Calcite Supersaturation and Precipitation Kinetics in the Lower Colorado River, All-American Canal and East Highline Canal

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In situ pH determinations and analysis of major ions in solution indicated that the lower Colorado River is supersaturated with respect to calcite throughout the entire daily cycle, in both winter and summer. Although the ion activity product was 4 to 6 times greater than the calcite solubility product, there was no detectable precipitation. Chemical analyses of water samples taken along 350 km of the river and canals from Parker Dam to the Salton Sea also revealed no evidence of calcium carbonate precipitation despite the inflow of saline and highly supersaturated irrigation return flows. Laboratory kinetic studies indicated that calcite crystal growth rates with Colorado River water are about 30% of the rate for pure $Ca-HCO_3$ waters and about 70% of that for synthetic Colorado River water. Calcite precipitation by crystal growth in the river is limited by the combination of short residence times and unavailability of reactive calcite. Critical supersaturation levels necessary for heterogeneous nucleation do not occur; a high suspended load limits algal photosynthesis and thus prevents large decreases in daytime H_2CO_3 levels.

INTRODUCTION

Predictions of calcium and alkalinity levels in rivers flowing through arid lands are particularly important for municipal and agricultural users alike. The objectives of this investigation were to determine the state of calcite saturation in the lower Colorado River system and whether $CaCO_3$ precipitation occurs, and, if so, whether it affects downstream water chemistry.

The irrigation of agricultural lands under conditions of minimized leaching [*van Schilfgaarde et al.*, 1974] reduces the total salt load of the drainage water, producing, in particular, less Ca and alkalinity after ion exchange equilibrium is established in the root zone. The effect that this will have on downstream water quality depends in part on the extent to which calcium carbonate precipitates in arid land river systems. Assuming chemical equilibrium in the river receiving the drainage water, *Suarez and Rhoades* [1977] evaluated the effects of reduced leaching for specific water types.

Earlier studies have shown evidence of rapid precipitation for supersaturated spring waters upon CO_2 degassing [*Barnes*, 1965; *Jacobson and Usdowski*, 1975]. However, calcium carbonate precipitation from supersaturated waters may not be a rapid process. *Back and Hanshaw* [1970] observed calcite supersaturation in Florida groundwaters. *Suarez* [1977] found that the drainage waters beneath irrigated lands were supersaturated with respect to calcite, with a mean ion activity product (IAP) value of $10^{-8.0}$ (as compared to the calcite k_{sp} of $10^{-8.47}$ [*Jacobson and Langmuir*, 1974]). Also, precipitation of $CaCO_3$ in the Wellton-Mohawk Drainage Canal does not occur despite more than tenfold calcite supersaturation in the 20-km section examined [*Suarez*, 1976]. It thus appears that waters with a short residence time (hours–weeks) may not precipitate calcium carbonate as theoretically predicted. The present study was undertaken to determine the downstream compositional changes that result from mixing drainage waters from the Palo Verde Project back into the Colorado River.

Drainage waters in the Palo Verde Project and the Colorado River from Parker Dam to Yuma and the All-American Canal and East Highline Canal were analyzed to ascertain if measurable precipitation of $CaCO_3$ occurs in agricultural drainage waters during conveyance to, or after mixing with, the Colorado River. Figure 1 shows the geographical location of the study area.

Above Palo Verde Valley, water flow in the lower Colorado River ranges from 9.8×10^6 to 220×10^6 m³ yr⁻¹ [*Irelan*, 1971]. The climate is dry and warm, with mild winters (occasional frosts) and hot summers (commonly $\simeq 38°C$ or higher at midday). Rainfall of about 7.5–13 cm yr⁻¹ derives from either local summer thunderstorms or gentle winter rain. The river cuts into mostly reworked alluvial sediments with outcrops of resistant igneous and metamorphic rock in isolated stretches. No saline deposits have been detected in this region [*Metzger et al.*, 1971]. Groundwater recharge below Parker Dam is quite low and consists mostly of irrigation drainage. There are numerous washes along this stretch of the river, but they supply insignificant quantities of water and only during large storm events. Siltation in the river has been extensive. The river is generally less than 1 m deep (with numerous sandbars), and at low flow, water meanders within the channel.

PROCEDURE

River Sampling Study

River locations and mileages were taken from the Bureau of Reclamation Colorado River maps. The starting point for this study, kilometer 0.0, corresponds to mile 240 on the Bureau maps and is just south of Needles, California. The Colorado River was sampled initially on February 7–8, 1977, to evaluate diurnal fluctuations in CO_2 and pH during the winter. River water samples were collected above the Palo Verde Drain at kilometer 215 just north of Horace Miller Park. Over a 24-hour period, a total of 18 samples were taken at a depth of 10 cm and 1 m out in the river from the bank. A few samples were taken at the surface and at a depth of 50 cm. In situ pH (± 0.01) was continuously measured, 1 m out from the riverbank, with a Beckman Expandomatic connected to an Omniscribe chart recorder. One portion of each water sample was immediately
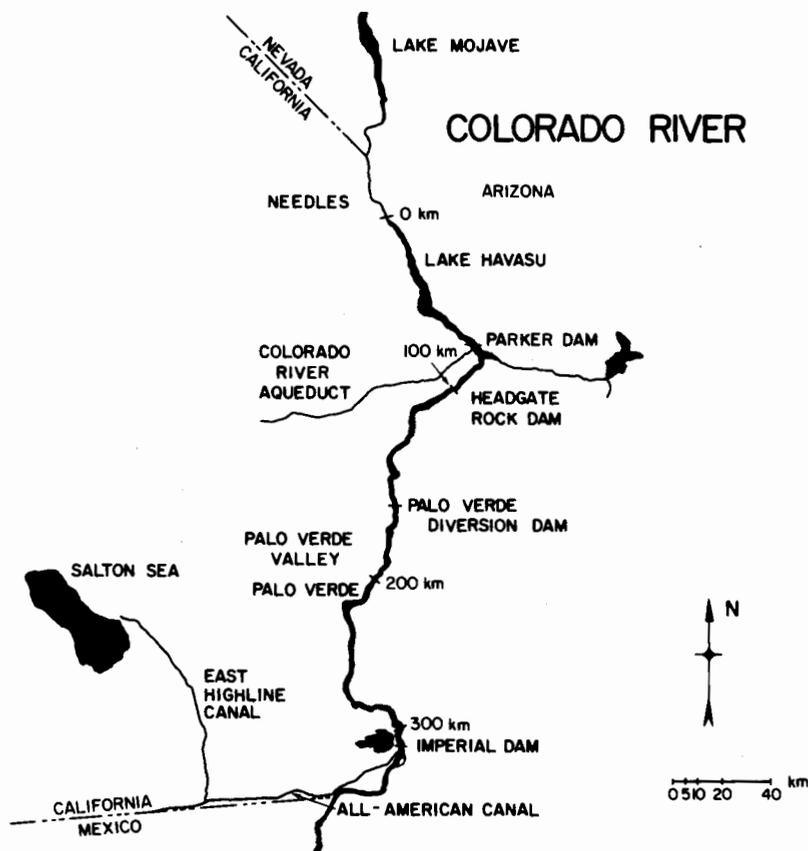
Fig. 1. Generalized map of the study area.

