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WATER QUALITY OF THE SAN MARCOS RIVER

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Abstract.—The San Marcos River exhibits a distinct pattern of changing chemical and physical characteristics as it runs its 133 km course to the confluence with the Guadalupe River. This evolution of water quality includes a shift from a primary influence of groundwater to a more runoff-dominated river ecosystem, anthropogenic influences of point and nonpoint pollution, and change in character as the river flows through different physiographic regions. The river is of a constant nature and has very high water quality in its headwaters, however it becomes a more variable, turbid lowland river closer to its confluence with the Guadalupe River.

The San Marcos River emerges from a series of 200 closely-spaced openings forming a spring outfall with the second highest discharge in Texas (Brune 1981). This artesian system is fed by the San Antonio portion of the Edwards Aquifer, a 290 km long, crescent-shaped limestone aquifer running along the southern and eastern edge of the Edwards Plateau (Abbott & Woodruff 1986). The headwater stretch of the river is known for its relatively constant temperature and flow (Hannan & Dorris 1970). The springs and upper river contains a very productive submerged macrophyte community, and harbors many endemic or range-restricted organisms. These include the federally listed endangered or threatened species *Zizania texana* (Texas wild rice), *Eurycea nana* (San Marcos salamander), *Etheostoma fonticola* (fountain darter), and *Gambusia georgei* (San Marcos gambusia). The constancy of the environment has also allowed for the invasion of a number of exotic species that have a significant influence on the system.

This river is a truly unique ecosystem within the state, and the purpose of this study was to characterize important chemical and physical aspects of the river from its origin to its confluence with the Guadalupe River. This effort included sampling at 14 sites along the entire length of the river, and additional sampling in the upper river to more closely examine nutrient loading and limitation within this stretch.

STUDY SITES

Sites were sampled from the headwaters and along the entire length of the river (133 river km) to its confluence with the Guadalupe River

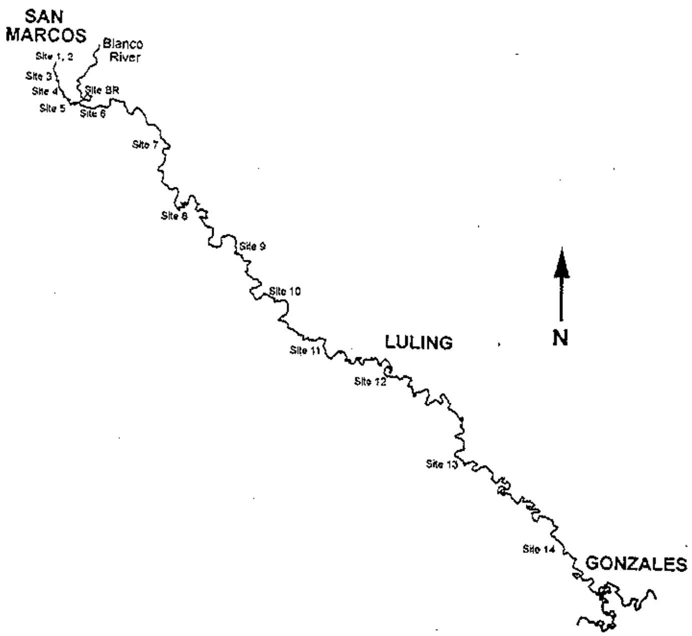

Figure 1. Sampling site locations on the San Marcos and Blanco rivers.

(Fig. 1). All river distances were taken directly from Texas Parks and Wildlife (Table A2 in TPWD 1994b) or interpolated from this source with USGS maps, and were measured from the headwater springs to the confluence. Two headwater sites were located at an artesian well behind the Freeman Aquatic Biology Building on the Southwest Texas State University campus (site 1) and in Spring Lake near the largest spring (site 2). Site 3 was 0.5 river km downstream of the springs at the Old Fish Hatchery Building in City Park. Site 4 was about 100 m downstream of the outfall of the A.E. Wood State Fish Hatchery (river km 3.5). Site 5 was 500 m below the outfall of the San Marcos Sewage Treatment Plant (SMSTP, river km 4.8). The Blanco River enters the San Marcos River 7.2 km downstream from the springs, and site 6 was at the Caldwell County Road 266 crossing (also known as Westerfield Crossing) (river km 9.5). Site 7 was at the Highway 1979 crossing just south of Martindale (river km 18), and site 8 was at the Highway 1977 crossing east of Staples (river km 27). Site 9 was at the State Route 20 crossing just south of Fentress (river km 42), and site 10 was at the Caldwell County Road 119 crossing (river km 54). Site 11 was at the U.S. Highway 90 crossing west of Luling (river km 64), and site 12 was at the U.S. Highway 80 crossing in Luling (river km 74), which is also near the USGS Luling gauging station. Site 13 was at the Highway 2091 crossing in Palmetto State Park (river km 97), and site 14 was at the Highway 2091 crossing directly west of Gonzales (river km 125), 8 river km above the San Marcos River confluence with the Guadalupe River. There was also a site on the Blanco River (site BR) located at the Old Martindale Road crossing (County Road 295) above the confluence with the San Marcos River.

