HYDROCHEMISTRY OF THE COMAL, HUECO, AND SAN MARCOS SPRINGS, EDWARDS AQUIFER, TEXAS

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ABSTRACT

The hydrochemistry of three of the largest springs emerging from the Edwards Aquifer was analyzed weekly for a year to determine if locally derived recharge could be enhanced through dam construction as a means of preserving spring flow. A recent model has predicted the cessation of spring flow to occur as early as the year 2020 due to Edwards Aquifer ground-water mining around San Antonio. This model did not consider the possibility of separate flow systems to the various spring orifices. Two recent tracer tests have verified differing flow patterns to the San Marcos Springs. Also, the hydrochemical analyses of six San Marcos spring orifices have demonstrated that two chemically different spring groups exist. The southern group of orifices display higher temperature, and tritium and dissolved oxygen concentrations when compared to the northern group of spring orifices. Also, changes in discharge have a more profound effect on water chemistry for the northern spring orifices.

A detailed potentiometric surface map was constructed around San Marcos during low spring-flow conditions (70 cfs, 2 cms). The highly fractured and faulted Edwards Limestone produced a very complex potentiometric surface configuration. The numerous faults associated with the Balcones fault zone can act as either ground-water barriers or avenues of enhanced ground-water flow. Pressure head distributions demonstrate the existence of two separate flow regimes, one of "older" water from the San Antonio region and the other of "younger" water moving to the springs from the Blanco River. The potentiometric surface map and one dye trace also demonstrate that the Blanco River is losing water to the Edwards Aquifer through highly fractured rock in the river bottom, directly recharging the San Marcos Springs. Therefore, by devising ways of artificial recharge, either by drilling holes in the river bottom or by diverting river water to bedrock sinkholes along the river banks, or by constructing a dam, up to 80,000 acre-ft/year (9.87 x 10^6 m^3/year) of enhanced recharge water could be contributed to the aquifer to maintain the...
flow of the San Marcos Springs.

Hueco Springs is composed of recent, locally derived recharge water as demonstrated by dye trace results, turbidity, and rapid fluctuations in water chemistry after storms. The flow of Hueco Springs could be enhanced by placing a recharge dam on Elm or Bleders Creek.

Some locally derived recharge waters reach Comal Springs as evidenced by chemical changes following storms. These changes are not large or long-lasting. Also, all attempted dye traces failed to reach the springs. Tritium values are low. Water-chemistry changes are gradual and are related to longer-term seasonal and discharge effects. Therefore, a local recharge dam would not enhance spring flow. San Antonio utilizes water levels in a reference well to determine when rationing must begin. To save Comal Springs, the chosen level for mandatory rationing must be increased to approximately 625 feet (above sea level).

Figure 1: Location of Barton, San Marcos, Hueco and Comal Springs.

Figure 2: Major orifices of the San Marcos Springs (Divergent, 100; Cabomba, 101; Deep, 102; Johnny, 104; Catfish, 106; Hotel, 107).

Figure 3: Location of sampled orifices of Comal Springs.

Figure 4: Location of Hueco Springs sampling sites, Comal County, Texas.

Figure 5: Flow paths of tracer tests performed by Ogden (1983) and Quick and Ogden (1985).

Figure 6: Dye-trace to Hueco Springs.

Figure 7: Potentiometric surface map of the San Marcos area.

Figure 8: Location of Tarbuttons Cave, the Halifax Ranch, and the Blanco River near Kyle, Texas.

Figure 9: Time series plot of temperature for Deep and Johnny spring orifices compared to total discharge of the San Marcos Springs.
Figure 10: Time series plot of dissolved oxygen concentrations for Deep and Johnny spring orifices compared to total discharge of the San Marcos Springs.

Figure 11: Time series plot of calcium hardness concentrations versus total springs discharge for the Deep and Johnny spring orifices.

Figure 12: Time series plot of total hardness and calcium hardness concentrations and discharge for Comal 1 Spring.

Figure 13: Time series plot of total hardness and calcium hardness concentrations for Hueco I Spring compared to precipitation data.

Figure 14: Time series plot of temperature and specific conductance data for Comal 1 Spring compared to discharge data.

Figure 15: Time series plot of temperature and dissolved oxygen for Hueco I Spring compared to precipitation data.

Figure 16: Time series plot of specific conductance and chloride concentrations for Comal 1 Spring compared to spring discharge data.

Figure 17: Time series plot of specific conductance and chloride concentrations for Hueco I Springs compared to annual precipitation data.

Figure 18: Plot of magnesium hardness, calcium hardness, specific conductance, pH, temperature, and discharge before, during, and after October 1982 storms around Comal Springs.

Figure 19: Plot of fecal coliform bacteria, chloride, sulfate, phosphate, nitrate, and discharge before, during, and after October 1982 storms around Comal Spring

Figure 20: Plot of magnesium hardness, calcium hardness, specific conductance, and discharge before, during, after March 1983 storms around Hueco I Spring.

Figure 21: Plot of chloride, nitrate, pH, and discharge before, during, and after March 1983 storms around Hueco I Spring.

