3.0 SUMMARY OF THE SYNOPTIC SURVEY RESULTS – AN INITIAL STEP IN CONCEPTUAL MODEL DEVELOPMENT

A side-by-side comparison of Lexington, Almaden, Guadalupe, and Calero Reservoirs, and their downstream creeks, provides insight into the behavior of mercury in the Guadalupe River Watershed. The four systems are very similar in their non-mercury chemical characteristics. Synoptic Survey samples were taken on July 28-31, 2003, and key water chemistry measurements made during this period are presented in a series of figures at the end of this section (see Figure 3-2). Most of the discussion below refers to these figures. The entire set of Synoptic Survey results can be found in the *Synoptic Survey Report* (Tetra Tech, 2003d.)

3.1 BACKGROUND WATER CHEMISTRY

Reservoirs: All four reservoirs are quite similar in terms of the water quality parameters believed to influence mercury concentrations in the water (pH, DO, DOC, SO_4, chloride, productivity). At the time of the synoptic survey each reservoir exhibited moderate thermal stratification (see Figure 3-1), which limited the mixing of epilimnetic (upper) and hypolimnetic (lower) waters. Epilimnetic total phosphorus levels ranged from 60 to 130 ppb, sustaining enough phytoplankton production and detrital rain to cause oxygen depletion in the hypolimnion. The alkalinities in the reservoir waters were high (2.6 to 4.0 meq/l) as were pH values (7.3 to 8.8). The pH depression in the lower water (1 to 1.5 units) was consistent with the build up of carbon dioxide (CO_2). Calculated CO_2 supersaturation in the hypolimnetic waters ranged from 20 to 27 times atmospheric level; epilimnetic CO_2 values were within a factor of 3 of saturation.

Dissolved organic carbon (DOC) can form a complex with dissolved mercury and prevent its removal from the water column by absorption to settling particles. DOC

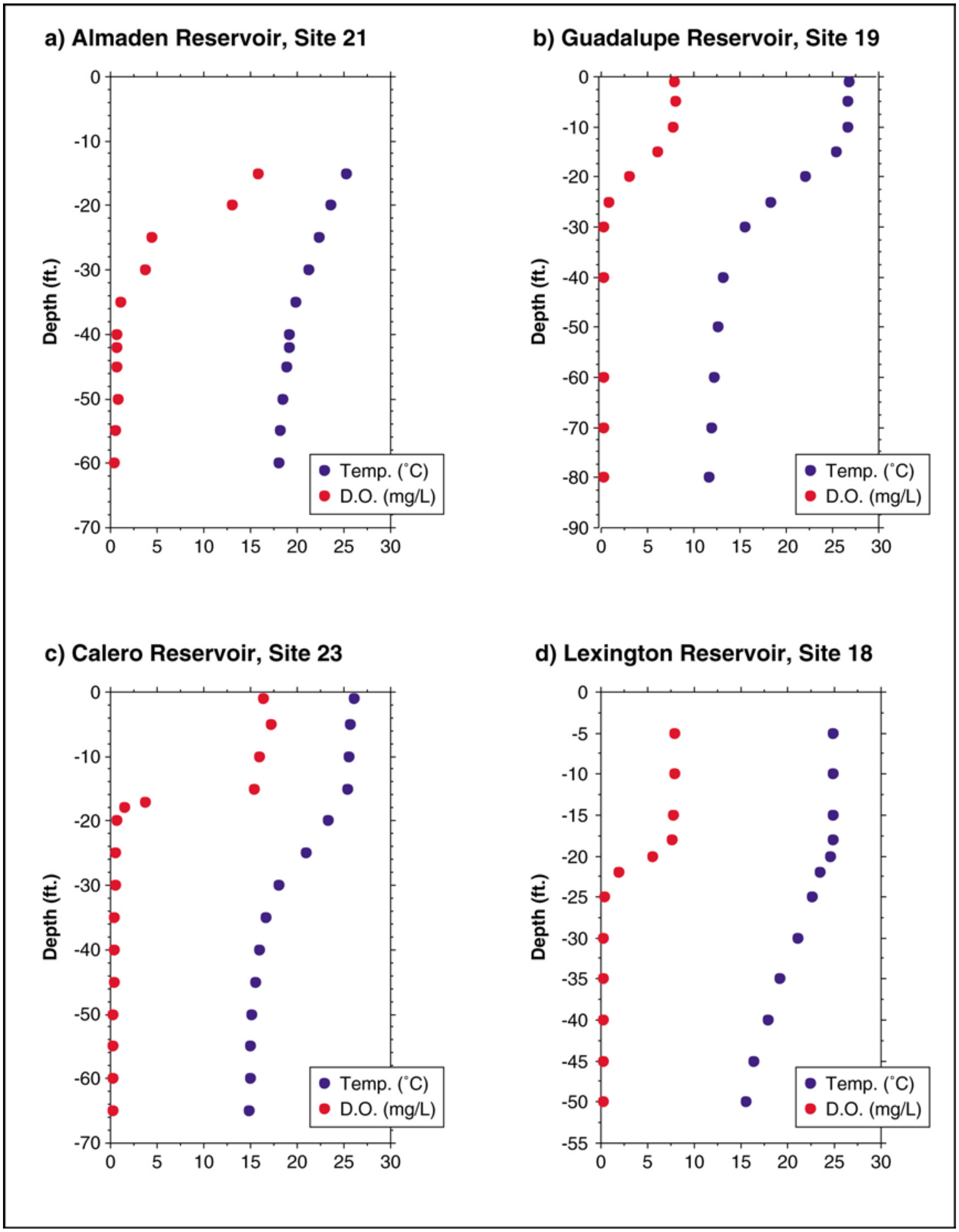

Figure 3-1. Dissolved oxygen profiles in a) Almaden, b) Guadalupe, c) Calero, and d) Lexington Reservoirs, (July 28-31, 2003).