filtered through a 0.1-μm Millipore filter using 0.5% CO_2 gas in the pressure filtration unit and then immediately acidified with HCl. Another portion was directly acidified, and the third was left untreated. All samples were placed in polyethylene bottles previously acid cleaned and rinsed with distilled water. The untreated samples were placed in bottles filled to the top, immediately capped, and placed in a cooler ($\simeq 2.0°C$). Water temperatures were also recorded at the times of collection. Most alkalinity titrations were made immediately on filtered and unfiltered samples. Some alkalinity titrations were made on the refrigerated samples within 6 hours. There were no differences, indicating that the temperature reductions and capping procedures prevented precipitation after collection. Dissolved oxygen in the river water was measured occasionally using a Yellow Springs model 51A oxygen meter. Measurements of specific conductance of the water were also made.

The Colorado River, Palo Verde Drain, All-American Canal, and East Highline Canal were sampled extensively during the week of March 7, 1977. The sampling procedure was similar to that described above. The Orion model 401 pH meter was calibrated (± 0.01) at field water temperatures using temperature-corrected pH buffers (6.00, 6.86, 7.00). The river was sampled from a boat in the center of the river at various locations between km 179 and km 307 (Imperial Dam). Other samples of the river and all canal and drain samples were taken near the edge. Samples were taken by boat near both banks of the river, beginning just downstream from the Palo Verde Drain and continuing downstream until the river was relatively well mixed, as determined from specific conductance measurements.

A summer sampling of the river was carried out September 19–21, 1977, at the same sites as before. The summer diurnal cycle was evaluated by sampling the river for 24 hours on September 19–20. The samples were collected by the procedure described previously.

Analyses of Ca and Mg were performed by atomic absorption, with addition of La to the samples to prevent interferences [Brown et al., 1970]. Na and K were determined directly by atomic absorption [Brown et al., 1970]. Alkalinity was determined by titration, Cl by potentiometric titration with an American Instruments chloride titrator, SO_4 by the $BaSO_4$ turbidimetric procedure [American Public Health Association, 1975], and NO_3 by direct measurement with an Orion solid-state $NO_3{}^-$ specific electrode.

Thermodynamic calculations of ion activities are based on the use of an extended Debye-Huckel equation [Truesdell and Jones, 1974] and correction for ion pairs considering temperature dependent dissociation constants [Suarez, 1977]. As a check on the degree to which Ca is complexed in the river, Ca^{2+} activities (indicated by $a_{Ca^{2+}}$) were determined directly with an Orion Ca^{2+} specific electrode on the samples collected in March 1977 (in addition to calculation of $a_{Ca^{2+}}$ from total Ca by correction for activity coefficients and complexing). Direct measurements were made to ensure that the calculated Ca^{2+} activity values were not in error due to possible complexing by organic species. The measured values are somewhat different and on the average slightly lower (4%) than the calculated ones (data not shown). The difference for any given sample is within the precision of the Ca electrode ($\pm 15\%$) error. The calculated Ca^{2+} activity values are considered accurate and were used for
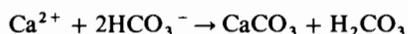
calculation of degree of calcite supersaturation. Use of electrode-measured Ca^{2+} activities would not significantly change the results.

Precipitation Rate Study

Plummer et al. [1979] pointed out that calcite dissolution experiments at low P_{CO_2} will result in CO_2 disequilibrium if the rate of dissolution exceeds transport of CO_2 across the air-liquid interface and CO_2 hydration. They observed this in dissolution experiments at 3×10^{-3} atm P_{CO_2} where pH changes were recorded (free drift method). Additionally, they observed slow removal of H_2CO_3 from solution for pH > 7.0 (production of CO_2 during dissolution) in experiments in which pH was controlled by addition of acid (pH-stat method).

Despite potential experimental complexities, precipitation kinetic studies on river water require low P_{CO_2} experiments, because rivers are at low P_{CO_2}. At high P_{CO_2}, Colorado River water is undersaturated instead of supersaturated. In order to properly simulate river conditions, experimental pH and P_{CO_2} values should match field values.

Under most natural conditions, pH ranges between 6 and 8.5, and HCO_3^- is the predominant carbonate ion. For these conditions the calcite precipitation reaction can be written as follows:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2CO_3$$

Previous precipitation experiments used free drift methods; thus P_{CO_2} increased during the reaction, as was pointed out by *Plummer et al.* [1979]. Fortunately, precipitation experiments can be conducted at low P_{CO_2} under fixed, controlled conditions using the pH-stat method. In this study I used Na_2CO_3 as the titrant; this results in the reaction

$$2Na^+ + CO_3^{2-} + H_2CO_3 \rightarrow 2Na^+ + 2HCO_3^-$$

The Na_2CO_3 was prepared in CO_2-free water with a specific conductivity of < 0.5 μmho cm^{-1}. The titrating container was completely filled with solution, minimizing the gas phase. Also, the air entry tube to the titrant container was connected to an ascarite trap to remove incoming CO_2. This procedure enables pH control by replacement of the precipitated CO_3; thus H_2CO_3 and P_{CO_2} remain constant.