Figure 22: San Antonio reference well.
INTRODUCTION

The Edwards Limestone is a complexly fractured and faulted, designated sole-source aquifer that provides the water needs for nearly two million people, including the city of San Antonio. Rapid urban development has increased the chances of contamination and has caused the average pumpage rate to now nearly equal the average yearly recharge rate of 595,000 acre-feet (7.34 x 10^9 m^3/year). The most significant natural discharge points for the aquifer are three of the largest springs in Texas, the Comal, Hueco, and San Marcos springs (Figure 1). These springs are major recreational areas for central Texas and contain several rare and endangered plant and animal species. Comal Springs ceased to flow during the drought of the mid 1950's and the drought of 1984. The San Marcos Springs continued to flow but reached a record low of 46 cfs (1.3 cms) in 1956 and 60 cfs (1.7 cms) in 1984. Tritium studies of the Comal Springs by Pearson et al. (1975) and time series analysis of fifteen water chemistry parameters by Rothermel and Ogden (1986) have demonstrated that the various Comal Spring orifices receive very little local recharge except during high-water-table conditions. In contrast, early tritium measurements of the San Marcos Springs suggested that the these springs receive a mixture of old and recent recharge (Pearson et al., 1975). Hueco Springs has the highest tritium content and is believed to be composed of very recent ground water.

Recent studies by Espey et al. (1975), Klemt et al. (1975), and Guyton and Associates (1979) have led to modeling predictions that suggest discharge from all three springs could cease by the year 2020, due primarily to ground-water mining in the San Antonio area. This hypothesis was based on uniform, homogeneous flow to the major orifices of the springs. For San Marcos Springs, samples taken by Pearson et al. (1975) were only from one orifice since the other are below the lake's surface (Figure 2). Preliminary sampling of each of the San Marcos Springs orifices by divers (Ogden et al., 1986) showed that, based on water chemistry, two seemingly hydrologically separate spring groups exist. If this hypothesis could be substantiated, then the predictions of the model could be wrong, and some method of preserving spring flow might be found. Therefore, the objective of the research was to utilize ground-water tracers and spring-water chemistry to determine if separate flow regimes actually exist at the San Marcos Springs, and if a similar situation occurs at Hueco or Comal Springs.
The study area is located along the Balcones fault escarpment in Hays and Comal counties, Texas. The study area lies between two major physiographic provinces of the southwestern United States, the Edwards Plateau and the Gulf Coastal Plain. The topographic expression that forms the dividing line for the provinces is the Balcones Escarpment. West of the escarpment is the karstic Edwards Plateau. The area immediately east of the escarpment is the Blackland Prairie of the Gulf Coastal Plain.

The Edwards Aquifer is composed of a group of Cretaceous carbonates that have a total thickness of approximately 450 feet (137 m) in the San Marcos area. The Edwards Aquifer is composed of the Comanche Peak Limestone, Edwards Limestone, and Georgetown Limestone. Rose (1972) raised the Edwards Limestone to group status in central Texas and divided it into the Kainer (lower) and Person (upper) members. The Edwards Aquifer was later divided into hydrostratigraphic units by Maclay and Small (1983) through a detailed analysis of cores and geophysical logs. Lithologically, the Edwards Aquifer consists of rudist limestones, burrowed tidal-flat wackestones, grainstones, dolomite, nodular chert, solution-collapse breccias, and weathered, honeycombed beds.

Recharge to the aquifer occurs through losing streams located primarily to the west and south of San Marcos and New Braunfels. Surface water moves across the impermeable rocks of the Glen Rose Formation until (drainage zone, Figure 1) the Edwards Aquifer is encountered at the Balcones fault zone. Most of this water moves in a general east/northeast direction where it discharges at the Comal, Hueco, and San Marcos springs. Complex "down to coast" faulting causes the Edwards Aquifer to lie deeper and deeper below the surface as one transects in a southeast direction. Where the aquifer is exposed at the surface, it is termed the recharge zone. Where the Edwards is completely saturated and buried beneath the impermeable Del Rio Clay and younger rocks, it is termed the artesian zone. The bad-water line represents the eastern edge of the aquifer where poor circulation has caused the water to have a high TDS (>1000 mg/l) and be non-potable.

The San Marcos Springs are the second largest spring group in Texas with a mean history flow of 161 cfs (4.50 m³/sec). They are located in the city of San Marcos in Hays County and are owned and operated as a tourist attraction by Aquarena Springs, Inc. The spring orifices are now under up to 40 feet of water due to a dam originally created for hydroelectric power. Water issues from six major orifices along the base of the Balcones Escarpment (Figure 2) as well as from numerous smaller openings; some are marked by sand boils. Samples from the six orifices were retrieved by divers. A temperature/dissolved oxygen (D.O.) probe was placed at each orifice during sampling and read from...
above by researchers in a glass-bottomed boat. The elevation of the lake surface is 574 feet (175 m) above sea level.