occurred at relatively low levels (1.8 to 3.9 mg C/l). Sulfate concentrations were high enough (16 to 54 mg/l) to not limit the metabolism of the sulfate reducing bacteria. Hypolimnetic SO_4, concentrations were only 1-2 mg/l lower than epilimnetic levels. Total suspended solids were less than 4 mg/l; typical values ranged from 1 to 2 mg/l. The concentrations of total dissolved solids, as reflected by conductivity, were all within 15 percent of a mean value of about 290 mg/l.

Relatively low values of chlorophyll a were measured in most upper waters, (2 to 4 μg/l), in the presence of high total phosphorus (TP) concentrations (60 to 130 ppb). If phosphorus alone was limiting algal growth, expected values for chlorophyll a could be as high as 30 to 60 μg/l (Lorenzen, 1979, Porcella, et al. 1983). Perhaps algal growth was being limited by something other than phosphorus (e.g., inadequate inorganic nitrogen (levels were less than 0.3 mg N/l), low light levels, or toxicities to algae). Based upon the other chemical measurements, and adequate fisheries, the reservoirs appear to be productive.

Streams: Flows in the four streams during the sampling were characteristic of the dry season (4 to 23 cfs). Reservoir releases were made from the lowest waters, below the hypolimnetic sampling points. As with many stratified reservoirs, these waters had essentially no dissolved oxygen[1], were supersaturated with CO_2, and had hydrogen sulfide odors. Typically within less than three miles downstream, oxygen concentrations in the water were approaching saturation. Measured pH values were increasing, and carbon dioxide partial pressures, calculated from measured alkalinity, pH, DOC, and temperature, were approaching equilibrium with the atmosphere. Dissolved organic carbon concentrations were dropping (aerobic metabolism), and total dissolved solids concentrations were increasing, along with phosphorus and sulfate levels.

3.2 ELEVATED MERCURY LEVELS

These surface waters, located elsewhere, with just atmospheric mercury inputs, would not be expected to have elevated mercury levels in fish. The waters were all very similar; they were quite alkaline, pH was not low, DOC concentrations were not high, sulfate concentrations were not unusual, and the systems appeared to be productive. The mine waste sediments that have entered these water bodies appear to be the source of the elevated mercury levels.

The Lexington Reservoir - Los Gatos Creek system served as a control. Its watershed likely has limited mercury in its bedrock, i.e., lower concentrations than found in the watersheds of the Almaden Reservoir-Alamitos Creek system, or the Guadalupe Reservoir-Guadalupe Creek system. The Calero Reservoir-Creek system has some mercury-bearing formations in its watershed, and the reservoir receives inputs of water from the California Central Valley Water Project and Almaden Reservoir.

[1] The Lexington outlet sampling was conducted downstream of the concrete lined outlet channel, downstream of a very turbulent section. The field measured dissolved oxygen was near saturation, but the sulfide odors were still strong.

3.3 MERCURY WATER CHEMISTRY

Reservoirs: Aquatic mercury measurements included total mercury (unfiltered), total methylmercury (unfiltered), filtered total mercury and filtered methlymercury. Methylmercury is of major concern because of its ability to concentrate in food chains, producing levels in fish tissue several million times higher than that in the water. The measured methylmercury concentrations at the Guadalupe and Almaden reservoir outlets were high[2]. The concentration at Calero was also high. The level at the Lexington outlet was lower but still of concern. In the four reservoirs, the fraction of the total mercury that was methylmercury (40-60%), was considerably higher than observed elsewhere in the U.S. Typical fractions are about one to five percent. The high ratios observed in the reservoirs and their outlets indicates that sulfide may be weathering (dissolving) mercury solids (cinnabar, and adsorbed Hg) followed closely by methylation. That is, much of the mercury entering the water from sediment may enter as methylmercury. The sulfate reducing bacteria (SRB) produce metabolic waste product (H_2S, HS^-) that may accelerate dissolution of HgS solids by complexing the mercury to form the soluble complexes HgS^o and $Hg\ (HS)_2{}^o$. These small, neutrally charged species are thought to readily pass through the SRB cell membranes to sites of methylation. The methylmercury produced is likely complexed with sulfides and readily passes outward through the SRB membranes and subsequently enters algal cells, possibly similarly complexed. It is thus possible that much of the mercury that is mobilized in these reservoirs, in particular in Almaden and Guadalupe, may be initially mobilized as methylmercury. This is not the case in waters where atmospheric deposition of mercury is the major source, supplying much of the mercury to the water body in the Hg (II) form.

An alternative hypothesis is that mercury methylated in the reservoirs originally enters the reservoirs in a dissolved rather than particulate form. Some researchers believe that the residual mercury in the calcines exists as salts and sorbed phases (e.g. Rytuba, J.J., 2000). Whether the methylmercury production is associated with sulfide weathering of mercury solids in the reservoirs or from methylation of dissolved mercury inputs, remains to be resolved. It is also possible that both pathways are quantitatively significant. Resolution of this uncertainty has strong implications as to the efficacy of potential remedial measures. Resolution also creates sampling and analysis needs that will be addressed in the upcoming Task 5.