Two additional sites were used for diel monitoring and nutrient limitation experiments. These included Thompson's Island (TI), located between sites 3 and 4 (just upstream from the Country Road 299 crossing, at river km 3.4), and Cummins Dam (CD), a site between sites 5 and 6 just upstream from the dam (downstream of the confluence with the Blanco River, at river km 8.7).

METHODS

The 14 sites along the river were measured on seven dates: 27 March 1992, 22 July 1992, 16 November 1992, 31 January 1993, 16 April 1993, 12 September 1993, and 10 October 1994. Temperature, pH, dissolved oxygen and specific conductivity were measured with a Hydrolab Surveyor II that was calibrated daily (Hydrolab 1985). Alkalinity was measured according to Wetzel & Likens (1991). Turbidity was measured with a HF Instruments model DRT turbidimeter. Nutrient analyses were carried out on an Alpkem RFA 300 autoanalyzer, and were based on the methods described by Strickland & Parsons (1972).

On October 10 and 11, 1994 sampling over a diel period was done at five sites (3, TI, 5, CD, and BR) in the upper river region in which all the variables described above were measured at 3 hr intervals.

In February, 1995 an experiment was carried out to determine the limiting nutrients in the upper river regions. Unglazed bathroom tiles (2.54 by 1.27 cm) were placed at sites TI and 5 to measure periphyton colonization rates through chlorophyll *a* accumulation upstream and downstream of the SMSTP. The tiles were suspended at a depth which 75% of the incident light at each site would penetrate to, and were left in the river for 14 d. Simultaneously, water samples were collected at each site for a nutrient limitation bioassay with the alga *Selenastrum capricornutum* (USEPA 1971). Samples were apportioned into 1 L cubitainers, and the appropriate nutrient additions were made. The treatments were control (no nutrient additions), +P (a K_2PO_4 solution was added to a final enrichment of $50\ \mu g\ P\ L^{-1}$), +N (a NH_4Cl solution was added to $100\ \mu g\ N\ L^{-1}$ final enrichment), and +M (metals, 100 μL of the micronutrient solution of Woods Hole MBL algal growth media (Nichols 1973) was added per cubitainer). Four combination treatments (nitrogen and phosphorus, +NP; nitrogen and metals, +NM; phosphorus and metals, +PM; and all three in combination, +NPM) at the same enrichments above were also included in this experiment. The metal solution included EDTA, iron, copper, zinc, cobalt, manganese, and molybdenum. All treatments were done in triplicate at both sites except for the control treatments, which had six replicates, and the cubitainers were incubated in 24 hr light (60 $\mu E\ m^{-2}\ s^{-1}$) and gently shaken on a shaker table for 14 d. Response to nutrients was quantified by change in chlorophyll *a* content within the cubitainers. Chlorophyll *a* was determined in DMSO-acetone extracts (Burnison 1980).

Data from the U.S. Geological Survey (USGS Water Resources data reports, USGS 1969-93) were compiled from three stations to provide more specific chemical characteristics and flow data of the waters of the San Marcos and Blanco rivers. Data were pooled from three wells and a spring (USGS local identifiers LR-67-01-801, LR-67-01-806, LR-67-09-105, and LR-67-09-111) in San Marcos which were very similar in chemical composition to the San Marcos Springs (Groeger & Gustafson 1994) to represent the ionic content of the river headwaters. Data were from USGS water years 1978-87, 1989-91, and 1993. A USGS site (USGS # 08172000) at Luling (corresponding to site 12 of this study, drainage basin area of 2170 km^2) was used to represent a site indicative of a greatly increased terrestrial influence (USGS 1969-93). The Blanco River USGS site (USGS # 08171000, drainage basin area of 919 km^2) was in Wimberley, and data from USGS water years 1974-76, 1979, and 1988-93 were used.

RESULTS

Temperature.—Variation in temperature of the San Marcos River was slight in the headwaters region (Fig. 2A). The range at site 3 during this study was 21.1-22.5°C, which closely corresponded to an earlier study (Hannan & Dorris 1970) at a nearby series of sites in which mean monthly temperatures ranged from 21.0-23.3°C over a 16 month period. Variation in water temperature increased at successive sites downstream from the artesian well, and this variation was much greater downstream of the confluence with the Blanco River (Fig. 2A). At site 14, the last sampling point before the confluence with the Guadalupe River, the temperature ranged from 11.9-27.3°C. The USGS temperature data collected near site 12 (corresponding to the data in Table 1) ranged from 6-30°C (n = 161).