Comal Springs is the largest spring group in Texas with a mean historic flow of approximately 300 cfs (8.31 m³/sec). This average has been decreasing in recent years as water-well withdrawals around San Antonio have increased. The springs are located in New Braunfels, Comal County, and issue from four major orifices above the lake surface (Figure 3). These orifices are located along a 1500-yard (372-m) stretch of the base of the Balcones Escarpment. The spring openings are at about 623 feet (190 m) above sea level. The lake is presently used for recreation and the production of hydroelectric power.

Hueco Springs is located three miles north of New Braunfels and is composed of two major orifices in limestone covered by Quaternary alluvium 300 feet west of the Guadalupe River (Figure 4). The altitude of the springs orifices are 658 ft (201 m) and 652 ft (199 m) above sea level. Spring flow is very variable and historically has not been measured as often as the Comal and San Marcos springs. The Hueco Springs commonly cease to flow during droughts. The maximum recorded discharge was 131 cfs (3.71 m³/s) in 1968 (Guyton and Assoc., 1979).

TRACER TESTS

Two ground-water tracer tests were performed to aid in interpreting flow directions and velocities to the San Marcos Springs. The first test was conducted in Ezell's Cave, located on the San Marcos Springs fault (Figure 5). Two pounds (0.90 kg) of sodium-fluorescein green dye were placed in the Ezell's Cave lake during a period of average (approximately 140 cfs (4 cms)) spring discharge. Prior to the test, charcoal packets for dye absorption were placed at six spring orifices and two wells. The dye was detected within nine days at the Southwest Texas State University artesian well and on the 10th day at one of the City's wells. Charcoal traps were retrieved from the San Marcos Springs by divers 11 days after dye injection and, surprisingly, only one orifice (102-Deep Spring, Figure 2) was positive. The velocity of travel was approximately 1500 ft/day (457 m/day). Nearly 30 days later, dye also emerged from the Catfish Spring orifice (106) of the San Marcos Springs. Continued monitoring of the spring orifices showed no presence of dye from any other spring orifice. The tracing experiment was repeated about six months later and the results were the same. A fault was mapped by Guyton and Associates (1979), which separates the southern set of spring orifices (Deep and Catfish) from the northern set (100-Divergent, 104-Johnny, 101-Cabomba, and 107-Hotel, Figure 2). This fault could have sufficient
displacement to act as a ground-water barrier. The fact that it took approximately 30 days to move only 230 feet (70 m), between the Deep and Catfish spring orifices, suggests minimal hydrologic connection and/or a zone of extremely slow ground-water movement possibly caused by a meeting of two separate pressure systems.

A second trace was conducted from a lake in Rattlesnake Cave during low flow conditions of the San Marcos Springs (60 cfs, 1.7 cms). Three ounces (86 grams) of sodium-fluorescein dye and five pounds (2.3 kilograms) of Tinopal CBS-X, an optical brightener, were utilized. Rattlesnake Cave is located approximately 4000 ft (1220 m) northeast from the head of Spring Lake (Figure 5). In eleven days the dye was detected at Sink Spring and a well approximately 500 feet (153 m) southwest of the cave. Finally, 40 days after the test began, the dye emerged from all six monitored orifices of the San Marcos Springs. The slower velocity of transport may be attributed to low spring discharge and the extremely flat water-table conditions brought about by the eight-month drought. The emergence of the dye from all spring orifices suggests that the fault boundary crossing Spring Lake also may act as a pressure-head boundary allowing reversals of flow directions during differing flow conditions. Another possibility is that water moving southwest from the Sink Creek drainage basin may bifurcate in a down-gradient direction, whereas, the water moving in a northeast direction along the San Marcos Springs fault may stay confined within a narrow pathway.

Five ground-water traces were performed around Comal Springs, but none of the dyes appeared at any of the spring orifices. This supports earlier hypotheses that very little recent, locally derived recharge waters emerge from Comal Springs (Pearson et al., 1975). Rettman (pers. comm., 1984) once injected dye into a well in Panther Creek about 500 feet (155 m) from the nearest spring orifice (Comal 1). Surprisingly, the dye emerged only from the Comal 3 orifice. The trace was repeated, and the results were the same. This demonstrates that at least some separate flow paths feed the individual spring orifices. Whether these limestone conduits are interconnected at some distance from the springs and merely bifurcate near the springs is unknown. Quinlan and Rowe (1977) have discovered similar bifurcation in some Kentucky springs documented by actual cavern explorations.

One successful trace was made to Hueco Springs. A pound (2.2 kg) of fluorescein dye was injected about two miles (3.2 km) southwest of Hueco Springs (Figure 6). Within five days, the dye detectors tested positive, indicating that recent storm waters contribute significantly to the discharge of the springs. The charcoal absorption packets were not
tested until five days after dye injection, so the travel time may have been significantly less.