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[2] For the purpose of these discussions, the following criteria are used to define high and low concentrations. In water, high concentrations are those over 1 ng/l for methylmercury and over 10 ng/l for total mercury. Low concentrations are those below 0.2 ng/l for methylmercury and below 2 ng/l for total mercury. For sediment concentrations, high total mercury concentrates are those above 2 mg/kg and low concentrations are those below 0.5 mg/kg.

The results of the USGS National Pilot Study of Mercury Contamination of Aquatic Ecosystems along Multiple Gradients (Krabbenhoft et al, 1999) provide a basis of comparison for the mercury concentrations. The median concentration of methylmercury in 106 samples was 0.06 ng/l. The median total mercury concentration in water was 2.28 ng/l. The median sediment mercury concentrations in the USGS study were 0.046 mg/kg.

Streams: In all four cases the streams served as net demethylators, reducing the methylmercury concentration as water flowed downstream from the reservoirs. From the stream sediment methylmercury concentrations (Tetra Tech, 2003d) there is little doubt that methylation was occurring in the streams, but instream methylmercury production did not keep up with the methylmercury dissipative processes. Nonetheless, reduced instream methylation would allow the methylmercury concentrations to decrease more quickly and to lower levels.

Although the levels of methylmercury wane downstream, total mercury concentrations did not always follow. In Alamitos and Guadalupe Creeks, total mercury concentrations increased as the streams flowed through reaches with mine wastes. Unlike the reservoir waters, the fraction of the total mercury in the streams that was methylmercury rapidly decreased downstream, to values closer to those observed elsewhere in the U.S.

3.4 ALMADEN LAKE

Although Almaden Lake is not part of the four reservoir-creek system, its behavior provides insights on mercury behavior in the watershed. The lake is an impoundment on the Alamitos Creek just upstream of its confluence with Guadalupe Creek. Most of the lake is shallow with a deep portion formed by an old gravel quarry. During the Synoptic Survey, the volumetric inflow to the lake was estimated to be about 10 cfs.

Background Water Chemistry: The lake is highly productive, with abundant emergent macrophytes. During the synoptic survey, the total phosphorus concentration was the highest measured, 680 ppb. Water temperature at 1 p.m., at a depth of one foot was 27.7°C; ten feet down the temperature was 23.7°C . The lake was highly alkaline, 3.8 me /Lq. One foot depth and 10 foot pH values were 9.4 and 8.6 respectively. Corresponding dissolved oxygen concentration were >20 mg/l, and 1.7 mg/l. Dissolved organic carbon (DOC) concentration was 3 mg/l at the one foot depth; sulfate concentration was 48 mg/l. From the alkalinity, pH, DOC, and temperature values, a partial pressure of carbon dioxide was calculated to be 26 percent of the atmospheric level at the one foot depth and 125 percent at ten feet. The degree of undersaturation in CO_2 near the surface in the early afternoon, and the very high dissolved oxygen concentration reflect the high degree of productivity in this waterbody.

Mercury: Almaden Lake had the single highest total methylmercury measurement in the synoptic survey, 17.85 ng/l. The dissolved methylmercury concentration, 1.72 ng/l, was considerably lower, but still high. (See Table 3.1) The relatively small fraction dissolved most likely reflects the high concentration of total suspended solids 53.8 mg/l, the highest observed in the survey. Total and dissolved mercury concentrations were higher than the values in the reservoirs tributary to Alamitos Creek.

With an inlet total dissolved mercury concentration of 6.65 ng/l, and an in-lake total methylmercury concentration of 17.85 ng/l, it is possible that some of the inlet inorganic particulate mercury, calculated as 19.23 ng/l, or sediment mercury, 21.5 mg/kg (just above the lake) is being solubilized and methylated. Although the synoptic data are preliminary, and limited in temporal extent, there does not appear to be enough dissolved mercury to directly support the methylation occurring in the lake. Inlet methylmercury concentrations were 0.306 ng/l, total, and 0.181 ng/l, dissolved.

Table 3-1
ALMADEN LAKE
Mercury Species Concentrations (ng/l)
SYNOPTIC SURVEY JULY 28-31, 2003

	Total Mercury ng/l	Total Dissolved Mercury ng/l	Particulate Mercury ng/l	Total Methyl Mercury[1] ng/l	Dissolved Methyl Mercury ng/l
Upstream Station[2]	25.88	6.65	19.23	0.306	0.181
Lake (At 1 ft below surface)	25.36	4.40	20.96	17.85	1.72

[1]Calculated: Total mercury minus total dissolved mercury
[2]Upstream station on Alamitos Creek at Mazzone Drive approximately 170 meters upstream of the Lake