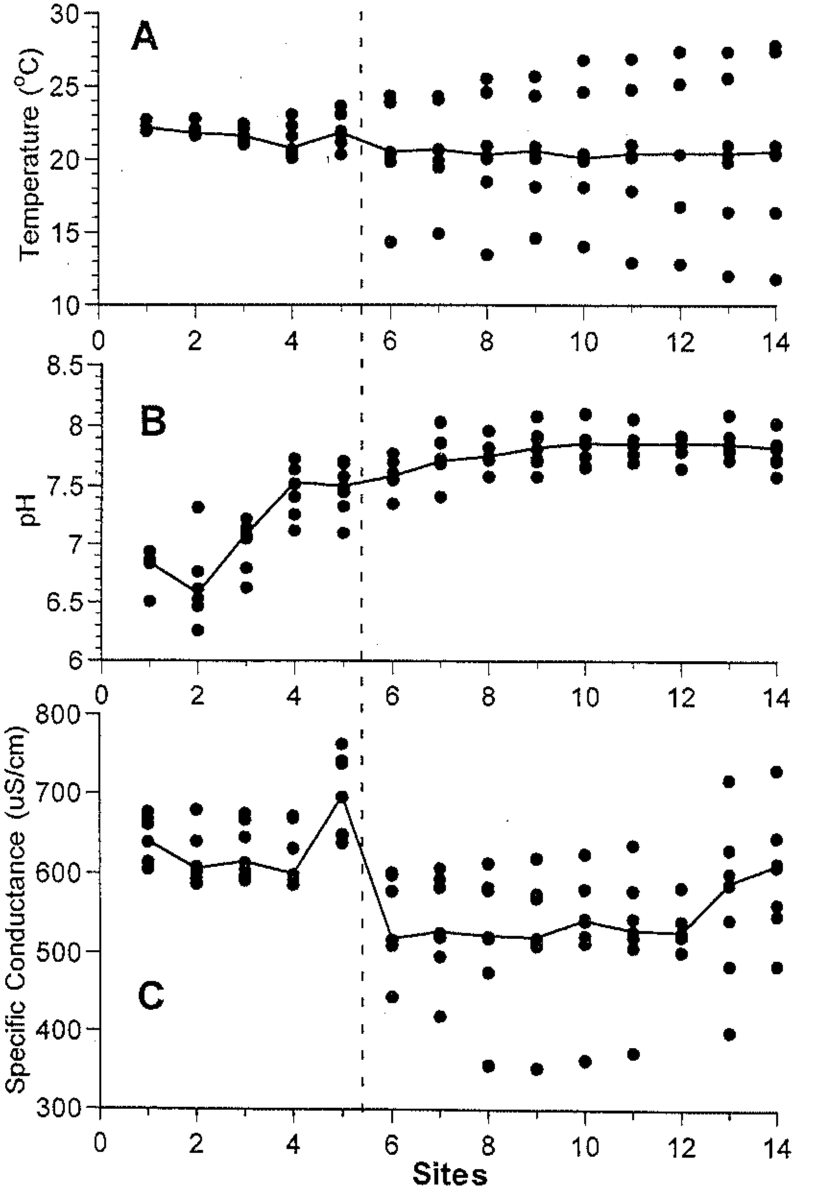

Figure 2. Temperature (A), pH (B), and specific conductance (C) on seven dates at sites along the San Marcos River. The solid line is the median value at each site. The vertical dotted line is the confluence with the Blanco River.

Table 1. Summary of USGS data, representing the chemical composition of the headwaters and a downstream site (Luling, TX) of the San Marcos River, and the Blanco River. Data are the median, mean, first to third quartile distribution (1-3 Q), range, and total number of samples (n). Sp. Cond. = specific conductance; Alk. = alkalinity.

Location	Sp. Cond. (μS/cm)	pH	Ca^{2+} (meq/L)	Mg^{2+} (meq/L)	Na^+ (meq/L)	K^+ (meq/L)	Alk. (meq/L)	Cl^- (meq/L)	SO_4^{2-} (meq/L)	Si (mmol/L)
San Marcos Springs										
Median	598	7.0	4.49	1.40	0.52	0.04	5.20	0.56	0.54	0.20
Mean	596	7.0	4.43	1.43	0.53	0.04	5.19	0.58	0.55	0.19
1-3 Q	581-617	6.9-7.1	4.24-4.59	1.34-1.48	0.48-0.60	0.03-0.04	5.08-5.25	0.51-0.65	0.50-0.60	0.18-0.20
Range	506-638	6.5-7.3	3.84-4.89	1.23-1.73	0.38-0.70	0.03-0.05	5.00-5.41	0.42-0.82	0.37-0.75	0.02-0.30
n	59	58	56	56	56	56	54	56	56	56
Blanco River										
Median	459	7.8	3.29	1.40	0.35	0.03	4.15	0.37	0.47	0.15
Mean	466	7.8	3.25	1.37	0.35	0.03	4.09	0.37	0.50	0.15
1-3 Q	444-491	7.6-7.9	2.97-3.54	1.23-1.48	0.33-0.37	0.03-0.04	3.84-4.42	0.34-0.39	0.40-0.62	0.14-0.17
Range	420-592	7.3-8.3	2.64-3.79	1.07-1.56	0.27-0.39	0.01-0.05	3.40-4.72	0.31-0.51	0.27-0.94	0.02-0.20
n	40	40	40	40	40	40	40	40	40	40
San Marcos River										
Median	578	8.0	3.84	1.48	0.87	0.05	4.60	0.96	0.60	0.18
Mean	570	8.0	3.67	1.47	0.87	0.05	4.36	0.95	0.63	0.18
1-3 Q	536-609	7.8-8.2	3.54-4.04	1.40-1.56	0.70-1.00	0.04-0.05	4.20-4.80	0.73-1.10	0.56-0.67	0.16-0.20
Range	125-835	7.1-8.6	0.85-4.59	0.21-5.10	0.17-1.57	0.03-0.13	0.86-5.18	0.34-3.36	0.13-1.21	0.01-0.40
n	180	142	179	179	143	134	179	179	179	179