**POTENTIOMETRIC MAP**

The first potentiometric map of the Edwards Aquifer in the San Marcos area was drawn by DeCook (1956). He utilized only 13 wells for the Edwards Aquifer in Hays County. His map failed to show the effects of faulting on the water-table configuration and suggested no flow to the San Marcos Springs from points to the north/northwest such as the Blanco River. A model of the potentiometric surface map was constructed by Klemt et al. (1975) for the entire aquifer region for the purpose of predicting the time of cessation of flow from the Comal and San Marcos springs. This map was also too generalized for Hays County. Therefore, a detailed potentiometric surface map was needed to determine the effect of faulting on ground-water flow and as a means of distinguishing ground-water flow directions.

A detailed potentiometric surface map was constructed utilizing 75 static water-level measurements within the 50-square-mile (130 sq km) study area within a short period of time in October and November of 1984 (Figure 7). Very little water-table elevation change occurred during this time as demonstrated by the monitored static water levels of twelve wells located throughout the study area. The precipitation that occurred during October and November had little effect on the water-table elevation. From this, it is evident that significant interconnected cavity porosity exists within the zone of water-table fluctuation as is predicted by theories on the evolution of solution cavities.

The configuration of the water table is very complex due to the structural complexity of the study area. There are numerous faults, cross faults, and joints that dissect the San Marcos area and cause ground-water movement to be impeded or enhanced. Only the major faults are shown on the potentiometric surface map. This new potentiometric surface map demonstrates that the movement of ground water has been modified by the Balcones fault zone. Several faults traversing the study area have vertical displacements of 50 to 350 feet (15 to 107 meters). These normal faults form en echelon fault blocks which create, in some places, isolated avenues of ground-water flow and ground-water barriers. Similar fault control of ground-water flow is also seen in Holt's (1956) potentiometric surface map of Medina County, which is also located in the Balcones fault zone. He demonstrated that faults with significant displacement create barriers to ground-water movement and that water will "spill out" into an adjacent fault block where the
displacement of the faults decreases.

The potentiometric surface map also suggests that ground water is moving from the San Antonio portion of the aquifer confined between the San Marcos Springs fault and Comal Springs fault. Each of these faults has over 300 feet (90 m) of displacement, and both are believed to form hydrologic barriers to ground-water movement. Some local recharge waters may enter the fault block when Purgatory Creek flows during major storm events. If this local water does enter the fault block, it must be insignificant compared to the amount in storage, because no chemical changes of the springs occur after storms.

In the San Marcos area, "local" recharge waters enter the study area from the west and move down-gradient to the southeast. The movement of ground water is then diverted by the Baptist Academy fault (Quick, 1985) because it has significant displacement in the western half of the study area. The displacement of the Baptist Academy and Bat Cave faults decreases in a northeast direction. As a result, ground water is believed to change direction and move towards the south to the San Marcos Springs along fractures and minor cross-faults. The potentiometric map also demonstrates that recharge is occurring from the north/northwest (Sink Creek-Blanco River) to the San Marcos Springs. A recent Blanco River loss study by Watson (1985) has shown that the Blanco River is losing water near the Halifax Ranch (Figure 8) to the Edwards Aquifer in the same area suggested by the equipotential lines. At one point along the losing stretch, a 30-foot (9 m) deep cave (Tarbuttons Showerbath Cave, Figure 8) occurs just 20 feet (6 m) from the river. The cave crosses beneath the river, but less than 1 cfs (0.03 cms) enters the cave as seepage from the roof. A dye trace was performed by Ogden et al. (1985) linking these cave waters to the San Marcos Springs. Watson's (1985) study stated that the annual volumes of recharge by the Blanco River into the aquifer, 1934 to 1977, varied from a high of 85,900 acre-feet (1.06 x 10^3 m^3/year) in 1975 to a low of 8,200 acre-feet (1.01 x 10^3 m^3/year) in 1950. The average annual recharge for the 1934 to 1977 period was 36,000 acre-feet (4.44 x 10^3 m^3/year). If recharge from the Blanco River were to be enhanced, it could provide the means of ensuring continued discharge from the San Marcos Springs.

HYDROCHEMISTRY - SAN MARCOS SPRINGS

Six orifices of the San Marcos Springs were sampled by divers at least every two weeks from August 1982 through July 1983. During this time, the total discharge of the springs increased from 60 cfs (1.7 cms) to 160 cfs (4.5 cms). Two of the measured parameters, temperature and dissolved oxygen, show distinct differences between the southern and
northern group of spring orifices. Figure 9 shows the temperature and discharge data for both the Deep and Johnny spring orifices of the San Marcos Springs. The Deep spring orifice (site #102, Figure 2) was chosen to represent the southern group because of its greater discharge. The Johnny spring orifice (site #164, Figure 2) was chosen to represent the northern spring group because it was spatially in the middle and also had a continuous high discharge rate throughout the study year. Each chosen orifice is statistically representative of its group, based on comparison of means for 15 chemical parameters. It is important to note that discharge was not measured at each individual orifice, since they were all under more than 10 feet (3 m) of lake water. The Deep spring orifice has a mean average temperature of 22.3°C. An analysis-of-variance test, F-probability 0.0001, designates a statistical difference between the two spring orifices at alpha equals 0.05. The temperature of Deep spring is always above 22.0°C and Johnny's is always below 22.0°C. The importance of Deep's higher temperature is that it is warmer than expected for shallow ground water in the Edwards Aquifer. All of the spring orifices of the northern group have an average temperature that is expected for shallow ground water. Hueco Springs, for example, is known to discharge almost entirely shallow ground water at an average temperature of 21.3°C. In areas around San Antonio where the Edwards is over 1500 feet (457 m) below the surface, ground water can be up to 25°C. Comal Springs, which receives little or no local recharge, has a mean average temperature of 23.2°C (Rothermel and Ogden, 1986). As the warm ground water beneath San Antonio moves upwards in its path to the Comal Springs, it is slowly cooled. As the underflow then continues northward to the Deep and Catfish orifices of the San Marcos Springs, it apparently cools another degree.