Filtered (0.1 μm) and unfiltered Colorado River water samples were collected from the All-American Canal and stored at 2°C. Solutions were analyzed for major species as described earlier. Orthophosphate was analyzed in 0.10-μm filtered and unfiltered samples. A synthetic phosphate-free water was prepared which had the same major ion composition and pH, and thus the same P_{CO_2}, $a_{Ca^{2+}}$, $a_{HCO_3^-}$, and $CaCO_3$ IAP as Colorado River water. Additionally, Ca-HCO_3-Cl water was prepared which had the same $a_{Ca^{2+}}$, $a_{HCO_3^-}$, pH, P_{CO_2}, and $CaCO_3$ IAP. The Brinkman E526-E535 pH-stat was calibrated to within ± 0.01 pH units of the reference buffers. All experiments were run in a temperature-controlled room in a temperature-controlled stirrer apparatus (± 0.2°C). A Teflon stir bar was rotated at 100 rpm. Precipitation rates were independent of stirring rate. This is consistent with the observations of *Plummer et al.* [1978] that only at pH ≤ 5 do stirring rates affect reaction rates. The initial solution pH values were adjusted between 8.20 and 8.50 by varying the P_{CO_2}. Solutions (usually 20 ml) were maintained with the pH-stat at the initial pH values. Negligible amounts of Na_2CO_3 were required to stabilize the pH at the desired level. Calcite seed material, washed with distilled water and then dried, was subsequently added to the solution. Different concentrations of Na_2CO_3 (5 and 10 mmol l^{-1}) and quantities of calcite (0.05 to 0.2 g) were used to ensure that the pH-stat could maintain constant pH during runs. Experiments at different pH values were conducted with Colorado River water, synthetic Colorado River water, Ca-HCO_3-Cl water, filtered Colorado River water, synthetic Colorado River water spiked with phosphate, and Ca-HCO_3 waters. Additional runs were made in which calcite was not added; negligible amounts of Na_2CO_3 were titrated.

Calcite surface area was determined on Mallinckrodt reagent grade $CaCO_3$ previously washed in distilled water to remove fine material. Preliminary wet sieving removed all > 100-μm particles; subsequent washing and decanting removed all material less than 20 μm in size. The calcite was subsequently resuspended in distilled water, and hydrometer measurements were continuously taken during settling. These readings allowed calculation of particle size in 2-μm intervals. For each interval, a surface area was calculated by assuming rhombohedric particles and multiplying by the particle frequency in that interval. Total surface area was calculated by summing the surface areas in each size fraction. Sixty percent of the particles were within the range 25–35 μm in size. The average surface area of the material was calculated at 0.070 m^2 g^{-1}. There was excellent agreement between dissolution rates using this material and dissolution rates observed with coarser wet-sieved calcite crushed from Iceland spar (data not shown).

DISCUSSION

River Diurnal Fluctuation

Schmalz and Swanson [1969] noted that carbonate supersaturation of ocean surface waters could be explained by the diurnal CO_2 cycle. They reasoned that equilibrium could exist between the most soluble calcium carbonate phase present and the water at the highest CO_2 level at night. During the daytime at low CO_2 levels, the ocean surface waters were supersaturated, but at the same Ca and alkalinity levels as during the nighttime. We needed to determine if the Colorado River is at calcite equilibrium at night and if precipitation is occurring during the day. If $CaCO_3$ does not precipitate during daylight hours when the water is most supersaturated with respect to calcite, it can be safely assumed that no precipitation occurs during the entire 24 hours.

Analyses of the Colorado River samples collected at km 215 in February 1977 indicate that the chemical composition was uniform with time. Diurnal fluctuations in P_{CO_2} were relatively small, with values very close to the atmospheric level, 3×10^{-4} atm. The minimum P_{CO_2} of 5.34×10^{-4} atm occurred at 1505; the maximum P_{CO_2} of 7.19×10^{-4} atm occurred at 0330 (see Figure 2). Maximum P_{CO_2} occurs just before daylight. Apparently, low water temperatures during winter limit bacterial respiration, and large amounts of suspended sediment limit algal photosynthesis; hence CO_2 levels are low, and diurnal fluctuations are small. Even though P_{CO_2} and pH fluctuated slightly over the 24-hour period, Ca and HCO_3 levels remained quite constant as shown in Figure 2. The river was supersaturated with respect to calcite throughout the 24-hour period. Determined values for pIAP ($-\log$ IAP), and thus degree of river supersaturation with $CaCO_3$, varied diurnally with P_{CO_2}; however, there was no evidence of $CaCO_3$ precipitation, such as loss of Ca. Samples with the highest pH and lowest pIAP values, 7.71–7.73, showed no evidence of $CaCO_3$ precipitation (no decreases in Ca or alkalinity) despite the increased degree of
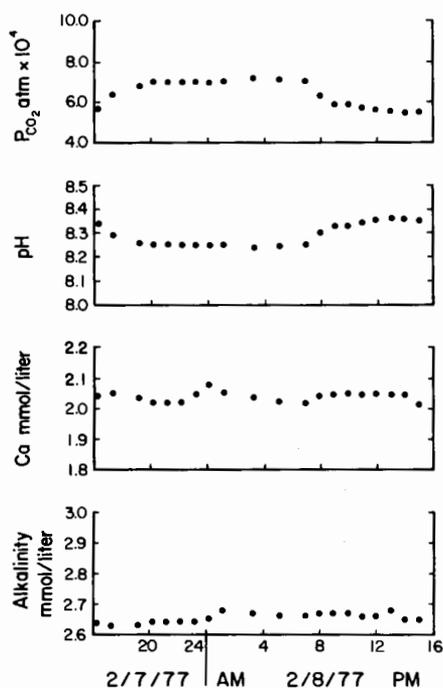
Fig. 2. P_{CO_2}, pH, Ca, and alkalinity versus time at kilometer 215 in the lower Colorado River on February 7-8, 1977. Alkalinity expressed as millimoles per liter of HCO_3^-.

supersaturation. The river was at or near saturation with O_2 during the entire cycle, indicating good aeration (data not given).