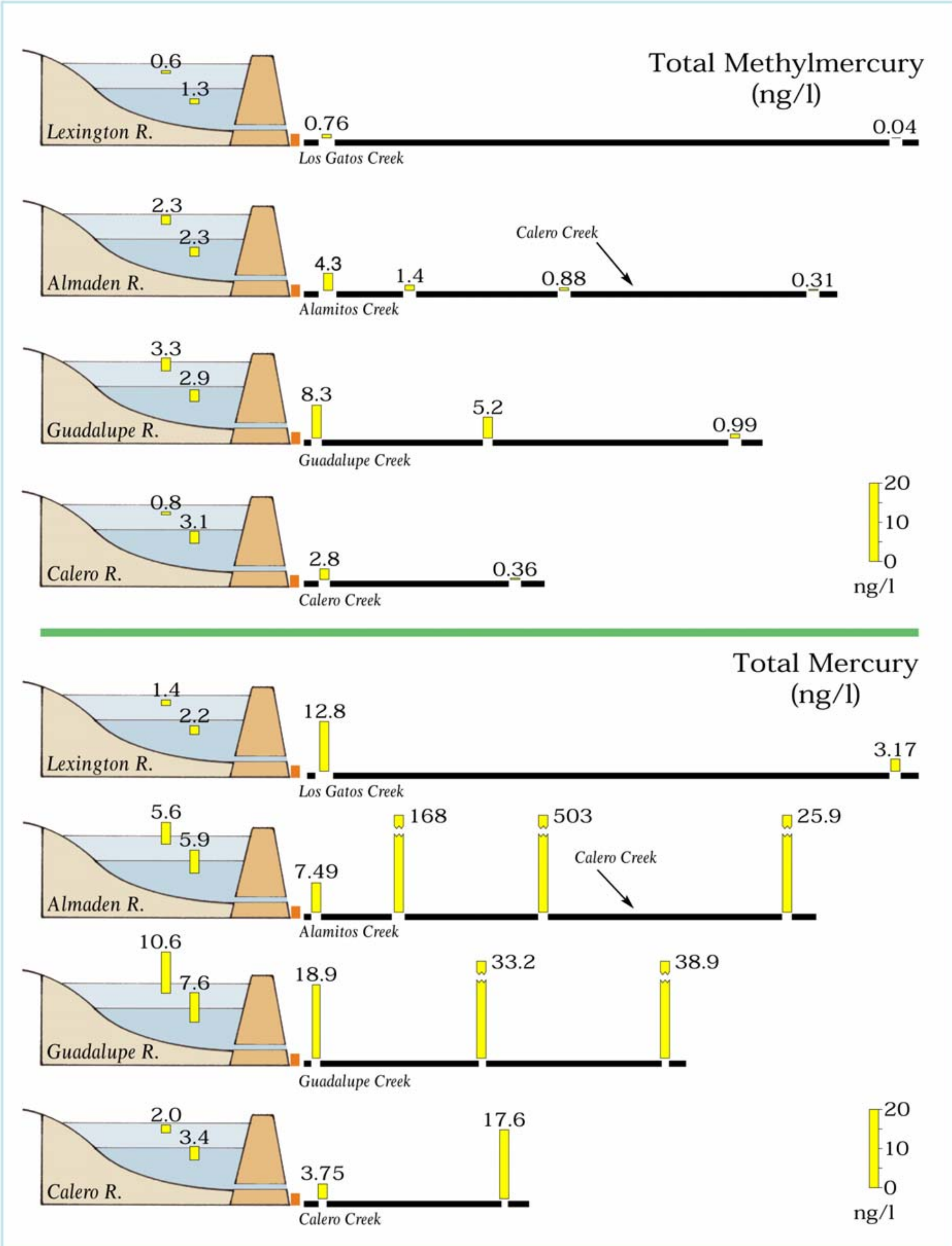

Figure 3-2a. Concentrations of total methylmercury and total mercury in the four reservoir-stream systems (July 28-31, 2003).

