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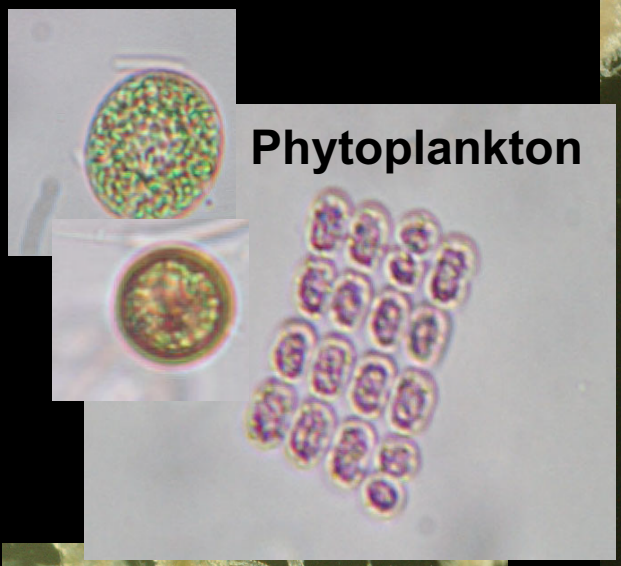

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By James S. Kuwabara[1], Brent R. Topping[2], Gerald E. Moon[3], Peter Husby[4], Andrew Lincoff[5], James L. Carter[6], and Marie-Noële Croteau[7]

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Executive Summary

The water columns of four reservoirs (Almaden, Calero, Guadalupe and Lexington Reservoirs) and an abandoned quarry pit filled by Alamitos Creek drainage for recreational purposes (Lake Almaden; Table 1) were sampled on September 14 and 15, 2004 to provide the first measurements of mercury accumulation by phytoplankton and zooplankton in lentic systems (bodies of standing water, as in lakes and reservoirs) within the Guadalupe River watershed, California. Because of widespread interest in ecosystem effects associated with historic mercury mining (Fig. 1) within and down gradient of the Guadalupe River watershed, transfer of mercury to lower trophic-level organisms was examined. The propensity of mercury to bioaccumulate, particularly in phytoplankton and zooplankton at the base of the food web, motivated this attempt to provide information in support of developing trophic-transfer and solute-transport models for the watershed, and hence in support of subsequent evaluation of load-allocation strategies. Both total mercury and methylmercury were examined in these organisms.

During a single sampling event, replicate samples from the reservoir water column were collected and processed for dissolved-total mercury, dissolved-methylmercury, phytoplankton mercury speciation, phytoplankton taxonomy and biomass, zooplankton mercury speciation, and zooplankton taxonomy and biomass. The timing of this sampling event was coordinated with sampling and analysis of fish from these five water bodies, during a period of the year when vertical stratification in the reservoirs generates a primary source of methylmercury to the watershed. Ancillary data, including dissolved organic carbon and trace-metal concentrations as well as vertical profiles of temperature, dissolved oxygen and pH, were gathered to provide a water-quality framework from which to compare the results for mercury. This work, in support of the Guadalupe River Mercury Total Maximum Daily Load (TMDL) Study, provides the first measurements of mercury trophic transfer through planktonic communities in this watershed. It is worth reemphasizing that this data set represents a single "snap shot" of conditions in water bodies within the Guadalupe River watershed to: (1) fill gaps in trophic transfer information, and (2) provide a scientific basis for future process-based studies with enhanced temporal and spatial coverage. This electronic document was unconventionally formatted to enhance the accessibility of information to a wide range of interest groups (Appendix 1). The following major observations from interdependent physical, biological, and chemical data were made:

Physical and Biological Characterizations

1. **Vertical gradients in the water column:** As a hydrologic context, the five water bodies were sampled within a period of vertical thermal stratification, approximately six months after peak storage (Fig. 2), but three months before minimal storage for calendar year 2004. The extent of thermal stratification varied with reservoir depth. Sub-oxic bottom-waters (that is, dissolved-oxygen concentrations less than or equal to 2 milligrams per liter) were observed in all reservoirs except Almaden (Fig. 3; Results and Discussion).