When the summer and spring rains occurred and discharge increased, the temperature at the Johnny spring orifice decreased, but Deep's did not. This suggests that during drought periods the hypothesized pressure boundary shifts northward and provides some older and warmer water to the northern spring group. Once the total discharge of the San Marcos Springs reaches approximately 100 cfs (2.8 cms), Johnny and the other orifices of the northern spring group then return entirely to younger and cooler local recharge waters, derived primarily from the Blanco River.

Figure 10 displays plots of dissolved oxygen concentration (D.O.) and discharge against time for the Deep and Johnny spring orifices. The average dissolved oxygen content for Deep spring is 5.7 mg/l and Johnny's is 4.1 mg/l. The coefficient of variation for Deep is 5.1% and Johnny's is 9.7%, demonstrating the greater variability of the northern group of springs. The analysis of variance, F-probability of 0.0001, statistically shows a significant
difference in dissolved oxygen content between the two orifices at alpha equals 0.05. Most outstanding is that Deep spring nearly always has higher D.O. content than Johnny. This again suggests that two different flow systems converge at the San Marcos Springs.

The average dissolved oxygen concentration of the six spring orifices of the San Marcos Springs gradually increases in a northward direction. Dissolved oxygen displays a negative correlation against discharge for Johnny (alpha equals 0.05) whereas Deep remains relatively unaffected. During low flow periods, Johnny's D.O. approaches that of Deep spring. When the drought ended in October, 1984, spring discharge increased and Johnny's D.O. dropped significantly. This further supports the independent flow regime hypothesis and that this separating boundary moves in response to changes in hydrostatic pressure between the two systems.

Other indicators that support this hypothesis are the calcium hardness and tritium values. Figure 11 shows a plot of calcium hardness and discharge versus time for the two spring orifices. Water emerging from the Deep spring orifice is nearly always harder due to the longer residence time associated with the greater transport distance. Tritium samples were taken in October 1984 during low flow conditions, but after several storm events took place. The tritium value for Deep spring was $7.1 \pm 0.5$ and Johnny's was $9.5 \pm 0.6$ tritium units. Current precipitation has approximately 9 tritium units at the Waco, Texas, station. Therefore, the data show that water emerging from the Johnny spring orifice is primarily from recent, local recharge.

**HYDROCHEMISTRY - COMAL AND HUECO SPRINGS**

Each of the four Comal Spring orifices and two Hueco Spring orifices were sampled weekly for a year in 1982 and 1983, and during a large storm to determine the effects of season, discharge, and recharge events on spring-water chemistry. One of the objectives of this study was to determine if all spring orifices discharge chemically similar water or if there are separate flow systems such as was demonstrated for the San Marcos Springs. Statistical comparison of the means of 15 chemical parameters showed no significant difference between any two spring orifices for each spring group, but significant differences did occur between Comal and Hueco Springs. Therefore, just the data from the Comal I spring orifice and the Hueco I orifice will be presented. A more in-depth analysis of all spring orifices and parameters can be found in Rothermel and Ogden (1986).

The Comal I orifice is the highest in elevation of the four and had the second highest
discharge. The water emerges from a shallow cave in brecciated Edwards Limestone. Numerous samples were taken during three monitored storm events during the year-long study period. The rain event data are included in the graphs and can usually be discerned by a series of points falling in a vertical column. Hueco I is the lowest in elevation of two Hueco spring orifices, and was chosen because Hueco II ceased flowing for several months during the study.

Total hardness and calcium hardness data (Figure 12) for Comal 1 show limited seasonal variation. A low occurred from September to mid-October, 1982, with a subsequent rise, and an apparent leveling off until mid-January, 1983. The hardness values then began to display a slow rise until late March, and they even out and begin to show a drop in the late summer. All the Comal springs displayed this seasonal trend in hardness. The lower fall and winter values for total and calcium hardness, and the rising trend of hardness in the spring, may be caused by rainwater and soil temperatures which affect dissolution kinetics. As seen in Figure 12, the months with lower total and calcium hardness are also the months with lower discharge. During these low water-table conditions, former wetted surfaces in the Comal flow system may have dried up, leaving calcium precipitate on the conduit walls. Since higher discharges occur in the spring, the conduit flow path would be more full of water and the flow may become more turbulent, thus redissolving the calcium "flakes" in the conduit and increasing the dissolution of conduit walls. Higher late-winter and spring recharge also may force harder water from the springs due to its longer residence time in the system. Trees and shrubs release carbon dioxide into the soil when active, but during the fall and winter months, when trees are dormant, up to three times less carbon dioxide is released by the roots than in the summer months. In addition, microorganisms in the soil contribute to soil CO$_2$, and the bacteria, molds, etc., may have lower activity in the winter, thus causing less soil CO$_2$. Fertilizers also increase CO$_2$ production in the soil and, of course, there is little fertilization in the winter months. Therefore, less carbon dioxide in the soil in winter months will reduce the dissolution of soil calcite and regolith as the recharge waters percolate to the flow system.

