15.31
Lava Warm Sp.	3.17	6.34	3.02	0.15	10.10	0.49	2.33	25.60
Emory Falls	1.56	3.19	0.83	0.04	5.00	0.41	1.39	12.42
Three Springs	1.23	5.57	0.87	0.06	4.50	1.87	1.41	15.51
Spencer Creek	1.30	4.65	1.11	0.06	6.40	0.68	1.69	15.89

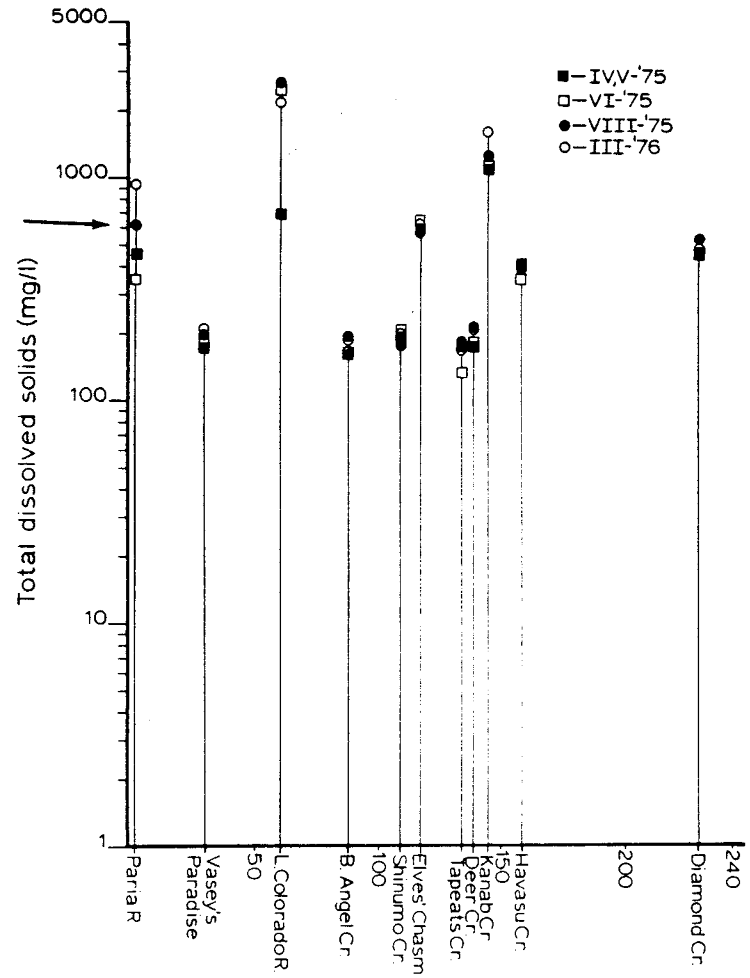

FIGURE 2. Total dissolved solids in 11 tributaries compared with the mean TDS in the Colorado River water at Lee's Ferry (arrow).

beds to swollen floods carrying enormous loads of sediment. The Paria River, Little Colorado River and Kanab Creek are good examples of this category. The second type is a short, relatively straight creek with steep gradients developed by headward erosion as the canyon deepened. Such streams carry clear water, but in times of flooding transport huge boulders to their mouths, producing many of the rapids so common in this section of the Colorado River. Most of the tributaries dealt with here are of this sort.

Table 1 presents available information on discharge rates of most of the tributaries included in this study. While some error is introduced by differences in the number and continuity of records, it is obvious that streams of the first type exhibit large-scale variations in flow compared with those of the second. This information and other discharge data from brooks in this region (Metzger 1961; Twenter 1962; Huntoon 1974) indicate that the average flow from measured streams between Lee's Ferry and Lake Mead probably does not exceed the sum of 750 cfs. This constitutes less than 10% of the mean modern discharge of the river as it passes Lee's Ferry. Thomas et al. (1963) estimated that the annual runoff of the Colorado River at Grand Canyon, Arizona, (Mile 87.4) averages about 95% of the total inflow to Lake Mead, including direct precipitation.

Figure 2 shows the total dissolved solids of 11 influent streams in relation to the average filtrable residue found in the waters of the Colorado River at Lee's Ferry. The figure points out that most waters entering the Colorado are comparatively dilute, serving to ameliorate the salt load contributed by others.

Relative ionic compositions and concentrations of the tributaries are presented in Tables 2, 3, and Figure 3, respectively. The chemistry of these streams is diverse, yet, for the most part, explainable on the basis of the lithology of their drainage systems or of the aquifers from which they arise. Very few of them have compositions like the mainstream Colorado; the Paria River and waters of Elves Chasm are closest in this respect.