2. **Phytoplankton communities**: Wide variation between water bodies was observed in both phytoplankton density (8596± 1771 to 112,218 ± 27042 cells per milliliter at Guadalupe Reservoir

and Lake Almaden, respectively) and phytoplankton biovolume (430,534 ± 99,766 to 9,268,520 ± 1,420,683 cubic micrometers per milliliter at Guadalupe and Almaden Reservoirs, respectively; (Table 1; Results and Discussion). Elevated phytoplankton density at Lake Almaden was due to a sub-surface (6 to 7 meter) bloom of the cyanophyte, *Merismopedia glauca* (Fig. 4). Despite Almaden Reservoir's second lowest phytoplankton density relative to the other reservoirs, its highest phytoplankton biovolume demonstrates conditions that favor a less diverse community of larger sized species. In contrast, Lexington Reservoir outside the major drainage area of the New Almaden Mercury Mines exhibited a high cell density (only exceeded at Lake Almaden), but a low biovolume (second only to Guadalupe River), reflecting conditions that support smaller phytoplankton species with consequently higher surface to volume ratios. This cell-size effect at Lexington Reservoir relative to the other reservoirs may be due to low mercury-species (toxicant) concentrations or low macronutrient (oligotrophic) conditions. At least an order of magnitude lower analytical detection limits are needed relative to reported nutrient data for the reservoirs to permit a quantitative examination of interdependent constraints on primary productivity due to nutrient availability.

3. **Zooplankton communities**: As observed with the phytoplankton communities in these five water bodies, the zooplankton communities exhibited wide (that is orders of magnitude) ranges for both density (78 ± 75 to 141,047 ± 70,293 individuals per cubic meter at Lexington Reservoir and Lake Almaden, respectively) and biomass (67 ± 49 to 312,228 ± 160,225 micrograms per cubic meter again at Lexington Reservoir and Lake Almaden, respectively; Table 3; Results and Discussion). Neither zooplankton densities nor biomass were significantly correlated with phytoplankton densities or biovolumes (r^2 consistently less than 0.33, Tables 2 and 3). This suggests that the planktonic communities were at disequilibrium relative to energy transfer or grazing pressures, and hence measured bioaccumulation factors may be skewed relative to a more temporally and spatially intensive sampling design.

Results from this work are the first to report the presence of the invasive species *Daphnia lumholtzi* to the South San Francisco Bay region (Fig. 5).

Chemical Characterizations

Note: The dissolved-mercury concentrations discussed in this section refer to samples filtered with 0.7-micrometer quartz-fiber filters pre-combusted at 500 degrees Centigrade for 12 hours. In the absence of the modifier "dissolved", the modifier "total" (as in "total mercury" or "total methylmercury") refers to concentrations determined for unfiltered samples (that is, including both particulate and dissolved phases).

1. **Mercury in the water column**: Concentration trends between the five sampled water bodies were consistent for both total and methylmercury in the water column (Table 4; Results and Discussion). The lowest concentrations of mercury species were seen in Lexington and Calero Reservoirs, with Lexington typically having the lowest concentrations. Lake Almaden and Guadalupe Reservoirs displayed the highest total mercury concentrations in both the dissolved and particulate phases, but the highest methylmercury concentrations were associated with Lake Almaden and Almaden Reservoir.

Methylmercury in the dissolved and particulate phases was typically less than 10 percent of the total mercury (that is, inorganic and methylmercury). Conspicuous exceptions were noted from Lake Almaden and Almaden Reservoir, previously noted with the highest methylmercury concentrations, where up to 31 percent of the dissolved mercury was methylmercury.

2. **Total mercury and methylmercury in phytoplankton**: Concentrations of total mercury associated with phytoplankton ranged from 22.8 to 172 nanograms per gram dry weight from Lexington and Guadalupe Reservoirs, respectively (Table 4; Results and Discussion). An overview of regressions that model mercury transfer pathways is provided in figure 6. Bioaccumulation factors, representing diffusive or sorptive assimilation by phytoplankton cells, varied relative to dissolved and total mercury speciation in water, but were of the order of 10^4, approximately four orders of magnitude greater than biomagnification factors (that is, diet driven, trophic-transfer coefficients) between fish trophic levels in this watershed.