A similar but better displayed trend is seen on the Hueco Springs plot of total and calcium hardness versus time (Figure 13). Again, note the rain event points which, although they display a definite effect from rainfall, should be ignored to observe the seasonal variations. A very definite increase is seen from fall to late winter for calcium hardness. Although the points are more scattered for total hardness, a rise in the late winter and spring is also observed. An additional control that may cause such a trend is the recharge temperature. It is known that there is an inverse relationship between temperature and calcite solubility.
Thus, since cooler recharge occurs in the winter months, more calcium may be dissolved in the shallow vadose zone of the Hueco flow system, increasing the calcium and total hardness of the Hueco ground waters.

All of the Comal Springs have similar and low coefficients of variation (C.V.) for total and calcium hardness, indicating that the water has a longer residence time to equilibrate with the limestone and the dolomite. Comal 1 has the lowest C.V. (6.7% for total hardness and 14.7% for calcium hardness), but it has the highest mean and median values, although all the means are close. The plot of hardness against time reflects a better seasonal trend at Comal 3, but the data points are much less scattered at Comal 1. This could indicate that the flow of water initially comes out of Comal 1, then proceeds to flow out of the other three orifices, with a possible mixing of more recent waters (or surface runoff or saturated soil flow from small rains) as it flows along the fault-line to Comal 4, which has the highest C.V. for total (9.4%) and calcium (19.9%) hardness.

Hueco I has almost twice the C.V. (11.5%) for total hardness than Comal 1, and the highest mean and median over all the Comal Springs, although Comal 4 has the widest range for total hardness (198 to 340 mg/l as CaCO₃). For calcium hardness, Hueco I, again, has a high C.V. (19.2%) and a much higher mean (209 mg/l as CaCO₃), median (217 mg/l as CaCO₃), and range (178 mg/l as CaCO₃) compared to Comal Springs. Additionally, the analysis of variance test (with an F-probability of 0.001) indicates a significant difference between Hueco 1 and the Comal Springs for both total and calcium hardness.

Comal 1 displays a statistically significant (alpha = 0.001) positive or rising trend in calcium hardness as discharge rises. Hueco 1 shows a strong negative (alpha = 0.004) relationship, in contrast. In shallow flow systems where local recharge rapidly moves towards the spring outlet, such as for Hueco 1, calcium hardness is diluted by the rapid influx of lower hardness water. For Comal 1, the increase in discharge is more a reflection of the hydraulic head increase from distance recharge areas.

There are several possible reasons why there is a difference in the hardness concentrations between the Hueco and Comal waters. The higher hardness at Hueco may be related to the turbulent nature of flow allowing more calcium carbonate to be dissolved. The longer flow paths and probable laminar flow for the Comal Springs system may cause calcium carbonate to precipitate in cavities before exiting from the springs. The temperature differences between the springs may also be affecting solution kinetics. Another
possibility may be related to the Edwards Group member through which the water primarily flows. It may be that water moves through more soluble and gypsum-rich beds in the Hueco Spring's drainage basin. It is interesting to note that the calcium hardness of Comal I is significantly less than that for any spring orifice of the San Marcos Springs and that the calcium hardness for Hueco I is closer to that of the Deep springs orifice at San Marcos.

Temperature of the ground water at Comal Springs is very consistent and shows negligible fluctuations with time, although the temperature does appear to rise slightly in the summer months (Figure 14). Temperatures at Comal 1 ranged from 22.0°C (71.6 degrees F) to 23.5°C (74.3°F) during the sampling period, with a C.V. of 1.3%. The scatter that appears on the first part of Figure 14 is due to rain event changes and errors in measurements made with a hand-held thermometer. In January, 1983, temperature measurements were taken with a YSI digital dissolved-oxygen/temperature meter, thus eliminating "eye-balling" error. The change in instruments is well seen in both the Hueco I (Figure 15) and Comal 1 plots. The relatively constant temperature of the Comal waters differs slightly from the mean annual air temperature at New Braunfels (the location of the springs) of 20.6°C (69.08°F). Recharge water that sinks in the western counties of the Edwards Aquifer region migrates to depths of over 2000 ft. before emerging at Comal Springs. Due to this deep circulation, the ground water is heated above the mean annual air temperature.