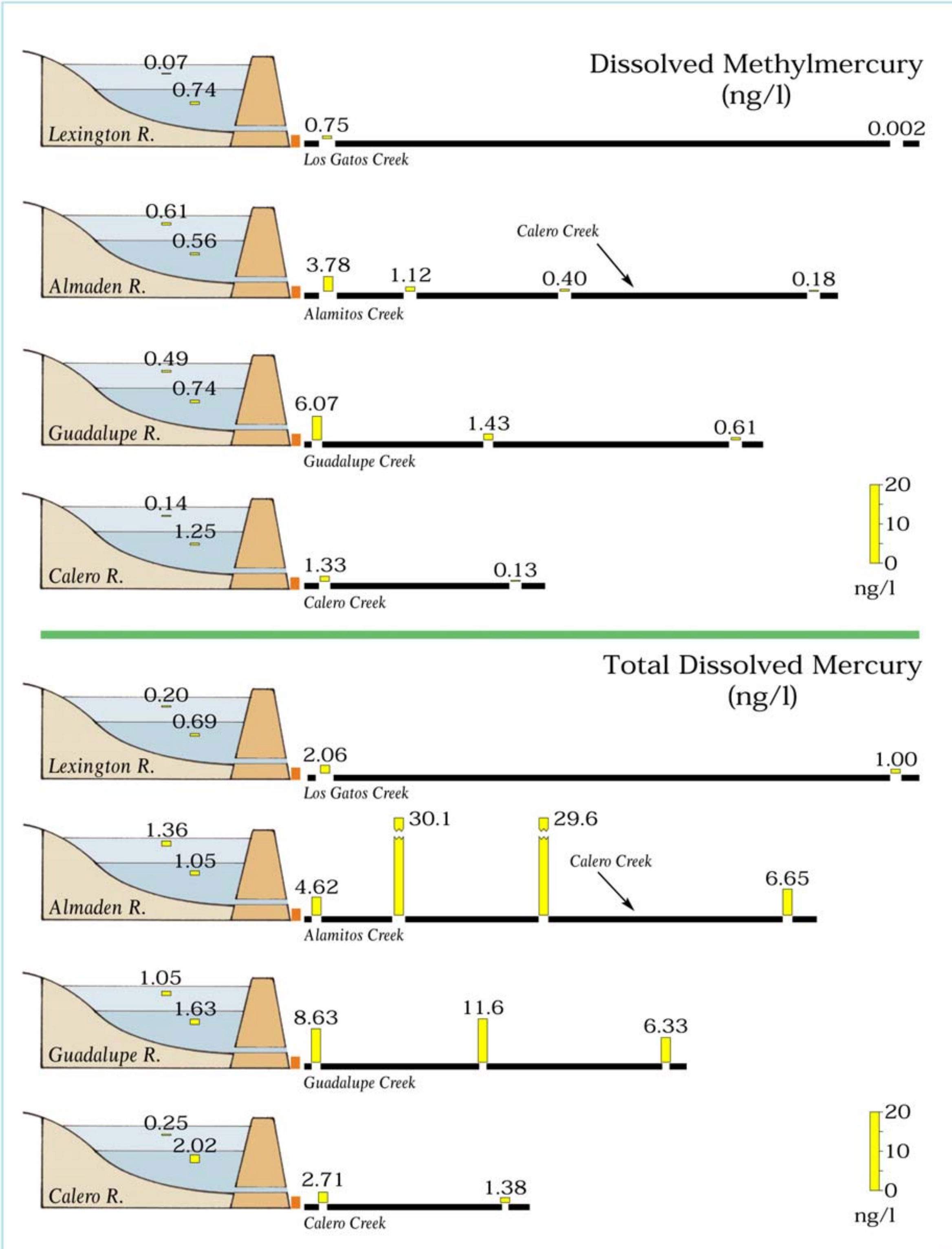

Figure 3-2b. Concentrations of dissolved methylmercury and total dissolved mercury in the four reservoir-stream systems (July 28-31, 2003).

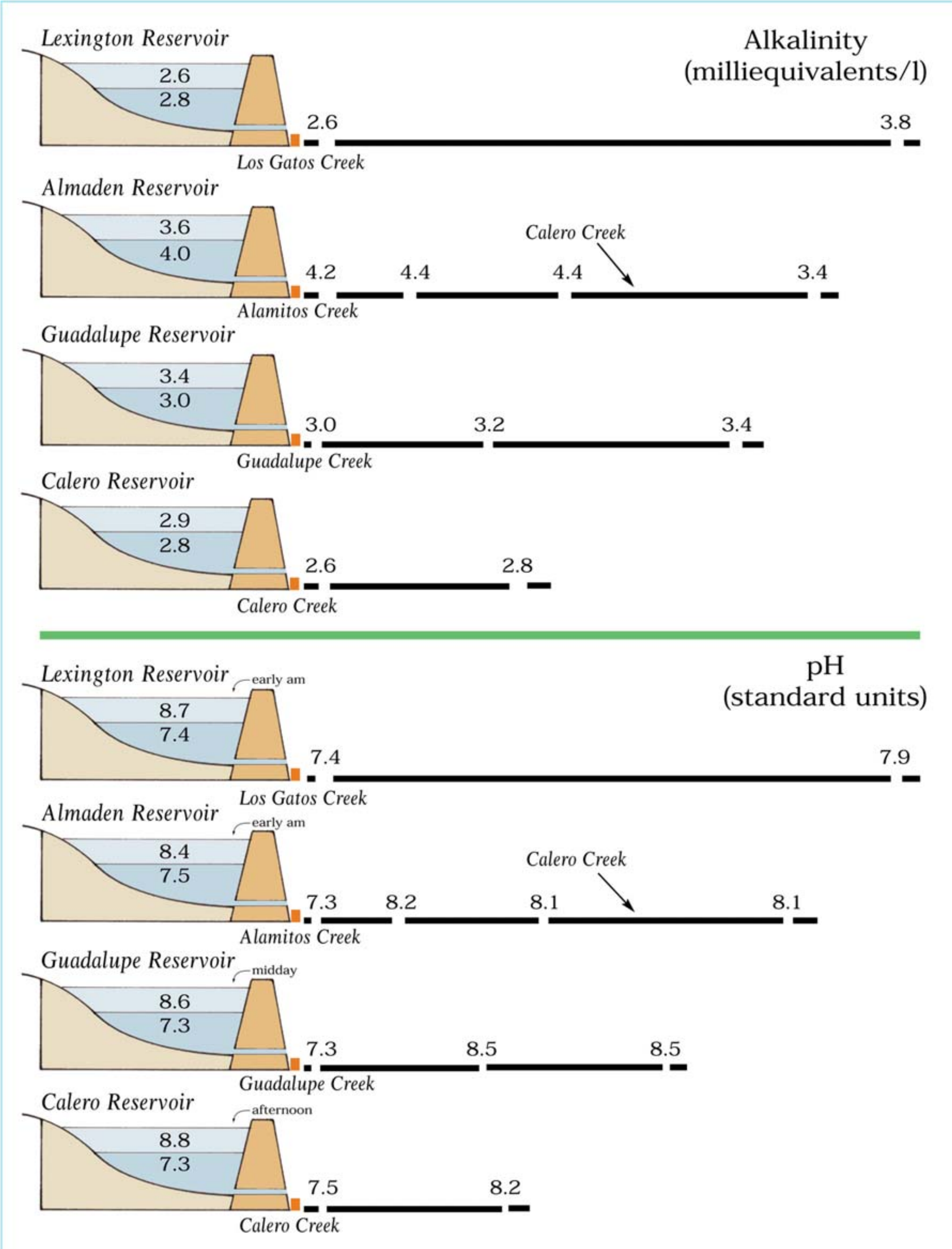

Figure 3-2c. Concentration of alkalinity and pH in the four reservoir-stream systems. (July 28-31, 2003)