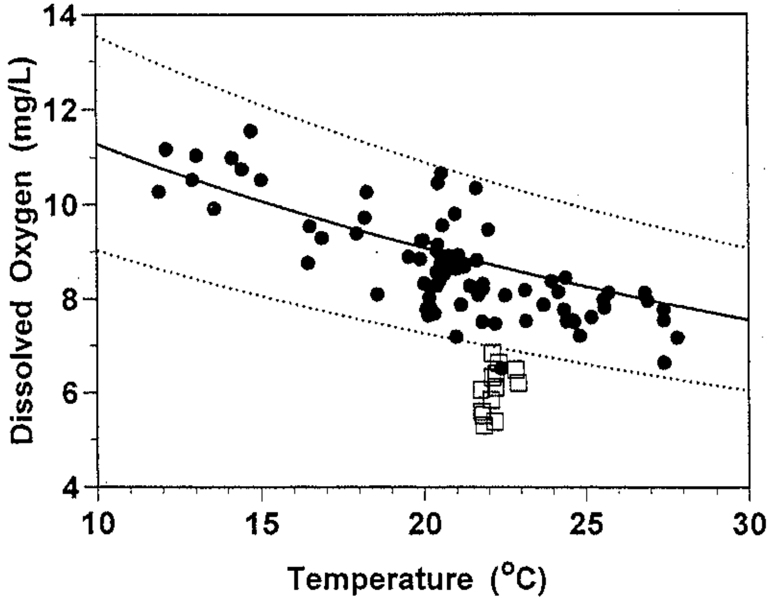

Figure 3. Relationship between dissolved oxygen and temperature in the San Marcos River at 14 sites. The solid and dotted curves represent 100% (± 20%) oxygen saturation concentration at an atmospheric pressure of 760 mm Hg at sea level. The unfilled squares represent sites 1 and 2, the artesian well and Spring Lake, respectively. The filled symbols represent the other 12 sites.

pH.—The pH in the artesian well and Spring Lake (sites 1 and 2) was much lower than other sites, indicating that aquifer CO_2 concentrations were higher than those in equilibration with the atmosphere. The pH increased rapidly downstream of site 2 (Fig. 2B). Downstream of the confluence with the Blanco River pH values were relatively constant and corresponded to those expected in a limestone-dominated drainage.

Dissolved oxygen.—Dissolved oxygen concentrations within the San Marcos River were within 20% of the temperature-dependent saturation concentration (Fig. 3) except for sites 1 and 2. Water is vigorously mixed as it leaves Spring Lake, either over a spillway or a very steep rapids, greatly increasing the rate at which dissolved gasses approach an atmospheric equilibrium concentration (Hannan & Dorris 1970).

Specific conductance and alkalinity.—Specific conductance was relatively constant in the upper river, though there was a distinct increase downstream of the SMSTP (site 5, Fig. 2C). Specific conductance was lower and much more variable downstream of the confluence with the Blanco River. Alkalinity, which was highly

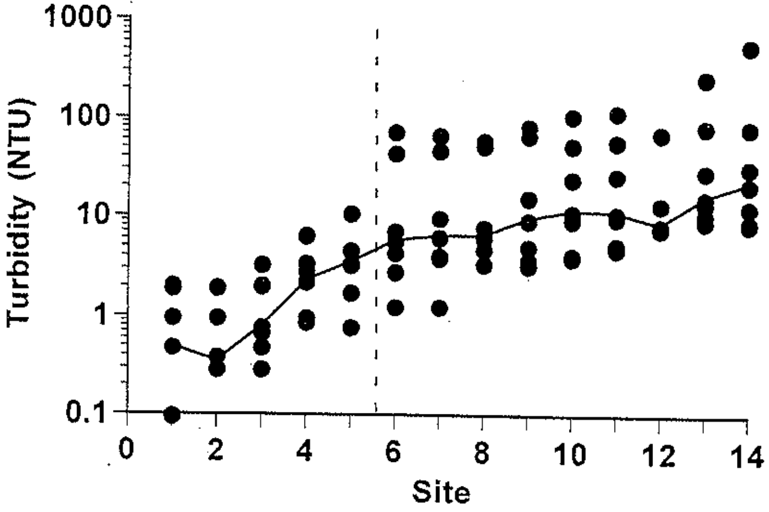

Figure 4. Turbidity on seven dates at sites along the San Marcos River. The solid line is the median. The vertical dotted line is the confluence with the Blanco River.

correlated with specific conductance (r = 0.79, n = 114), exhibited a very similar pattern to that of specific conductance (data not shown) except alkalinity did not exhibit a corresponding increase below the SMSTP.