Partial analyses of samples collected in September 1977 at the same location are given in Figure 3. There was some variation in the composition of the river with time. The chloride concentration (shown in Figure 3) was lowest between 2230 and 0130. Based on depth measurements made in the river, maximum flow in the river occurred at least 8 hours before the time of the chloride concentration minimum. Releases from Parker Dam are made in a daily cyclical manner, primarily to generate hydroelectric power at times of peak demand. Downstream from Parker Dam, the Poston Drain (drainage return flow from the Colorado River Indian Irrigation Project) enters the Colorado River at km 130.8. The lowest chloride value would be expected to occur at maximum flow (when there is the largest amount of upstream dilution) immediately below the drain. Within the 84-km distance between the Poston Drain and our sampling site, however, the pulse of water moves ahead of the water (and salinity front). Consistent with this salinity pulse being caused by a mixture of drainage water with the river, the fluctuations in alkalinity (shown in Figure 3) mirror the changes in chloride. Figure 3 shows a sharp drop in CO_2 after 0600 due to the onset of photosynthesis at sunrise. The decrease in CO_2 between 0600 and 1400 would cause a similar decrease in HCO_3 if precipitation were occurring. As shown in Figure 3, alkalinity did not drop during these hours. P_{CO_2} levels fluctuated between 1.12 and 1.49 $\times 10^{-3}$ atm. These values are about 4 times the atmospheric value but still relatively low and quite constant. It appears that the large amounts of suspended sediment in the river reduce photosynthesis by algae. The higher level of CO_2 in the summer is interpreted as the result of higher temperatures which allow for higher rates of bacterial respiration.

The pIAP values obtained for the summer cycle, shown in

Figure 3, ranged from 7.79 to 7.93, indicating supersaturation throughout the 24-hour cycle. The level of supersaturation in the summer months was thus lower than in winter, because of higher CO_2 levels in the summer. The highest level of supersaturation occurred during the afternoon (around 1500 to 1800) for both winter and summer. No corresponding decreases of alkalinity or Ca were observed during that interval. Apparently, the diurnal change in the CO_2 level in the river is insufficient to cause $CaCO_3$ precipitation (or a daily precipitation-dissolution cycle) between Parker Dam and the Palo Verde Drain.

Downstream River Compositions

Partial results of the March 1977 samplings of the Colorado River waters are given in Figures 4 and 5. Sample 1 (km 7.1), sample 2 (km 43.8), and sample 3 (km 69.8) were taken along the edge of Lake Havasu, and sample 4 was taken at Parker Dam, km 76.8. The estimated residence time of water in Lake Havasu is approximately 2 months [*Slawson*, 1972]. On the basis of these limited data, $CaCO_3$ precipitation in Lake Havasu under winter conditions was not detected. The minimum daytime CO_2 level is expected to be considerably lower in the summer, and CO_2 might be sufficiently depleted in the surface waters to cause precipitation then. The sample taken at Parker Dam was likely more representative of the entire lake than the first three samples from shore.

The data in Figure 4 show the effect of additions of Palo Verde drainage water to the Colorado River (at km 243.6). Downstream from the drain, samples were taken from the east and west banks of the river at each of several sampling distances along the river (drainage water is indicated by open triangles in Figures 4 and 5) until no differences in specific conductance between east and west banks were observed.

Figure 4 shows the Cl concentrations in the Colorado River, All-American Canal, and East Highline Canal on March 8-9,
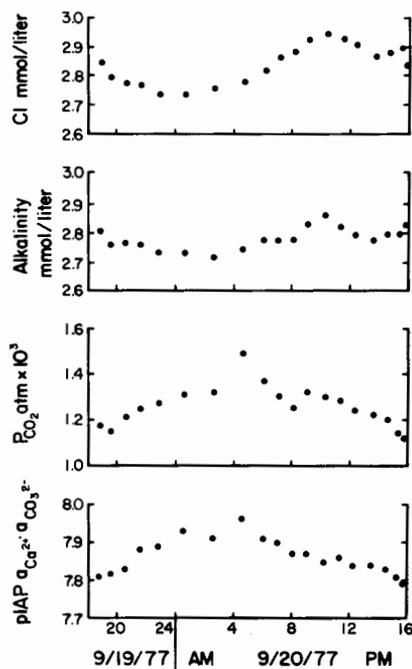

Fig. 3. Cl, alkalinity, P_{CO_2}, and pIAP versus time at kilometer 215 in the lower Colorado River on September 19-20, 1977. Alkalinity expressed as millimoles per liter of HCO_3^-.

1977. The values given in the figure correspond to the concentrations at those locations. High Cl values at km 243.5 to km 251 correspond to samples of the Palo Verde Drain. Cyclic fluctuations in the Cl concentrations of the river just downstream from the Palo Verde Drain reflect the changes in the relative proportions of Palo Verde Drain water to upstream Colorado River water, whose flow is controlled by the daily cyclic water release from Parker Dam. Fluctuations below Parker Dam (km 76.8) and above the Palo Verde Drain reflect inputs of small volumes of water from the Poston Drain at km 130.8. Concentrations of Na, Mg, K, SO_4, and NO_3 were 4.50–5.92, 1.23–1.41, 0.123–0.131, 3.05–3.69, and 0.083–0.125 mmol l^{-1} respectively.