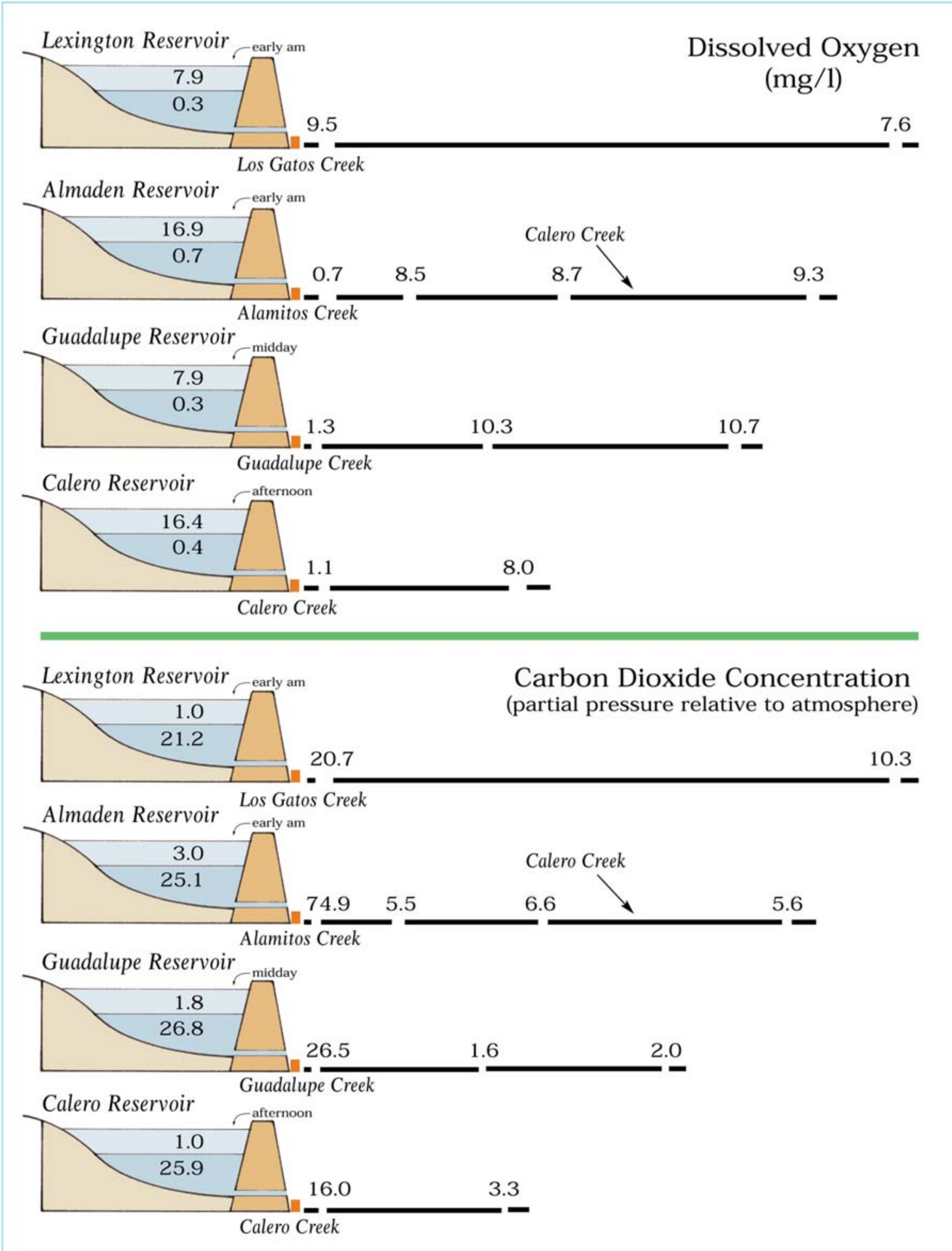

Figure 3-2d. Concentrations of dissolved oxygen and carbon dioxide in the four reservoir-stream systems (July 28-31, 2003). Carbon Dioxide concentrations are expressed as the ratio of the calculated partial pressure of CO_2 in the water to that of the atmosphere.