   Unlike total mercury concentrations, the highest methylmercury concentrations were from Lake Almaden (8.2 nanograms per gram dry weight). Methylmercury consistently represented a small fraction (less than 1 to 11 percent) of total mercury in phytoplankton. This is in stark contrast to methylmercury in fish, which typically represent greater than 90 percent of the total mercury in fish tissue.

3. **Total mercury and methylmercury in zooplankton:** Similar to trends in mercury concentrations measured in phytoplankton, total mercury associated with zooplankton ranged from 102 $\pm$ 2 to 764 $\pm$ 14 nanograms per gram dry weight from Lexington and Guadalupe Reservoirs, respectively. Methylmercury associated with zooplankton ranged from 84 to 780 nanograms per gram dry weight, as with total mercury, at Lexington and Almaden Reservoirs, respectively. In contrast to trends seen for methylmercury in phytoplankton, and total mercury in zooplankton, Almaden Reservoir and Guadalupe Reservoir (notably, not Lake Almaden) showed the highest methylmercury in zooplankton. Although this shift in uptake pattern cannot be explained with the existing data set, it is important to note that this shift is consistent with the next trophic level (small fish; see section below). That is, the methylmercury assimilated by zooplankton is highly correlated with the mercury (presumably methylmercury) in small fish ($r^2 = 0.90$; Fig. 6A). In both Almaden and Guadalupe reservoirs, methylmercury in zooplankton already exceeded the U.S. Environmental Protection Agency Water Quality Criteria of 300 nanograms per gram for human consumption of fish, one to three trophic transfers above zooplankton.

   Biomagnification factors for zooplankton relative to phytoplankton were inconsistent for total mercury (a range of 2 to 11; Table 4; Results and Discussion), and even more so for methylmercury (a range of 20 to greater than 1000). These factors, for both mercury species, are one to four orders of magnitude less than those describing the initial accumulation of mercury by phytoplankton from the water column. Only the biomagnification factors for zooplankton relative to total mercury in phytoplankton were similar in magnitude to those reported between fish trophic levels in this watershed.

4. **Associations with mercury in small (prey) fish:** Biomagnification factors for age-1 largemouth bass (prey fish) relative to mercury in zooplankton were consistent within the five lentic systems for methylmercury (5.5 $\pm$ 1.0, $r^2 = 0.90$) (Table 4; Fig. 6A; Results and Discussion) and for total mercury (4.8 $\pm$ 0.7, $r^2 = 0.94$; Fig. 6B). These values were also consistent with those describing mercury transfer between prey and piscivorous fish in this watershed (3.8 to 7.1) and others (estimated at about 0.5 log units), but approximately four orders of magnitude smaller than bioaccumulation factors describing initial accumulation of mercury by phytoplankton from the water column (approximately 26,000 and 19,000 for total and methylmercury, respectively).

Potential Management Implications

Remediation efforts and Total Maximum Daily Load (TMDL) allocations along the Guadalupe River have linked objectives of decreasing concentrations, loads to down-gradient systems and reducing the bioaccumulation of mercury in biological resources (for example, fish consumed by humans and wildlife). The bioaccumulation factors determined in these studies, consistent with previous mercury trophic-transfer studies in other lakes, indicate that accumulation of mercury is heavily weighted at the base of the food web. This data set provides initial measurements of the phytoplankton and zooplankton bioaccumulation factors for mercury at one time only, during a period of the year marked by dissolved-oxygen stratification, when the reservoirs serve as a significant source of dissolved methylmercury to receiving lotic systems. Therefore, this data may begin to fill an information void in our understanding of mercury trophic transfer, particularly by base trophic levels within the watershed that regulate subsequent mercury accumulation by predatory fish. However, in the absence of any quantification of temporal variability, this limited set of bioaccumulation factors requires prudent interpretation and application (Fig. 7). Relationships between prey and predator can change over space and time (that is, distributions of prey and predator species vary in quality and quantity). This complexity seriously challenges our ability to accurately model the accumulation of a solute like mercury from one trophic level to the next.

Background

The Guadalupe River watershed represents a significant spatial component of a Comprehensive Environmental Response Compensation and Liability Act (CERCLA) site affected by drainage from the New Almaden Quicksilver Mines. The economic, historic and geochemical significance of these mines have been thoroughly discussed (Goss, 1958; Johnson, 1963; Lanyon and Bulmore, 1967; Schneider, 1992; Rytuba and Enderlin, 1999; Alpers and Hunerlach, 2000; Topping and others, 2004). Positive regional, national and international contributions of this historic mining operation are adversely offset by the legacy of mercury accumulation in sediment, water and biota. The bioaccumulation of mercury within this watershed has been heretofore poorly quantified.