Fluctuations in pH, P_{CO_2}, and $pIAP$ for the first three samples are due to inability to properly sample the river from the banks as indicated earlier. The pH levels were lower in the drain waters than in the river; P_{CO_2} levels and all other dissolved species were higher in the drain waters, as expected. The small fluctuations in Cl, alkalinity, and Ca downstream from the Palo Verde Drain (Figure 4) coincided, as did pH (Figure 5). The pH values were determined during the day so the fluctuations downstream reflect changes in the relative proportion of drain water to river water and not the diurnal CO_2 cycle. Similar fluctuations in the ion activity product $a_{Ca^{2+}} \cdot a_{CO_3^{2+}}$ were found (see Figure 5). The relative degree of supersaturation of $CaCO_3$ increased in the river immediately below the Palo Verde Drain and then depended on the proportion of drainage to river water.

Despite the lack of further inputs to the river below the Palo Verde Drain, the level of calcite supersaturation showed no evidence of decreasing downstream from the drain, a distance of 220 km (Figure 5). The calcium and alkalinity concentrations also indicate no measurable precipitation. There was also no measurable suspended $CaCO_3$ in the river, on the basis of analyses of filtered and unfiltered samples.

X ray analyses of the filters revealed the presence of calcite in suspension when large quantities of water were passed through the filters from samples that had a high turbidity and high

Fig. 5. Plots of pH, P_{CO_2}, and $pIAP$ versus distance along the Colorado River in March 1977. Irrigation return flow and partially mixed irrigation return flow and Colorado River water are indicated by open triangles.

suspended solids. Montmorillonite and quartz were abundant on these filters. Filters from waters with low suspended load did not have X ray detectable calcite (or any other carbonate phase) despite filtering of large quantities of water (about 2 l in some instances). It is concluded that suspended calcite, when present, was not a fresh chemical precipitate but part of the sediment load of the river. The presence of suspended calcite is expected, since the soils in the region contain abundant calcite.

The relative proportion of upstream Colorado River water and Palo Verde drainage making up each downstream water sample can be calculated from the chloride concentrations of upstream water, downstream water, and Palo Verde drainage waters using the relationship

$$X = [Cl_{downstream} - Cl_{upstream}] \div [Cl_{drainage} - Cl_{upstream}]$$

where X is the fraction of drain water in the downstream samples. Approximately 4 to 10% of the downstream Colorado River water volume consisted of Palo Verde drainage. On the basis of these percentages, expected solute concentrations were calculated for each downstream sample. Predicted minus observed concentrations for each solute were correlated to downstream distance for all samples below Palo Verde Drain. Some variation still existed; however, it was not cyclical, and there was no statistically significant correlation with distance even at the 20% confidence level. The variation was within the range ± 0.06 mmol l^{-1} for all but three samples. These values correspond to less than $\pm 2.7\%$ of the Ca concentrations. These values, calculated from differences in concentration, are within analytical error. This is a further indication that during the winter months there is no evidence for $CaCO_3$ precipitation occurring in the lower Colorado River following drainage inflow.

Results of the September 1977 sampling along the lower Colorado River are shown in Figures 6 and 7. Chloride levels along the river are shown in Figure 6. Above the Palo Verde Drain at km 243 the mixing of Colorado River water and Poston Drain water can be detected by Cl fluctuations. Below
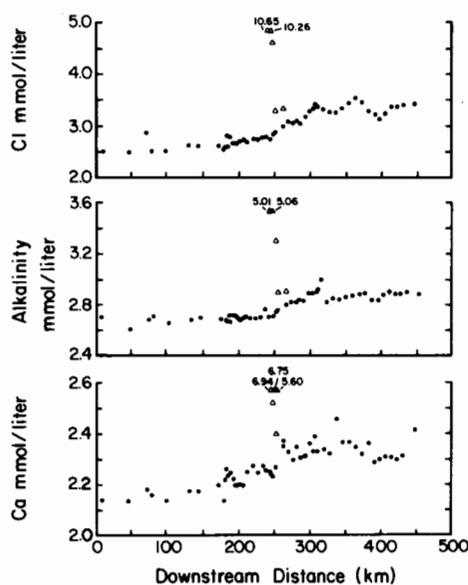

Fig. 4. Cl, alkalinity, and Ca versus distance along the Colorado River, All-American Canal, and East Highline Canal in March 1977. Irrigation return flow and partially mixed irrigation return flow and Colorado River water are indicated by open triangles.
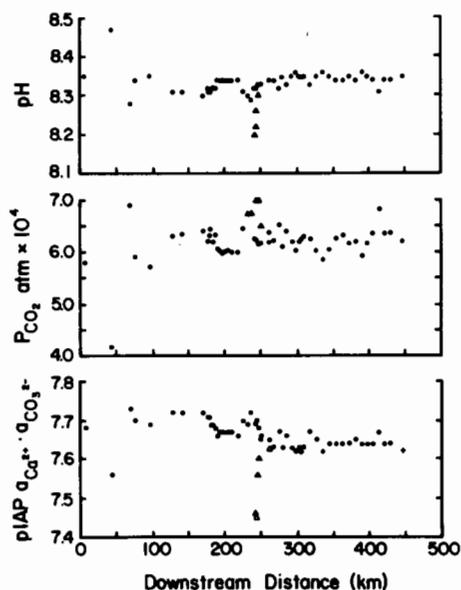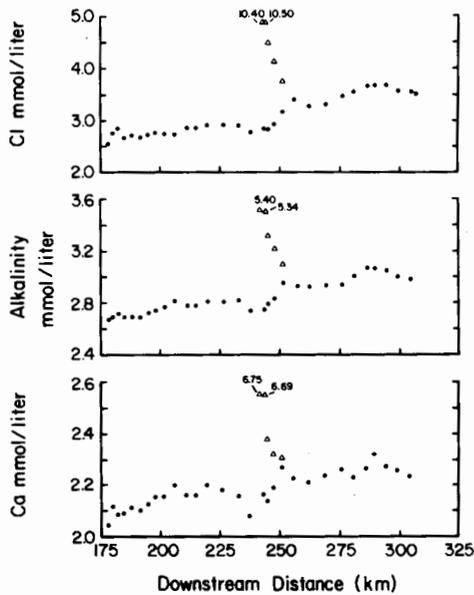
Fig. 6.   Cl, Ca, alkalinity, and pIAP versus distance along the Colorado River in September 1977. Alkalinity expressed as millimoles per liter of HCO_3^-. Irrigation return flow and partially mixed irrigation return flow and Colorado River water are indicated by open triangles.