Dilute Dolomitic Tributaries

At least eight tributaries, all arising as springs from the Karstic groundwater system of the Kaibab Plateau north and east of the mainstream, may be placed in the category of calcium-magnesium bicarbonate waters (Table 2, Figure 3C). These streams, emerging between Mile 32 and Mile 136.2, include Vasey's Paradise, Red Wall Moss Spring, Clear Creek, Bright Angel Creek, Shinumo Creek, Stone Creek, Tapeats Creek and Deer Creek. Vasey's Paradise (Mile 32) and the nearby Redwall Moss Spring (Mile 34.5) are unusual in that they gush directly from the Redwall limestone forming the canyon walls. The entrance of other springs beneath the river's surface near Mile 32 has been documented by Moore (1925) and Lange (1956).

The fact that these waters are of the strong carbonate type with more or less equal proportions of calcium and magnesium and very low quantities of sulfate, chloride and sodium may be attributed to the geochemical nature of the Paleozoic limestone formations comprising much of the system. Chemical analyses reveal that these so-called limestones contain much calcitic dolomite (Noble 1922; McKee and Gutschik 1969; Galbraith and Brennan 1970). Specifically, the Kaibab, Redwall and Muav limestones are the major formations in contact with the groundwater sources of these streams.

TABLE 3. Means of the principal ions and their sums from the sodium-bicarbonate, the sulfate, and the saline sodium-chloride waters entering the Colorado River. Values expressed in meg/liter.

	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^-	$SO_4^=$	Cl^-	Sum
$NaHCO_3$ Waters								
Diamond Spring	2.49	1.73	0.77		3.73	0.31	0.68	9.71
Diamond Creek	1.53	2.91	3.64	0.12	6.51	0.79	1.85	17.35
Travertine Falls	0.76	2.96	10.40	0.15	8.86	1.40	4.12	28.65
Sulfate Waters								
Paria River	3.18	3.13	2.96	0.12	3.54	5.02	1.03	18.98
Kanab Creek	7.12	6.63	1.74	0.15	2.61	13.73	0.72	32.70
Elves Chasm	3.24	3.80	0.99	0.08	3.03	4.36	1.24	16.74
NaCl Waters								
Blue Sp. (source)	13.17	6.50	22.32	0.59	15.80	3.06	22.99	84.43
Blue Sp. (mouth)	4.75	5.60	29.47	0.18	7.79	3.22	34.04	85.05
Blue Sp. - L. Colo.	2.64	1.15	5.39	0.11	4.92	0.62	6.43	21.26
Pumpkin Sp.	3.92	4.20	149.12	0.33	30.80	6.19	122.39	316.95

The dolomitic waters are dilute when compared with all others measured in the Marble Canyon-Grand Canyon system (Figure 2). Their rapid response to high precipitation and snow melt (Huntoon 1974), as evidenced by heightened discharge, implies a relationship between concentration and residence time. However, as Huntoon pointed out, the actual time necessary for any given particle of water to travel through this system may be years, owing to storage in the large Paleozoic aquifers.

The dolomitic streams have the highest Ca/Na, CO_3/Cl and CO_3/SO_4 ratios, and the lowest monovalent to divalent cation ratios of the entire system discussed here. Furthermore, their silica content is at the bottom of the list, and most of them have low N/P ratios; the latter are the result of both low nitrogen content and high phosphorus levels.

Impure Dolomitic Waters

Streams placed in this category are higher in dissolved constituents, have magnesium exceeding calcium, and contain greater amounts of sulfate, chloride and sodium than members of the previous group (Table 2, Figure 3A). All waters in this assemblage, Havasu Creek, Lava Warm Springs, Three Springs, Spencer Creek and Emory Falls, enter the Colorado River from the south rim of the Grand Canyon. They also arise from aquifers in Paleozoic formations, chiefly the Muav limestone.

Havasu Creek, one of the major sources of water supply from the south rim (Cooley 1963), arises as a series of seeps called Havasu Spring some 10 to 12 miles up a narrow canyon in the Supai formation (Moore et al. 1960). Havasu Spring and its outflow serve as an excellent example of solubility 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. Source water we have collected and analyzed had a ratio slightly greater than 2.0. By the time these waters reach the mouth of Havasu Creek, significant amounts of calcite have precipitated leaving an average Ca/Mg ratio of 0.65. Visual evidence for this precipitation exists in the blue hue of the water and the travertine deposits in the creek bed. The water is still supersaturated with $CaCO_3$ at the mouth of the stream. The change in Ca/Mg ratio is accompanied by a decrease in the CO_3/Cl ratio from 6.8 at the spring to 4.2 at the junction with the Colorado. Havasu Creek has a high silica content (ca. 14.5 mg/liter), which may be derived from the Supai sandstone.