Many fundamental processes affect the transport, partitioning, speciation and fate of toxic metals like mercury within aquatic systems. These processes, which have been recently examined as part of the Guadalupe River Watershed Mercury TMDL Project (Tetra Tech, 2005), ultimately have a cascading effect on the trophic transfer of mercury (Fig. 7). Biomagnification and subsequent toxicity of methylmercury through the food web is of particular concern (Wren and others, 1995). Typically, trophic transfer of mercury is dominated by the initial accumulation of mercury at the base of the food web (Mason and others, 1995; Mason and others, 1996). Unfortunately, no direct measurements for the bioaccumulation of mercury by phytoplankton or zooplankton have heretofore been available for this study area, or for adjacent, down-gradient ecosystems currently beginning extensive wetland-restoration (California Department of Fish and Game, 2005). This work begins to fill that information gap.

As a result of physical, chemical, and biological processes operating through the water column of lakes and reservoirs, geochemical gradients take on a variety of forms that have been previously reported (Kuwabara and others, 2003a; Fig. 8). Associated gradients in solute concentrations can thereby result in conditions conducive to a net increase in methylmercury concentrations, particularly in hypolimnetic waters of reservoirs within the Guadalupe River watershed (Tetra Tech, 2003). Scientists have recently determined that mercury bioaccumulation predominantly occurs within lower trophic levels (Watras and others, 1998). To complement ongoing geochemical and fish studies, this work provides initial, reservoir-specific bioaccumulation factors for those lower trophic levels.

Water-quality managers are often compelled or required to assess and prioritize remediation strategies for aquatic systems that have been adversely affected by anthropogenic activities. In the case of the Guadalupe River watershed, mercury associated with decades of productive mining at the historic New Almaden Quicksilver Mines has been fluvially transported and deposited in sediment. Frequent demands have been made by regional managers and the public to quantify the connections between fluxes of contaminants and the health, abundance, and distribution of biological resources (Kuwabara and others, 1999). As part of ongoing efforts by the USGS Toxic Substances Hydrology Program to examine processes affecting trace-contaminant transport in San Francisco Bay, this study focuses on a poorly understood, yet potentially important, step in the bioaccumulation of mercury upgradient of the estuary: lower-trophic level mercury uptake by phytoplankton and zooplankton in major reservoirs within the watershed. We hypothesized that the observed exceedances in the mercury concentration of piscivorous fish are driven by the same fundamental processes observed in watersheds unaffected by a legacy of mercury mining, that is, water-column availability of dissolved-mercury species to phytoplankton followed by enhanced methylmercury assimilation by zooplankton.

The results described here followed from the integration of current project studies with information needs identified by the Guadalupe River Watershed Mercury TMDL Working Group, a stakeholder group including environmental-interest, water-quality management, water-supply, and water-treatment organizations. Elevated mercury concentrations in fish, and consequent human-health consumption advisories (California Office of Environmental Health Hazard Assessment, 2005), reflect on the ecological status of aquatic systems within and downstream of the watershed. Quantifying and understanding the magnitude and variability of mercury sources to these fish represent a critical building block to the development of appropriate trophic transfer models and remedial programs for this mining-affected system, and potentially others as well.

To help enable science-based programmatic decisions related to water and ecosystem quality in the Guadalupe River watershed and downstream aquatic systems, the purpose of this study is to provide initial measurements of mercury bioaccumulation by phytoplankton and zooplankton (at the base of the mercury-cycling

food web) and to examine associations betwen this bioaccumulation to water-quality and mercury concentrations in fish (that is, existing end-member information). In so doing, the intent is to clarify and refine conceptual and numerical models describing mercury dynamics within the watershed.