Hueco I has a greater temperature fluctuation with a C.V. of 2.9%. The mean of 21.5°C (70.7°F) and median of 21.3°C (70.34°F) are almost two degrees celsius lower than the temperatures at Comal and are much closer to the mean annual air temperature at New Braunfels. This is partially due to the shallower nature (as compared to Comal) of the ground-water system and the faster flow-through rate of the water.

The variations caused by rain are smoother at Comal than Hueco, but the range in temperature variation due to rains was slightly greater at Comal. The analysis of variance test confirmed the significant difference in temperature between Hueco I and all the Comal Springs.

Specific conductance also remained relatively consistent for the sampling period at Comal Springs. Although there is some scatter in the plot for Comal 1 (Figure 16), a slight rising trend is observed for May and June. The conductivity meter had to be repaired in the middle of the sampling period; thus there is a break in the graphs of the data between late December, 1982, and early February, 1983. Hueco I has a very scattered plot of specific
HYDROCHEMISTRY OF THE COMAL, HUECO, AND SAN MARCOS SPRINGS, EDWARDS AQUIFER, TEXAS

conductance (Figure 17), indicating the greater influence of precipitation and recharge on the spring waters. The C.V. at Hueco I was 8.1%, higher than the 7.0 for Comal I. Comal I showed a positive statistical correlation between conductivity and discharge, while Hueco I demonstrated a negative correlation. Generally, there is a greater range and more fluctuation in specific conductance during storm events at Hueco than at Comal. This again depicts a shallower flow system at Hueco. The variations in conductance at Comal during rains are very abrupt, have less range, and are not as lasting as at Hueco. An in-depth discussion of the effects of storm events on the water chemistry of Comal and Hueco springs is presented in the following section.

Dissolved oxygen was measured only during the last seven months of the investigation. These parameters, however, show some interesting and important results. On the plot of D.O. against time for Comal I (Figure 14), two peaks and one low are seen. The peaks occurred just between April and May, 1983, and from beginning to mid-August, 1983, where the D.O. appears to drop by the end of August. It is important to note that there was essentially no rain during April and early May, and that this corresponds dramatically with the decrease in D.O. for Comal 1. This demonstrates an impact from local precipitation events on water chemistry even when most recharge may be distant. A trough in the D.O. graph for Comal 1 also occurred from late June to mid-July, 1983. Even though there is a lack of data, the variations seem to be real. Comal 1 statistically has a higher range (4.41 - 5.80 mg/l), mean (5.77 mg/l), and median for dissolved oxygen compared to the other three orifices. This suggests for the first time that Comal I may have a shallow flow component or that some nearby recent, oxygen-rich meteoric waters are mixing with the spring water. It is also important to note that the maximum temperature of Comal 1 is about one degree celsius cooler than the other three Comal Springs. Hueco I has even higher D.O. values (4.58 mg/l to 6.38 mg/l) than Comal 1, with a mean of 5.77 mg/l and a median of 5.88 mg/l (Figure 15). It also has the highest C.V. of 9%. This is due to a much shallower and quicker flow-through system than Comal Springs. The analysis of variance tests confirm the dissolved oxygen differences between the spring groups.

Storm Responses

The effects of storm events on spring-water chemistry are demonstrated at Comal Springs by plots of selected chemical and physical parameters versus time for a few October rains (Figure 18 and Figure 19). All spring orifices reacted similarly. Small rains occurring on October 6th and 8th, 1982, did not significantly change the spring-water chemistry, but an inch of rainfall on October 10th did. This larger rainfall increased the temperature and
brought in soil nitrates. Fecal coliform bacteria and phosphate levels did not change. Calcium hardness increased but magnesium, sulfate, and chloride levels decreased. These data definitely demonstrate that some recent, local recharge waters are reaching the springs. This is contrary to prior thought, based on low tritium values (Pearson et al., 1975). A tritium value of $5.0 \pm 0.5$ T.U. was made for Comal 1 on a sample collected in October, 1984, during a severe drought. It is possible that during larger storms, a ground-water "wedge" of recent water may form near the Comal Springs orifices. There may be a few spots along the Comal Springs fault southwest of the springs where a limited amount of recent recharge can infiltrate and build up a wedge, temporarily causing a steeper hydraulic gradient than other ground-water avenues providing spring flow. The amount and length of the effect of this ground-water wedge is related to the amount of precipitation and to the ground-water stage. During low water-table conditions, the effects of large storm events will be greater. It is also possible that during very high water-table conditions, ground water may "spill over" the Comal Springs fault that usually acts as a ground-water barrier. This barrier usually prevents recharge waters west of the fault from reaching the springs. Monitoring of several storm events during the study year demonstrates that effects on spring-water chemistry remain three days to approximately three weeks, but in most cases, it is just a few days. A few future tritium measurements should be made at Comal Springs immediately after storm events to determine the validity of the ground-water wedge hypothesis.