the outfall the chloride fluctuations were more pronounced and dependent on the ratio of Colorado River water to Palo Verde drainage water. Samples were collected for a short distance downstream from the Palo Verde Drain from opposite banks. P_{CO_2} values were higher for the drainage water (Figure 7) and fluctuated only slightly downstream. Calcium and alkalinity concentrations (Figure 6) were higher in the drainage water than in the river; hence they increased in the river below the drain. Figure 6 shows no evidence to support $CaCO_3$ precipitation. As found in the winter, the variations in Ca and HCO_3 were similar to those of Cl (Figure 6) and reflect the varying ratio of river water to drainage water. The pIAP values were lower for the drainage waters (more supersaturated) than the river water. The river became more supersaturated upon receiving the drain water and remained essentially constant thereafter (see Figure 7). It thus appears that despite considerable supersaturation, $CaCO_3$ does not precipitate in measurable quantities in the Colorado River upon receiving irrigation drainage below Parker Dam.

Precipitation Rate Study

Laboratory precipitation studies provide the opportunity to examine the reasons for lack of precipitation in the river. Laboratory experiments were conducted within the pH range observed for the river. The Colorado River water used in the study was within the composition range determined earlier. The pH was 8.27, and the following values were calculated:

$$a_{Ca^{2+}} = 1.09 \times 10^{-3} \qquad a_{HCO_3^-} = 2.39 \times 10^{-3}$$

$$P_{CO_2} = 8.39 \times 10^{-4} \text{ atm} \qquad a_{Ca^{2+}} \cdot a_{CO_3^{2-}} = 10^{-7.72}$$

The orthophosphate concentration in filtered Colorado River water was $1.0 \,\mu\text{mol l}^{-1}$.

The pH-stat data for Colorado River water, synthetic Colorado River water, and the Ca-Cl-HCO_3 water are given in Figure 8. Each value represents the mean of 8 to 16 replicate runs. As expected, the rate of precipitation was faster at higher pH values (lower P_{CO_2}). For Colorado River water the rate at

$pH = 8.20$ was $0.50 \times 10^{-7} \text{ mmol s}^{-1} \text{ cm}^{-2}$. At $pH = 8.50$ the rate, 2.88×10^{-7}, was 5.8 times greater than the rate at $pH = 8.20$. Synthetic Colorado River water increased from $0.65 \times 10^{-7} \text{ mmol s}^{-1} \text{ cm}^{-2}$ at $pH = 8.20$ to 4.20×10^{-7} at $pH = 8.50$, an increase of about 6.5 times. Colorado River water precipitated at a rate between 78 and 69% of the rate for synthetic Colorado water. This reduction in rate can be ascribed completely to PO_4 inhibition. When $1.0 \,\mu\text{mol l}^{-1}$ of Na_3PO_4 was added to synthetic Colorado River water, precipitation rates were slightly below those found for PO_4-free synthetic Colorado River water and Colorado River water (data not shown). It thus seems possible that some of the determined phosphate in the river water is complexed with soluble organics.

The precipitation rates for Ca-HCO_3-Cl water, also given in Figure 8, were between 3 and 4 times greater than those for Colorado River water. These results are consistent with the substantial reductions in precipitation in the presence of Mg and SO_4 at constant $a_{Ca^{2+}}$, $a_{HCO_3^-}$, and pH (D. L. Suarez, unpublished data, 1978). Assuming Mg has as much affinity as Ca for calcite surface sites [*Berner*, 1966] reduces expected precipitation growth rates by 40% (from calculated $a_{Ca^{2+}}$ and $a_{Mg^{2+}}$ values). The rates shown in Figure 8 indicate that most of the inhibition to crystal growth for Colorado River water is inorganic rather than organic. This is concluded from the fact that the Colorado River water and the PO_4- and organic-free synthetic Colorado River water had precipitation rates within 30% of each other and the Ca-HCO_3-Cl water precipitated 3 to 4 times faster than Colorado River water.

The very low or nonexistent precipitation rate in the Colorado River must reflect the unavailability of clean calcite rather than inhibition by dissolved species. Calcite is abundant in the sediment but is apparently coated by precipitation-inhibiting material. At pH values higher than 8.5, in the laboratory, when IAP's exceed $10^{-7.5}$, spontaneous precipitation (heterogeneous nucleation) occasionally occurred. Fast precipitation rates in earlier field studies [*Barnes*, 1965; *Jacobson and Usdowski*, 1975] were likely due to heterogeneous nucleation,
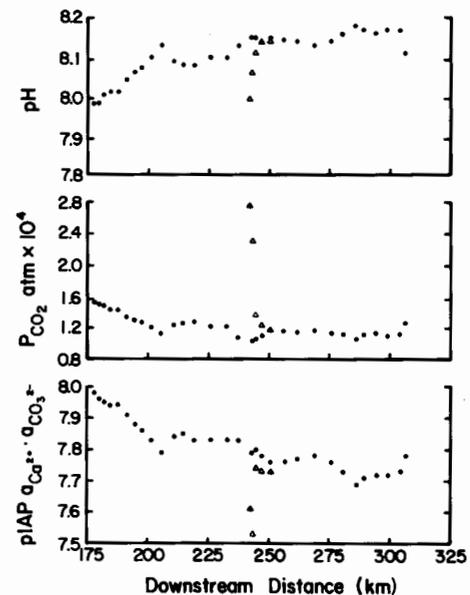