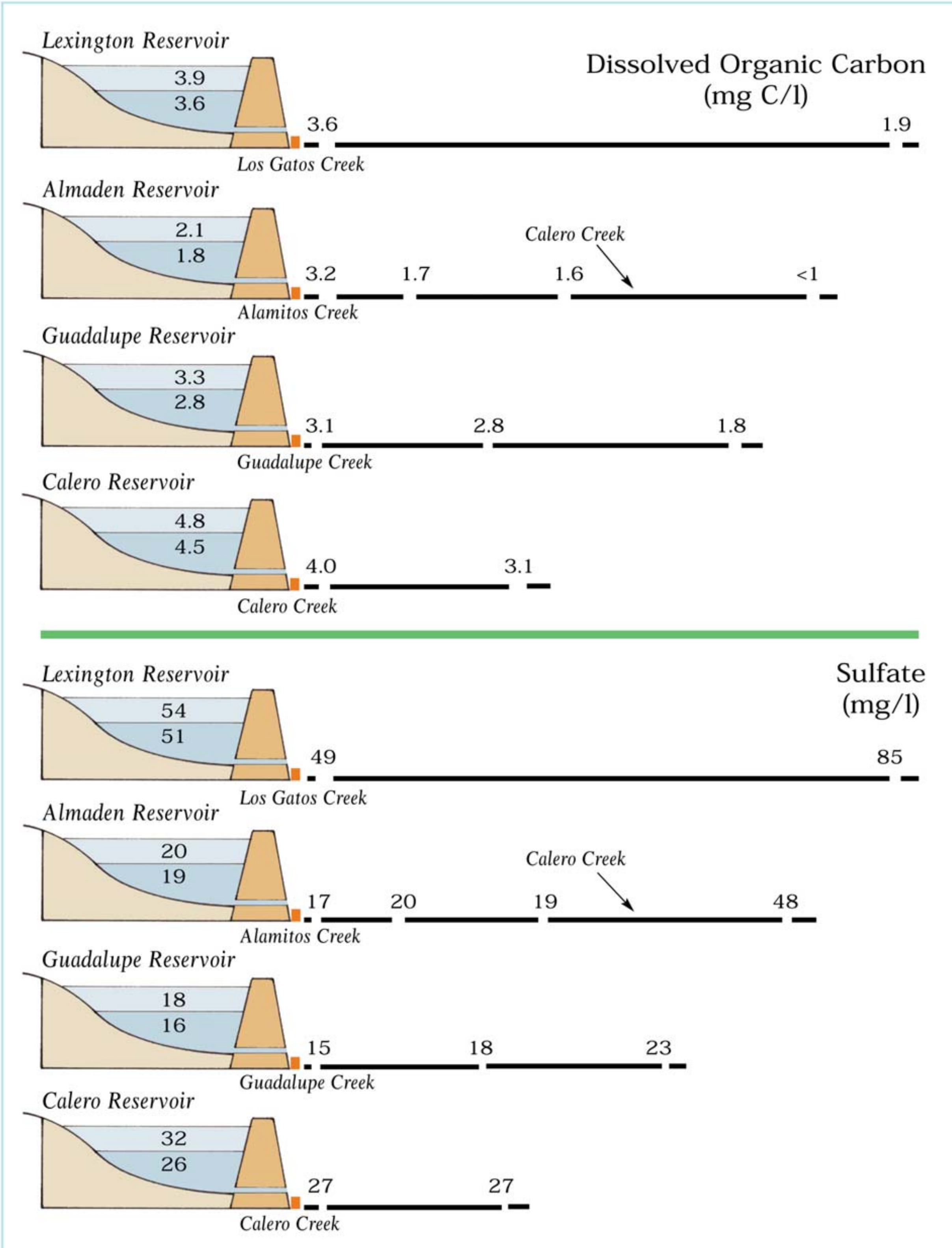

Figure 3-2e. Concentrations of dissolved organic carbon and sulfate in the four reservoir-stream systems (July 28-31, 2003).