Spencer Creek exits from McKee's (1945) Rampart Cave member of the Muav formation some distance from the Colorado River, while Lava Warm Spring arises from the upper part of the Muav at the mouth of Prospect Valley just above the level of the mainstream (Twenter 1962). We know of no documented evidence for the sources of Three Springs Creek and Emory Falls, but their geographic location and chemical composition suggest a Muav limestone origin.

Sodium Bicarbonate Waters

Diamond Creek and Travertine Falls provide examples of waters rare in Arizona--those which can be classified as the sodium bicarbonate type (Table 3, Figure 3A). Diamond Creek has its source in a group of springs exiting from the Muav limestone on the south side of the mainstream (Twenter 1962). The location and extensive travertine deposits of Travertine Falls suggest it also arises from the Muav. The soda nature of these streams is unexpected in light of the other waters emerging from the Muav. In fact, the major source of Diamond Creek, Diamond Spring, produces water of the impure dolomite type (Table 3, Figure 3A). This transition, involving a decrease in Ca/Mg ratios from 1.44 to 0.53, is probably due to a combination of factors, including: differential precipitation of calcium due to loss of CO_2, increase in temperature, and evaporation; inclusion of saline waters from the Tapeats Sandstone (Twenter 1962); and possibly, ion-exchange in alluvial sediments forming the channel of Diamond Creek.

Diamond Creek water carries the highest concentration of SiO_2 in the entire system described here. It and Travertine Falls consistently show phenolphthalein alkalinity, are extremely oversaturated with calcite and, except for the Little Colorado River and Pumpkin Spring, have the highest monovalent-to-divalent cation ratio.

Sulfate Waters

Tributaries having their anionic components dominated by sulfate (Table 3, Figure 3B), include two with the largest drainage systems, the Paria River and Kanab Creek, as well as the least extensive drainage, Elve's Chasm. Both the Paria and the Kanab arise in the high plateau regions of southern Utah and flow to the Colorado as meandering streams with relatively low gradients. Undoubtedly their abundant sulfate is provided by gypsiferous material common in the Jurassic and Triassic sediments which comprise considerable portions of their drainage areas (Gregory and Moore 1931); these deposits are so susceptible to erosion that they have been almost completely stripped from large portions of the Kaibab Plateau (Strahler 1948).

Elve's Chasm is somewhat of an anomaly in terms of expected vs. observed ionic components. This small tributary arises a short distance from the south bank of the mainstream, apparently from Paleozoic limestones, and flows to the Colorado as a series of falls and pools. In this respect, we would expect its waters to be of a dolomitic character, with anions dominated by carbonate rather than sulfate.

Kanab Creek is an example of gypsum water, although contaminated by magnesium (Figure 3B). The other sulfate waters are more like the Colorado River itself (see Figures 1 and 3B) and probably have less impact on its chemical make-up.

The Paria is unique in that it contributes more concentrated water when it is flooding than when its discharge is low; dilute-water springs near its confluence with the Colorado account for this. At times of flooding, however, it brings in much suspended sediment which mixes thoroughly with the Colorado River at a point somewhere more than five miles downstream. The Paria ranks first among the members of the Marble-Grand Canyon system in nitrogen and is very high in phosphorus. Its silica content is tied for third place with the other sulfate waters, Elve's Chasm and Kanab Creek ($\bar{X}$, 11 mg/liter); only Havasu and Diamond creeks carry more silica.

Saline Sodium Chloride Waters

The most highly concentrated waters entering the mainstream of the Colorado in the Grand Canyon are Pumpkin Spring and Blue Spring (Table 3, Figure 3B). Sodium and chloride are the dominant ions in these waters.