Fig. 7.   Plot of pH, P_{CO_2}, and pIAP versus distance along the Colorado River in September 1977. Irrigation return flow and partially mixed irrigation return flow and Colorado River water are indicated by open triangles.
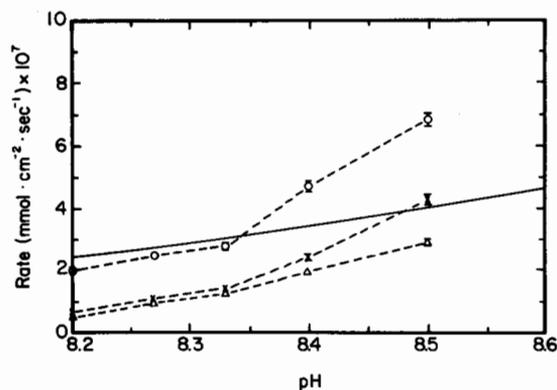
Fig. 8. Calcite precipitation rates at pH 8.20–8.50 for Colorado River water (open triangles), synthetic Colorado River water (crosses), and Ca-HCO₃-Cl water (open circles) at the same $a_{Ca^{2+}}$, $a_{HCO_3^-}$, pH, and P_{CO_2}. Values plotted represent the mean of 8 to 16 measurements for each point. Error bars represent ±1 standard error. Also shown by the solid curve are calculated rates based on the model of *Plummer et al.* [1979].

probably algal-induced precipitation in regions of depleted CO_2.

The calcite kinetic rate equation of *Plummer et al.* [1978] was used to predict precipitation rates for Colorado River water, synthetic Colorado River water, and Ca-HCO₃-Cl waters. The following expression from *Plummer et al.* [1978] was used:

$$R = k_1 \cdot a_{H^+} + k_2 \cdot a_{H_2CO_3} + k_3 \cdot a_{H_2O} - k_4 \cdot \frac{K_2}{K_{sp}} \cdot a_{Ca^{2+}} \cdot a_{HCO_3^-}$$

where

$$k_4 = k_1' + \frac{1}{a_{H_{s^+}}} \cdot (k_2 \cdot a_{H_2CO_3} + k_3 \cdot a_{H_2O})$$

where at 25°C, $k_1 = 0.051$; $k_2 = 3.45 \times 10^{-5}$; $k_3 = 1.18 \times 10^{-7}$; K_2, the second dissociation constant of carbonic acid, equals $10^{-10.33}$; and K_{sp} for calcite $= 10^{-8.47}$. *Plummer et al.* [1978] suggest that a value of k_1' of 10 to 20 times k_1 be used. The value $k_1' = 0.51$ was used, although in the P_{CO_2} and pH range of the present experiment its effect on k_4 was minor. The term $a_{H_{s^+}}$ is the H^+ activity at the surface. It is assumed to be the a_{H^+} at calcite saturation where P_{CO_2} at the surface equals P_{CO_2} in the bulk solution. These values were calculated using a modified version of the program described by *Suarez* [1977] by keeping P_{CO_2} constant and solving for the saturation values $a_{Ca^{2+}}$, $a_{HCO_{3^-}}$, and $a_{H_{s^+}}$.

The solid curve in Figure 8 represents the calculated precipitation rates. The fit of the model to the Ca-HCO₃-Cl water at pH 8.20, 8.27, and 8.33 is remarkable. Experimental runs at pH 8.4 and 8.5 showed higher precipitation rates than predicted (although only by a factor of less than 2). The sharp increase in precipitation beginning at pH 8.40 is not predicted by the model.

The present data do not support the suggestion by *Plummer et al.* [1979] that for precipitation experiments at low P_{CO_2} the surface P_{CO_2} values differ from those in the bulk fluid. This was given as an explanation for the 10 to 20 times slower than predicted precipitation rates found by *Reddy* [1975, and unpublished data, 1978] (as given by *Plummer et al.* [1979]). In the earlier precipitation experiment (free drift), P_{CO_2} increased during the reaction; in contrast it remained constant in the present experiment (pH-stat using Na_2CO_3). The present data are very close to predicted values at the lower pH values. If P_{CO_2}

at the calcite surface exceeded solution P_{CO_2}, it would result in observed rates dropping below predicted rates at the higher pH values (when the rates are fastest). As seen in Figure 8, experimental rates were greater than predicted rates for the higher pH measurements. An additional $a_{Ca^{2+}} \cdot a_{CO_3^{2-}}$ back reaction term could account for the break in slope. Leakage of CO_2 into the Na_2CO_3 titrant was not a factor, since values of titrant pH did not decrease. Also, reaction rates at pH 8.50 for Colorado River water were below those at pH 8.33 for Ca-HCO₃-Cl water; thus the deviations from the *Plummer et al.* [1978] model were not related to the quantities of Na_2CO_3 added.

Precipitation of $CaCO_3$ in Lake Havasu

Irelan [1971] lists volume-weighted yearly average concentrations of dissolved major ionic species in the Colorado River below Hoover Dam, at Lake Havasu, and at Imperial Dam. There is considerable year to year variation in concentration of individual species. A t test based on the yearly means for 1941 to 1965 revealed no significant differences at the 10% level. However, using the paired t test relationship [*Snedecor*, 1962]

$$t = (\bar{d} - \mu_D)/S\bar{D}$$

and pairing the values for each year, differences in alkalinity Ca, Mg, Na, and Cl below Hoover Dam and Lake Havasu were all significant at the 0.1% level. The Na, Mg, and Cl concentrations were slightly higher at Lake Havasu, consistent with evaporation. The Ca and alkalinity concentrations were slightly lower at Lake Havasu, consistent with precipitation of 0.075 mmol l^{-1} $CaCO_3$. The statistical analysis does not prove that precipitation is occurring in Lakes Mohave and Havasu since (1) the U.S. Geological Survey samples were not filtered and Lake Havasu samples have less suspended material, including calcite, than samples taken below Hoover Dam, (2) there is no assurance that the samples collected from Lake Havasu properly represent the average chemistry of the lake water, and (3) differences in sample collection or storage from the two locations could result in small but different amounts of $CaCO_3$ to precipitate before analyses were performed.