Turbidity.—The river, known for it clear headwaters, becomes increasingly turbid downstream (Fig. 4), a characteristic of the river obvious to the casual observer. Both the State Fish Hatchery and SMSTP were apparently responsible for increased turbidity in the upper river, though construction and suburban and agricultural land practices in the upper river's drainage probably contribute also. The Blanco River can have dramatic effects on turbidity in the San Marcos River during high flow periods (Fig. 4), but is not particularly turbid during normal flows (median turbidity at the USGS station on the Blanco River was 1.9 NTU (n = 40).

Nutrient concentrations.—Nutrient concentrations in the water emerging from the aquifer tend to be relatively constant. Soluble reactive phosphorus (SRP) usually ranges from approximately 5-15 μg P L^{-1} and total phosphorus (TP) approximately 15-30 μg P L^{-1} (Fig. 5A). Nitrate ranged from about 1500-1700 μg NO_3+NO_2-N L^{-1} (Fig. 5B), and ammonium 1-30 μg NH_4-N L^{-1} (Fig. 5C). In the upper river SRP and TP concentrations were relatively constant until they were greatly enriched by the SMSTP, and were reduced below the confluence with the Blanco River. Nitrate also increased downstream of the SMSTP,

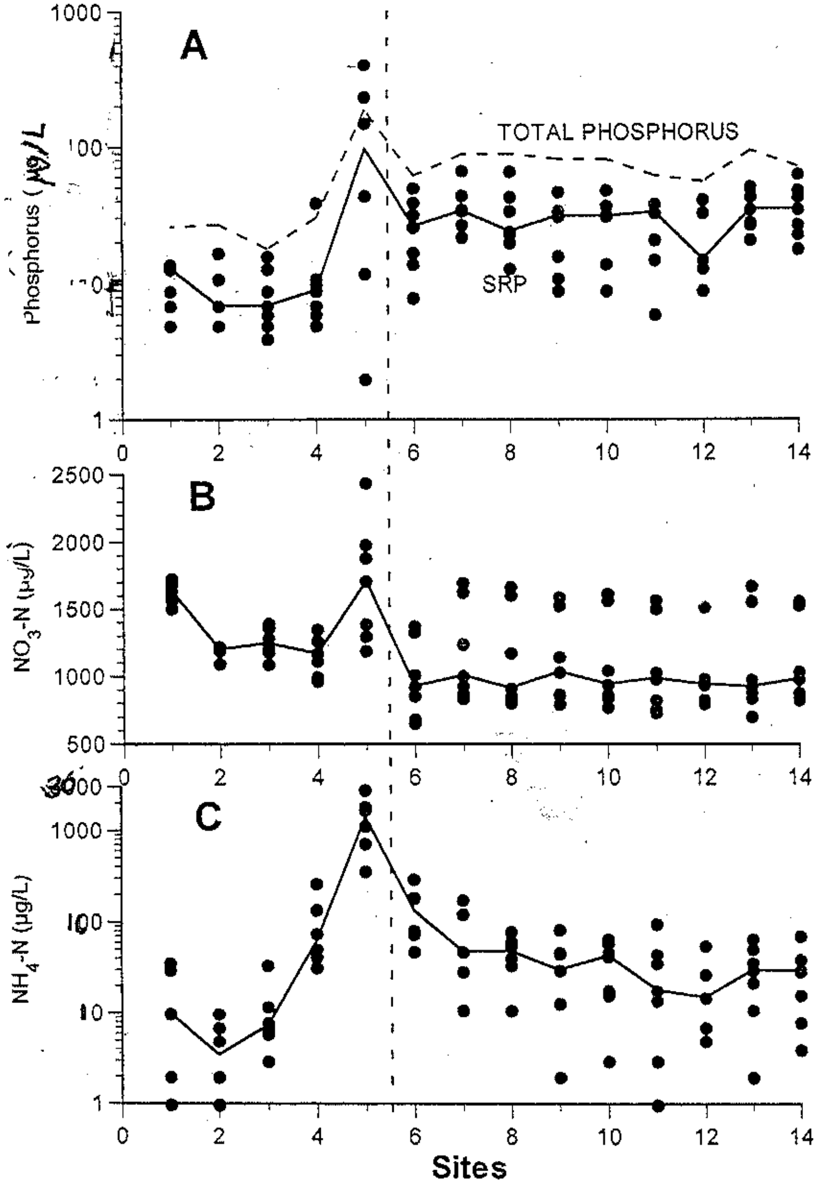

Figure 5. Phosphorus (A), nitrate-N (B), and ammonium-N (C) concentrations on seven dates at sites along the San Marcos River. The vertical dotted line is the confluence with the Blanco River. In A, the points represent SRP concentrations and the solid line is the SRP median concentration. The dotted horizontal line is the median concentration of total phosphorus.