Pumpkin Spring is a warm spring (32^0C) situated near the river's edge at Mile 213. Discharge

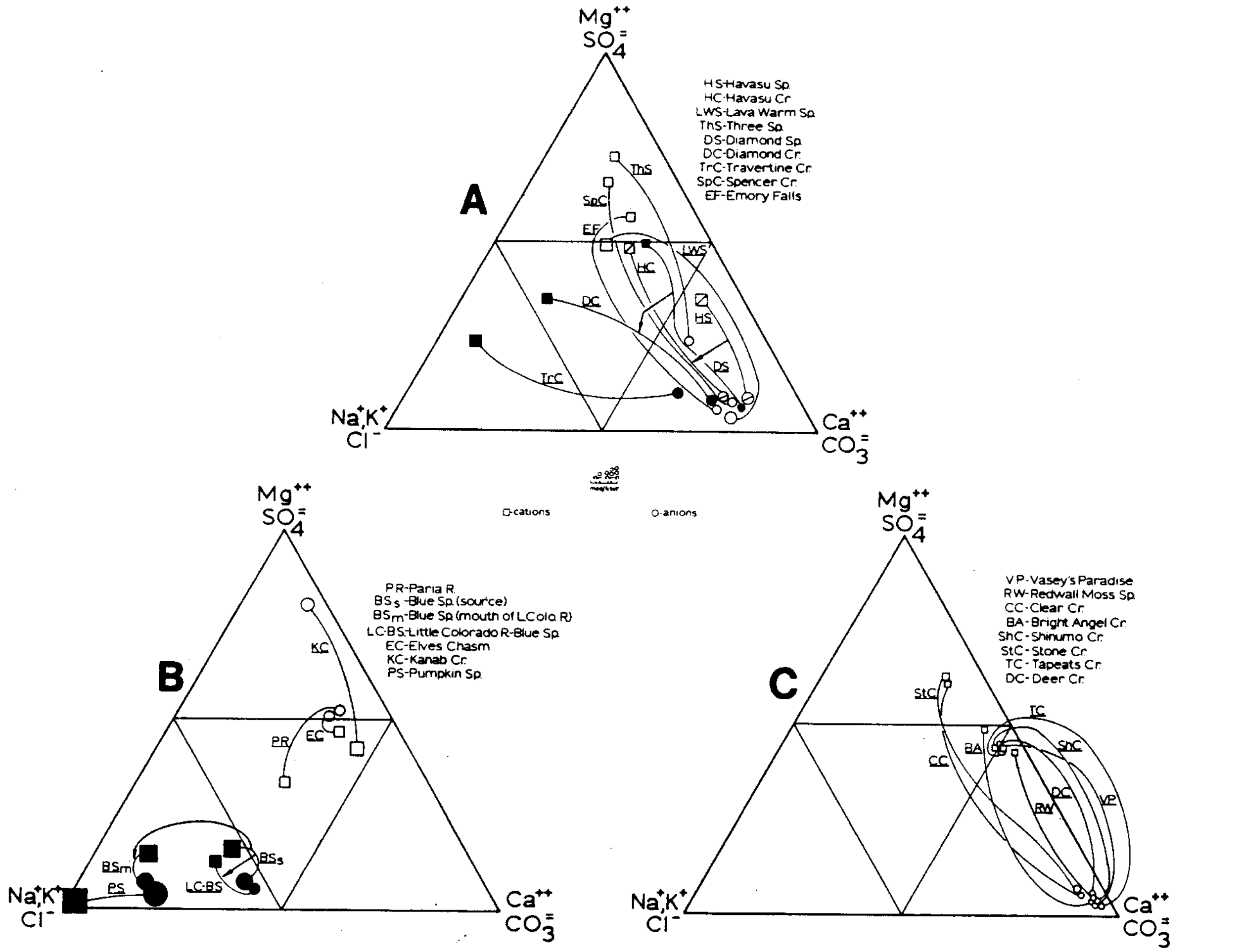

FIGURE 3. Triangular coodinate plots of the major ions in waters entering the Colorado River. Ordinations show percentages of milliequivalents. Circles = anions; squares = cations.

and, therefore, impact on the mainstream from this seep is negligible. Travertine and evaporite deposits have formed a yellow-orange bowl-shaped structure surrounding the water, accounting for the name Pumpkin Bowl. It has a great amount of carbonate also, a fact revealed by violent reaction when concentrated acid is introduced during a Winkler oxygen analysis. Its water is acid because of CO_2, easily seen as it bubbles from the underground source.

Blue Spring produces a relatively constant and considerable flow to the Colorado River (Table 3), giving it the infamous distinction of being the largest point-source contributor of dissolved solids in the region (Blackman et al. 1973). The spring, actually a series of springs and seeps, arises from the Redwall limestone in the canyon of the Little Colorado River from 3 to 13 miles above its confluence with the Colorado River (Johnson and Sanderson 1968). Cooley (1963) estimated that Blue Spring serves as a discharge point for about two-thirds of the groundwater in the aquifer of the 28,000-mile^2 Black Mesa hydrologic basin.