The effects of a March, 1983, storm event on water chemistry at Hueco Springs was also monitored. For this study, an ISCO Model 2100 automatic sampler was utilized. The rains caused the water to become cloudy to muddy for up to several hours after a particular rain event. The discharge rose from 21.0 cfs (0.6 cms) before the first rain to a high of 53.0 cfs (1.5 cms) about 6.5 hours after the first rain (Figure 20). Generally, conductivity and calcium hardness decreased and magnesium hardness increased. Initially, a slug of calcium-rich water was pushed out of the spring system by the first rain. This could be due to the turbulent nature of the water causing increased dissolution, or it could be related to rapid dissolution of dried calcium minerals precipitated in the soil and along fractures. This hypothesis is possibly substantiated by the corresponding changes in pH (Figure 21).

Another explanation for fluctuations in calcium concentrations could be water reaching the spring from different recharge areas along different flow paths. It is possible that harder water residing in one flow pathway being recharged near the spring was initially flushed out, causing a subsequent lowering of calcium concentration. Later, harder water in a second, more distantly recharged flow path reached the spring outlet causing a second
rise of the calcium concentration. Once the harder water was flushed out and dried calcium particles had been dissolved, the second storm had little effect on altering the amount of dissolved calcite.

Nitrate and chloride showed marked increases with discharge. As rain waters moved through the soil, sodium chloride was dissolved and soil nitrates added, since it was March and just the beginning of the growing season. Also, the percolating waters may have carried surface contaminants to the spring from animal and human wastes. Although not plotted, fecal coliform counts increased as well. The analysis of these trends further supports the idea that rain waters rapidly move through the Hueco Springs system to emerge in a short period of time. The flow paths are shallow, and the water is therefore extremely susceptible to contamination.

IMPLICATIONS OF THE RESULTS AND RECOMMENDATIONS

The hydrochemistry data from the various orifices of the San Marcos Springs suggest that two nearly independent flow regimes contribute water to the springs. In addition, the ground-water tracer tests and the potentiometric surface map demonstrate that ground water from the San Antonio region moves northward, confined within a narrow fault block, and emerges primarily from just the southern orifices of the San Marcos Springs. This ground water appears to be separated from ground-water contributions from the Blanco River and Sink Creek areas by a fault-controlled pressure boundary. The pressure boundary is believed to move slightly in response to changes in hydrostatic head between the two ground-water flow systems.

This new evidence now presents the possibility of preserving the springs and their endangered species by constructing a recharge/flood-control dam on the Blanco River. The proposed dam would have benefits whether placed on the Glen Rose Formation or on the Edwards Limestone along a major losing stretch of the Blanco River. If an approximately 80-foot (24 m) dam is placed on outcrops of the Edwards Limestone, it could provide an effective means of raising the water table and likely would supply water to both the San Marcos and Kyle areas. Also, the ground-water divide between Barton Springs in Austin and the San Marcos Springs might change significantly due to the ground-water mound created by the dam. Therefore, both groups of springs may benefit. Siltation may prove to be a problem with time if the dam is built directly on the Edwards Aquifer. If the dam were to be built upstream on the Glen Rose Formation, the recharge rate could be controlled. A continued release of 120 cfs (3.4 cms) would provide the same
maximum annual recharge rate of 85,900 acre-feet ($1.06 \times 10^3$) that occurred in 1975. This method would also prevent excessive siltation of recharge points, but may not raise the water table as greatly. A good site for the proposed dam would be about two miles (3.2 km) upstream from the Halifax Ranch (Figure 13). In addition to recharge effects, the dam would significantly decrease downstream flooding and sustain flow longer into the summer when the Blanco River usually ceases to flow. The new lake created by the dam could have limited recreational use, but shoreline development would have to be controlled to preserve water quality. Due to monetary problems and legal battles, it would probably be ten years before the dam could be completed. In the meantime, a diversion channel from the Blanco River to Tarbuttons Showerbath Cave should be constructed. Since the cave is within 20 feet of the river, cost would be minimal.

Faulting has hydrologically isolated Comal Springs from any large sources of local recharge. Therefore, a recharge dam cannot enhance the flow of the springs. Hueco Springs, on the other hand, receives significant amounts of local recharge, and its longevity could be ensured through building recharge structures at the headwaters of such creeks as Elm and Blieders. If the flow of Comal Springs is to be preserved, the amount of ground-water use by San Antonio must not increase significantly in the future. By converting, in part, to surface-water supplies, reduction of ground-water pumpage would be possible. The building of major dams would be costly and unpopular in the San Antonio area. The present political atmosphere of federal budget cutting makes such a scheme appear even more unrealistic. A more logical and inexpensive method of preserving the Comal Springs flow would be to require mandatory water rationing in San Antonio sooner than presently dictated by the city reference well. Figure 22 shows the San Antonio reference well and the ground-water elevations used to determine which water conservation measures should take place. Since these elevations were somewhat randomly chosen based on the record low in 1956, it is recommended that the City Council raise the level at which voluntary and mandatory rationing begins to 640 feet and 625 feet, respectively. Since experts agree that the majority of summer water use in San Antonio is for watering lawns, such a regulation change would not pose a significant hardship to residents. The present monitoring system encourages ground-water waste at the expense of other aquifer uses. San Antonio residents would still enjoy low water bills, and the springs would continue to flow.

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