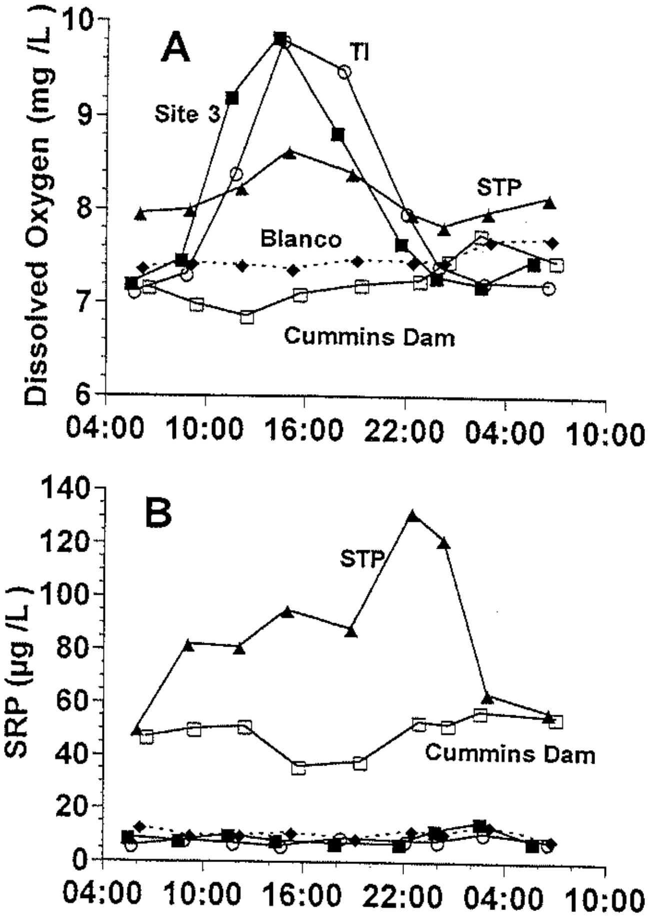

Figure 6. Diel concentrations of dissolved oxygen (A) and soluble reactive phosphorus (B) at five sites on the upper San Marcos River on 10-11 October, 1994. TI is the Thompsons Island site, and STP is site 5, right below the San Marcos sewage treatment plant.

though much less dramatically than SRP, and tended to decrease downstream to <1000 µg L^{-1}. Ammonium concentrations increased both downstream of the State Fish Hatchery and SMSTP, and decreased further downstream (Fig. 5C).

Ions.—The water emerging from the San Marcos Springs was enriched in all the major ions, except magnesium and possibly potassium, relative to the Blanco River (Table 1). The San Marcos River at Luling has a lower specific conductance relative to the water coming from the springs (Table 1), which can mostly be attributed to a

loss in calcium and alkalinity. Conversely, sodium and chloride increased over the same stretch of river. At all three USGS sites, calcium accounts for over 62% of the equivalent charge of cations and alkalinity accounts for 75% or more of the anions (Table 1).

Diel.—On the upper river, above the SMSTP, dissolved oxygen concentrations varied on a diel cycle (Fig. 6A) driven primarily by macrophyte photosynthesis and respiration (Hannan & Dorris 1970). This diel cycle was dampened below the SMSTP (site 5), apparently because effluent released from the plant was always close to atmospheric saturation. Nutrient concentrations at the SMSTP site were pulsed during the day, apparently corresponding to releases from the plant. SRP (Fig. 6B), NH_4-N, TP, and NO_3-N (data not shown) all increased from 0600 to about 2400 hrs, and then concentrations decreased, with a distinct peak about 1800 to 2200. Both at upstream sites and in the Blanco River there was no discernible diel pattern of nutrient fluctuation.

Algal biomass.—Tiles incubated in the river downstream of the SMSTP accumulated significantly more algal biomass, 20.0 ± 4.5 µg chlorophyll *a* cm^{-2} (mean ± 95% confidence interval), than those at the upstream site, 5.8 ± 0.9 µg chlorophyll *a* cm^{-2}. The bioassay experiment clearly showed that algal biomass responded only to the addition of phosphorus in water from the upstream site (Fig. 7). All treatments that included a phosphorus addition yielded about 100 µg chlorophyll *a* L^{-1} after 14 d, and there was no additional increase with any nutrient in addition to phosphorus. All other treatments yielded < 10 µg chlorophyll *a* L^{-1}, including the control. Water from downstream of the SMSTP supported a much higher growth of algae (control = 46.4 µg chlorophyll *a* L^{-1}), and the only significant increase over the control was due to the addition of both nitrogen and phosphorus (99 µg chlorophyll *a* L^{-1}) . The addition of metals inhibited algal growth in the downstream waters.