Although the Blue Spring series emerges from the Redwall limestone, the major aquifer system discharging through these springs is the Coconino and De Chelly sandstones (Cooley et al. 1969). Fracturing in the Supai formation, ordinarily the major aquifer to this system, allows water movement downward to the Redwall. It is also the Supai formation, with its contained salt beds, which probably acts as the source of the high dissolved-solid content in the waters of the overlying Coconino Sandstone and ultimately of the Blue Spring issue.

Although dominated by sodium and chloride, Blue Springs waters at the origin also contain significant amounts of calcium and carbonate (Table 3, Figure 3B). Following emergence, CO_2 release upsets the equilibrium resulting in precipitation of $CaCO_3$; this brings about a shift to waters relatively higher in sodium and chloride (Figure 3B). It should be mentioned, however, that source water diagrammed here is from the main Blue Spring head (Hem 1959), which is augmented to a small degree by input from more saline seeps and springs in the series.

Another modification of Blue Spring water occurs with its dilution by the Little Colorado River during certain times of year. With significant input by the Little Colorado River, Blue Springs waters are carried to the mainstream with approximately the same relative composition as at the source, but with greatly decreased concentrations. This modification, illustrated in Table 3 and Figure 3B, is based on measurements made April, 1975, with the Little Colorado River discharge at approximately 950 cfs.

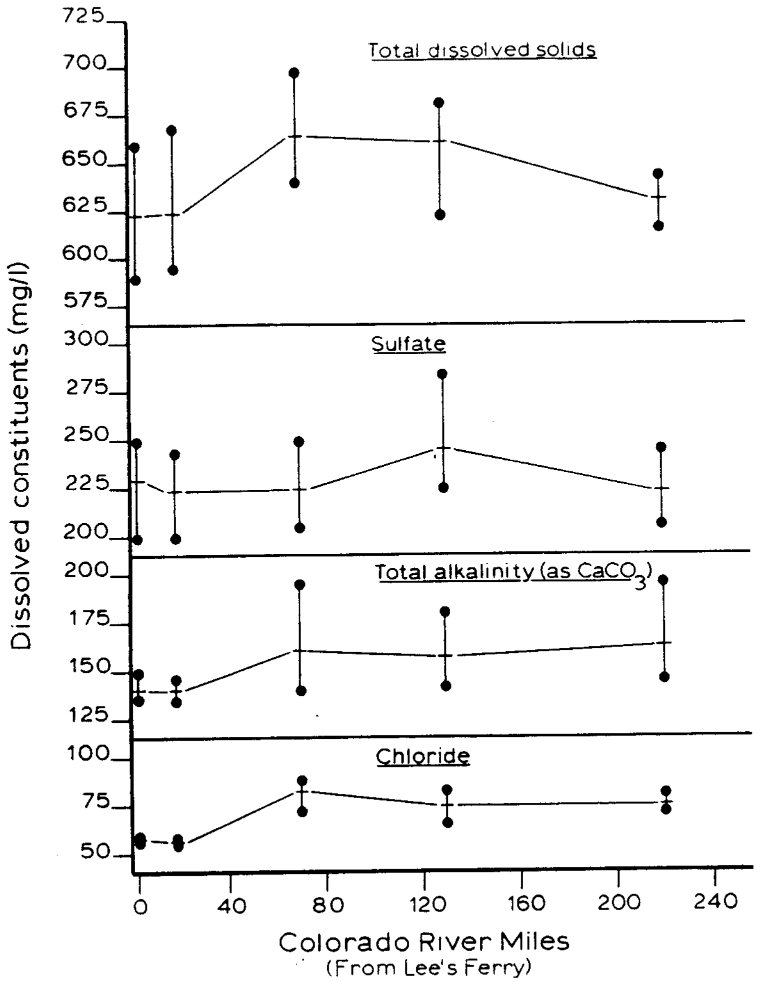

FIGURE 4. Changes in selected water chemistry--anions and total dissolved solids--from Lee's Ferry to Diamond Creek, Colorado River, 1975-76.

Figure 4 shows that there is a rise in total dissolved solids in the Colorado River water below Mile 61.5, where the Little Colorado enters. By the time the river reaches Diamond Creek (Mile 226), the salt concentration has diminished because of the dilution effect of subsequent influent streams.

The extreme turbidity introduced by the Little Colorado River when flooding modifies the Colorado and is not noticeably alleviated by clear tributaries down stream. It reduces the transmission to less than 0.001 percent and this opacity persists to the upper waters of Lake Mead.

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