If calcium carbonate precipitation occurs in Lake Havasu, it is not inconsistent with the data from the present study. Assuming a residence time of 3 months in Lakes Havasu and Mohave and a constant precipitation of 0.075 mmol l^{-1} yields a precipitation rate in the lake of 0.00083 mmol l^{-1} d^{-1}. The 1-week travel time between Parker Dam and the end of the East Mainline Canal would result in a precipitation of 0.0059 mmol l^{-1} if the same rate is used. This small quantity of precipitation is not detectable with the direct methods used in this study and can be neglected in mass balance calculations for the river. Also, using the data of *Irelan* [1971] and the P_{CO_2} values found in this study and calculating a yearly IAP value, no correlation was found between the level of supersaturation below Hoover Dam and estimates of Ca or alkalinity losses. The data calculated from *Irelan* [1971] from 1941 to 1965 show that the Ca and alkalinity concentrations and degree of supersaturation were higher in water at Imperial Dam (downstream) than either Lake Havasu water or water below Hoover Dam. These results are consistent with the data collected in the present study and indicate that the river is not in equilibrium with any $CaCO_3$ solid phase.

The levels of supersaturation and the lack of precipitation observed in the lower Colorado River can be contrasted to previous studies by *Barnes* [1965] and *Jacobson and Usdowski*

[1975]. *Barnes* [1965] examined a travertine-depositing creek (fed by groundwaters) under arid conditions. Groundwaters were near calcite equilibrium and precipitated $CaCO_3$ upon CO_2 degassing. Within 0.5 km of the spring, continuous crusts of travertine were observed in the creek bed, with additional evidence of precipitation based on the collected water samples. Data recalculated from *Barnes* [1965] using the ion pair model of the present study indicated that very rapid $CaCO_3$ precipitation occurred when pIAP values were below 7.6, although equilibrium was not attained. *Jacobson and Usdowski* [1975] also examined calcite precipitation in a supersaturated spring (distance of 0.13 km). The degree of supersaturation and rate of precipitation increased during the day (low CO_2 due to photosynthesis), and high precipitation rates occurred when values of pIAP were 7.5 or below.

In both studies, clear water allowed for substantial CO_2 depletions during daylight hours. The fast precipitation rates observed in both studies were likely due to heterogeneous nucleation rather than calcite crystal growth. The lack of calcite precipitation in the lower Colorado River, despite much longer travel times at only slightly lower levels of supersaturation, can be related to insufficient supersaturation for heterogeneous nucleation and unavailability of suitable nuclei.

Precipitation in the lower Colorado River, if it occurs, is only by crystal growth. An estimate of calcite crystal growth rates in the lower Colorado River can be made using the measured laboratory precipitation rates, the 1-week travel time between Parker Dam and the end of the East Mainline Canal, and an estimate of suspended calcite in the river. Using Bureau of Reclamation data (H. Carver, personal communication, 1982), volume-weighted 1-year average sediment load values were calculated for the five measuring locations in the lower Colorado River. The values ranged from 50 to 224 ppm suspended solids. It was assumed that calcite was 5% by weight of the suspended load (typical for adjacent soils) and that the mean calcite particle size was between 10 μm and 50 μm (also typical for adjacent soils). The range in calculated surface area was combined with the range in suspended load, resulting in a suspended calcite surface area range of 1.1 to 22 cm^2 l^{-1} of river water. Using a pH value of 8.30, the laboratory-measured precipitation rate was 1.1×10^{-7} mmol cm^{-2} s^{-1}. This corresponds to a total estimated precipitation of 0.073 to 1.5 mmol l^{-1} from Parker Dam to the end of the East Mainline Canal. Calcite precipitation of this magnitude would have been detected by the field measurements had it actually occurred. Evidently, the river-suspended calcite was not as reactive as was the laboratory calcite. It seems reasonable to assume that the river-suspended calcite was coated with organic materials, thus limiting precipitation rates below those predicted.

Conclusions

Lower Colorado River waters are supersaturated with respect to calcite and aragonite throughout the diurnal CO_2 cycle in both winter and summer. On the basis of earlier studies, large amounts of precipitation would be expected at these measured levels of supersaturation. $CaCO_3$ does not precipitate in the Colorado River between Lake Havasu and the Palo Verde Drain, nor is it precipitated upon admixture of the river with Palo Verde drainage waters (even more supersaturated) for a distance of 220 km. Mass balance calculations averaged for 1941 through 1965 indicate that a 5% reduction in Ca and HCO_3 may occur in Lake Havasu and Lake Mohave.

Lack of measurable precipitation downstream from the lake (despite higher levels of Ca and HCO_3) is due to short residence times and the high sediment load which limits algal photosynthesis and thus prevents sharp drops in CO_2 levels. The pH-stat precipitation experiments showed that Colorado River water does not contain any unusual inhibitors to precipitation. Decreases in precipitation below rates for pure systems were consistent with surface adsorption of foreign ions and slight PO_4 'poisoning' of calcite surfaces. If precipitation occurs in Lake Havasu, its calculated rate is not inconsistent with measurements in this study. Assuming a precipitation rate similar to that calculated for Lake Havasu from the data of *Irelan* [1971], only 0.0059 mmol l^{-1} of Ca precipitates during the 1-week travel time between Parker Dam and the end of the East Highline Canal. This quantity is not measurable with our procedures and can be neglected in mass balance calculations for the river. The Ca and HCO_3 content of the river is not controlled by a solid phase in the region between Parker Dam and the end of the East Highline Canal; therefore changes in irrigation management in Palo Verde would affect the Ca levels found in the lower portion of the river.

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