DISCUSSION

The chemical and physical quality of the San Marcos River evolves spatially and temporally as it flows from spring source to its confluence with the Guadalupe River. The changes in quality may be sudden or gradual, and the causes are both natural and anthropogenic. The first change is the exposure of aquifer water, which has typically been isolated from the atmosphere for a number of years (< 20 years, Guyton et al. 1979), to the atmosphere. Due to respiratory activity as the water percolates into and through the aquifer, high CO_2 concentra-

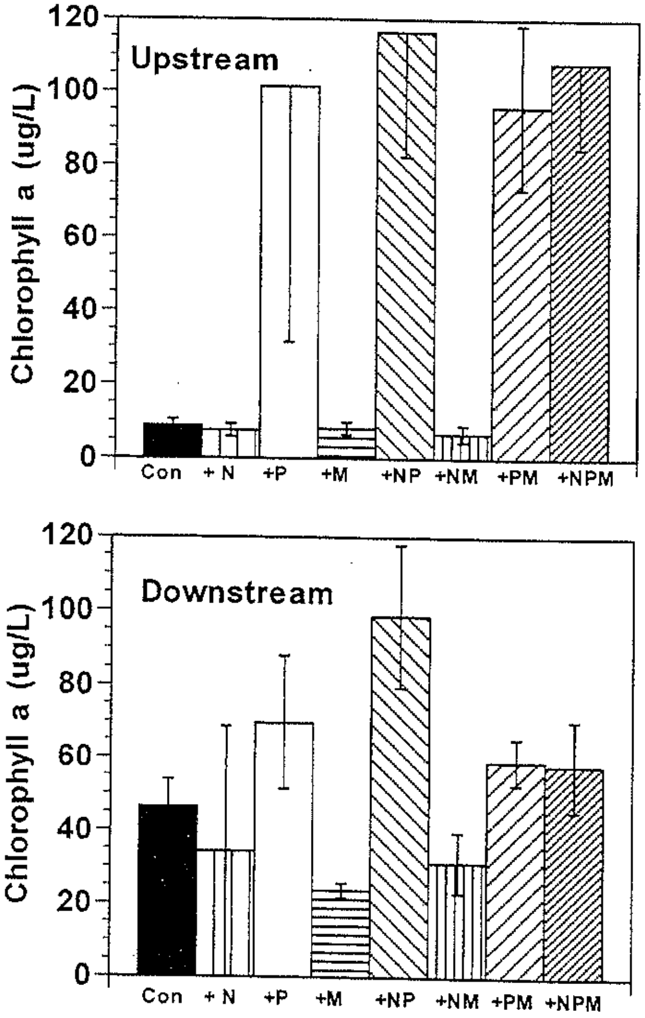

Figure 7. Final chlorophyll *a* concentrations for the nutrient limitation bioassay on samples collected upstream and downstream of the San Marcos sewage treatment plant. Error bars represent ± 95% confidence intervals.

tions (and resulting low pH) and depressed dissolved oxygen concentrations result, a common feature of groundwater ecosystems (Chapelle 1993). The low pH within the aquifer allows for more rapid chemical weathering and higher capacity for these ground waters to carry ions, particularly calcium and alkalinity. This accounts for the San Marcos River carrying higher ionic concentrations than the surface streams which feed it on the Edwards Plateau. The Blanco River (Table 1), which is one of the source rivers for the aquifer, is quite similar in its ionic chemistry to the other rivers that recharge the aquifer (Groeger & Gustafson 1994). Physical mixing processes allow the river waters to quickly reach atmospheric equilibrium with O_2 and CO_2, particularly as they leave Spring Lake. The damming of the river to form Spring Lake has created a very productive ecosystem, and metabolic processes of macrophyte communities within the lake and upper river have a great effect on certain parameters, such as the diel variation in O_2 and CO_2 and reduction of NO_3-N concentrations (Fig. 5).

At the confluence with the Blanco River, the variability of physical and chemical characteristics increased dramatically. This variability was most pronounced during storm events (22 July 1992 and 10 October 1994), with the highest turbidity and lowest specific conductance occurring shortly after large storms within the Blanco drainage basin. The Blanco River has a drainage basin of 1070 km^2 and therefore when these two rivers flow together, the terrestrial influence that is typical for rivers (e.g. diel light and temperature cycles, storm events, seasonality) begins to have a much larger effect on the spring-fed San Marcos River. Specific conductance downstream of the confluence reflected the lower concentration of ions in the Blanco River relative to the headwaters of the San Marcos River. The change in water chemistry in the San Marcos River downstream of this point can be partially attributed to the dilution effect of the Blanco River (Table 1). The long-term mean discharge from the San Marcos Springs (4.67 $m^3 s^{-1}$, 1957-91) and from the Blanco River at Kyle (4.19 $m^3 s^{-1}$, 1957-91) account for 42 and 38% of the mean discharge in the San Marcos River at Lulling (11.07 $m^3 s^{-1}$, 1940-92). Nutrients tended to be low in the Blanco River, and were generally diluted downstream of the confluence.