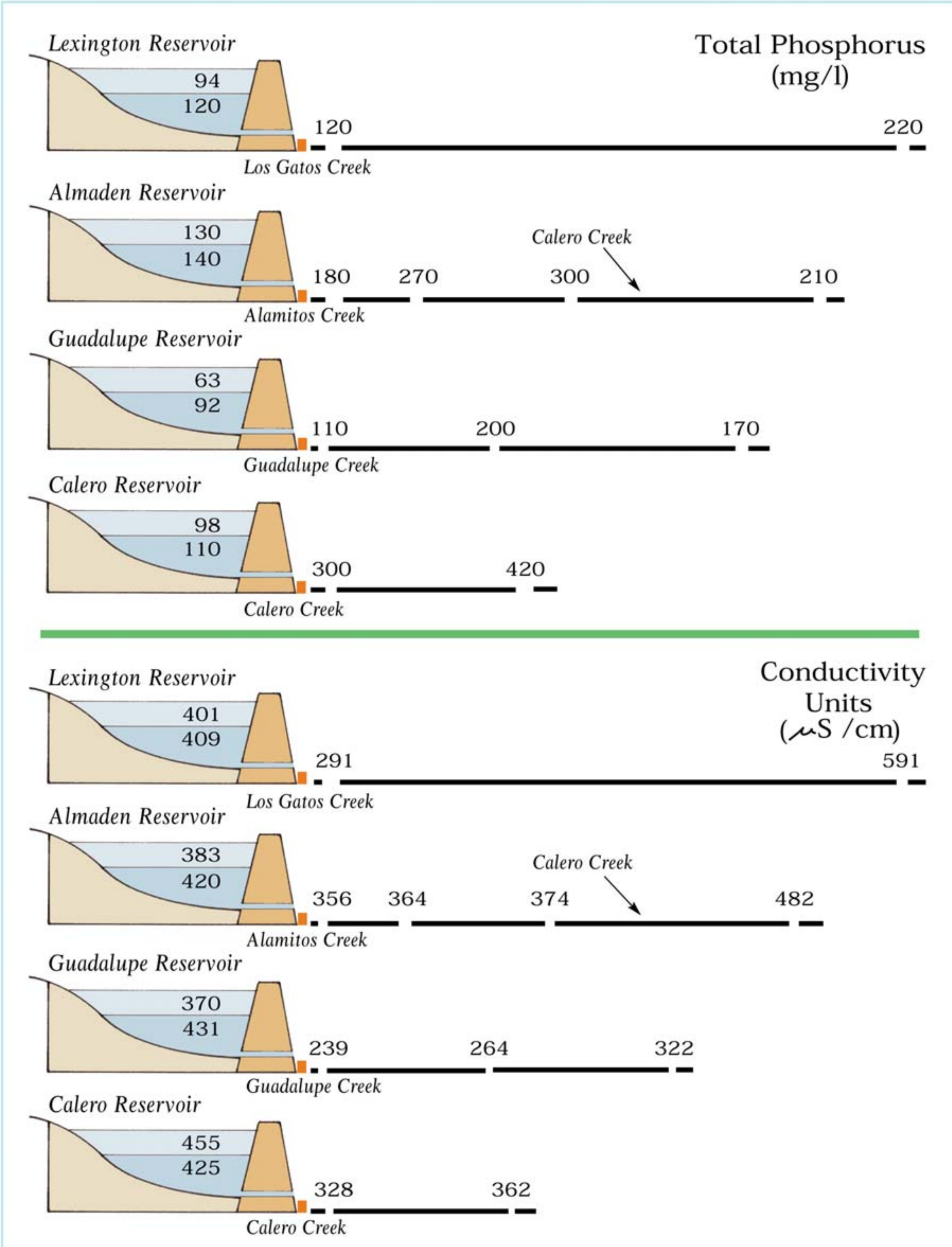

Figure 3-2f. Concentration of total phosphorous and conductivity in the four reservoir-stream systems (July 28-31, 2003).

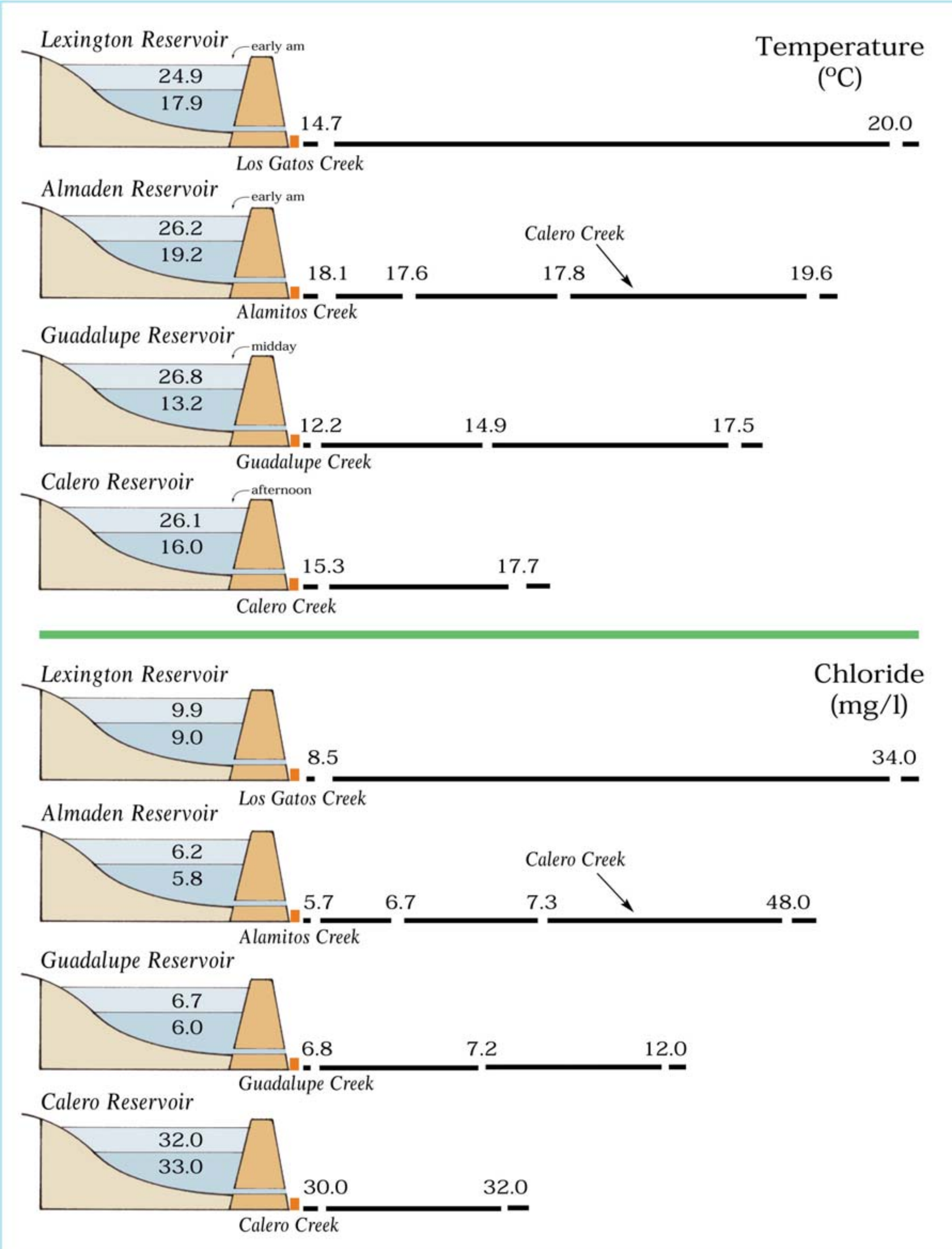

Figure 3-2g. Water temperature and chloride concentration in the four reservoir-stream systems (July 28-31, 2003).