The SMSTP was a major point source of nutrients in the upper river. SRP, TP, NH_4, and NO_3 all increased at this point. Both nutrient data and bioassay results suggest the river upstream of the SMSTP was strongly phosphorus-limited. At site 3, nutrient ratios (atomic) of dissolved inorganic nitrogen (NO_3+NO_2-N + NH_4-N) to SRP were 411:1, and for dissolved inorganic nitrogen to TP was 60:1. Other data (USGS provisional data) suggests these ratios are a regular feature of this stretch of the river. Normally, ratios > 10:1 or 20:1 are thought to be the point at which phosphorus becomes limiting (Sakamoto 1966; Forsberg et al. 1978), and the ratios reported here are very high relative to other phosphorus-limited ecosystems (Grimm & Fisher 1986; Hecky

& Kilham 1988; Morris & Lewis 1988; Lohman et al. 1991). The addition of phosphorus to the upper river greatly increases the capacity for algal growth. The State Fish Hatchery increased NH_4^+ in the river, and at least occasionally released high quantities of algae (and therefore TP) downstream, as they empty their ponds (TPWD 1994a). The increase in specific conductance below the SMSTP was due mostly to elevated concentrations of sodium and chloride in the treated sewage (USGS provisional data), as has been commonly associated with increased loading of domestic sewage in other systems (Feth 1981; Smith et al. 1987).

Increase in turbidity over the length of the river is probably due to both natural causes, as the river flows through the Blackland Prairie and Post Oak Belt physiographic zones, and land use patterns. Land use along a 1 mile corridor on either side of the river consists of 44% pasture and 18% cropland (Pulich et al. 1994). These types of land uses are often responsible for increases in suspended sediments (Gregory & Walling 1973). One of the apparent consequences of increased turbidity was a shift away from a macrophyte-dominated community in the lower river, but the increased variability in flow and changing bottom substrates may also be very important in this change. Sodium and chloride concentrations, and to a lesser extent sulfate, were higher at the Luling site due to oil field activity in Caldwell and Guadalupe counties, though these concentrations have been decreasing since the late 1960's with deep-well injection of brine and decreased oil pumping (Rawson 1968).

The San Marcos River suffers the same fate that other rivers draining the southcentral Texas Cretaceous limestone. Nutrients in these rivers are greatly increased by sewage inputs from population centers along the eastern edge of Edwards Plateau region corresponding to the Interstate 35 corridor. These include the San Gabriel River and the city of Georgetown, the Colorado River and Austin, and the Guadalupe River and New Braunfels. The city of San Marcos has concluded, along with the Texas Natural Resources Conservation Commission, that the city will reduce phosphorus concentrations in sewage effluent from a proposed upgrade of their plant down to 1 mg TP L^{-1}. This should cause a significant increase in the water quality of the river.

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PERMUTATIONS AND CHANGE RINGING

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Abstract.—Computers have long used permutations in ordering/sorting routines. Now permutations are using computers. The connection is change ringing. The mark ordering algorithm techniques of the 1960s, used to generate permutations for computer usage, are similar to an early method of change ringing known as Plain Bob. Now computers are instrumental in solving a 350 year-old problem concerned with generating all possible permutations on a set of seven bells subject to certain restraints. This paper describes various methods of generating permutations in change ringing, gives algebraic formulations for some of them and ends with a discussion of the centuries old problem mentioned above.

ENGLISH CHANGE-RINGING

There are more than 5000 churches with belltowers in England today. Canada and the USA have a total of 35. The most famous one in the United States is Old North Church in Philadelphia (Paul Revere was a bell ringer there and thus had access to the tower). Texas has two working belltowers for English change ringing, one in Houston (St. Thomas Episcopal Church, eight bells, 7-0-7, 1971) and one in Abilene (Church of the Heavenly Rest, six bells, 6-1-5, 1982). Bell weights are expressed in hundred-weights (cwt), where 1cwt = 112 lbs., quarter hundred-weights (=28 lbs.) and pounds, with an expression such as "6-1-5" referring to the heaviest bell in a tower. In Abilene the heaviest weighs 705 lbs. ($6*112 + 1*28 + 5 = 705$).

English change ringing consists of ringing n tuned bells ($4 \le n \le 12$ with 8 quite common, in which case the bells are tuned to the notes of an octave such as C to the next lowest C) in a steady rhythm so that the bells ring some subset of the group of all possible permutations of n. There are n! possible changes or permutations on n bells. Each tone row is the result of applying a permutation and consists of ringing each of the n bells exactly once. There is usually a one-beat pause at the end of every second row. An extent on n bells consists of ringing $n! + 1$ changes beginning and ending with the bells in the row $123\cdots n$ and with no other change repeated. Bell 1 is called the Treble and is the lightest bell in a tower. The weights get progressively heavier as one goes from bell 1 to bell n with the heaviest bell called the Tenor.