Results and Discussion

Physical Data

The five water bodies within the Guadalupe River watershed were sampled in September 2004, months after peak storage (Fig. 2), and during a period of vertical stratification. Maximum depths at the time of sampling ranged from approximately 12 meters (Lake Almaden) to 23 meters (Lexington Reservoir). In terms of thermal stratification, the deepest two reservoirs (Lexington and Guadalupe) exhibited thermoclines at a depth of approximately 10 meters, consistent with observed dissolved oxygen stratification (Fig. 3). Calero Reservoir (16-meter depth) showed depth-uniform temperatures until within a meter of the bottom, well below the oxycline described above. Thermal stratification was minimal (less than 2 degrees Centigrade gradient) at Almaden Reservoir and occurred primarily at a depth of approximately 3 meters, the position of the first dissolved-oxygen-profile step. Lake Almaden was the last water body sampled on September 15, 2004, at dusk. The thermocline at Lake Almaden occurred at approximately 1-meter depth, slightly shallower than the oxycline (Fig. 3B) and at least 5 meters shallower than the subsurface chlorophyll-*a* maximum depth generated by a bloom of the cyanophyte *Merismopedia glauca* (Fig. 4A) At a depth of 2 meters in Lake Almaden, nearer to the observed oxycline and thermocline, the phytoplankton community was dominated by bacillariophytes (diatoms) at cell densities at least an order of magnitude lower than the subsurface *Merismopedia* layer (Fig. 4B). Under approaching darkness, perhaps the cyanophytes, distinctly layered between 6 to 7 meters, were shifting from photosynthetic oxygen production to respiration.

Biological Data

1. **Phytoplankton Community**: The depth and vertical extent of the chlorophyll-a maximum was highly variable between reservoirs. For example, at Calero and Lexington Reservoirs, a chlorophyll-a maximum was not discernable in the water column so sampling was taken at approximately 2 meters (m). In contrast, the chlorophyll-a maximum was well defined between depths of 6 to 7 m in Lake Almaden, so water-quality and phytoplankton samples were taken at 6.5 m.

   Variability between reservoirs is exhibited by both phytoplankton densities and biovolumes (Fig. 9). Cell densities (that is, abundances) and biovolumes did not correspond between sites (r^2 =0.18). Calero Reservoir, upstream of the mercury-mining area, consistently had cell densities (54,000 $\pm$ 15,352 cells per milliliter) and biovolumes (1,887,836 $\pm$ 380,416 cubic micrometers per milliliter) in the mid-range among reservoirs with significant representation by cyanophytes (blue-green algae), bacillariophytes (diatoms), cryptophytes (for example, *Cryptomonas*), dinophytes (dinoflagellates), and chlorophytes (green algae) (Table 2). Two taxa, *Nannochloris* sp. (Chlorophyta) and *Aphanothece smithii* (Cyanophyta) made up an average of 55.9 percent and 23.6 percent (approximately 80 percent) respectively, of the phytoplankton in Calero Reservoir. A total of 11 different taxa represent at least 1 percent of the total individuals. Although *Nannochloris sp.* and *A. smithii* were numerically dominant, because of their extremely small size they represented just over 2 percent of the algal biovolume in Calero Reservoir. A number of taxa contributed to the total biovolume, including the extremely large dinoflagellate, *Peridiniopsis polonicum* (Dinophyta) and very large centric diatom, *Stephanodiscus tenuis* (Bacillariophyta).

   In contrast, Almaden Reservoir had lower cell densities (16,552 $\pm$ 3,438 cells per milliliter) but higher biovolumes (9,268,520 $\pm$ 1,420,683 cubic micrometers per milliliter) due to the dominance of large dinoflagellates and diatoms. *Aphanothece minutissima* (Cyanophyta) made up over 55 percent of the total individuals identified. *Chlorella minutissima* (Chlorophyta) and *Fragilaria crotonensis* (Bacillariophyta), 17.8 percent and 14 percent respectively, made up most of the remaining individuals. Although *A. minutissima* dominated numerically, it is extremely small and therefore made up little of the biovolume. Two taxa, the large dinoflagellate *Ceratium*

hirundinella f. *hirundinella* (Dinophyta) and moderate size *Fragilaria crotonensis* (Bacillariophyta), constituted 64.2 and 31.4 percent, respectively, making up approximately 96 percent of the phytoplankton biovolume in Almaden Reservoir. The addition of *Lyngbya birgei,* a cyanophyte, *Komma caudate*, a cryptophyte, and *Closterium aciculare,* a chlorophyte made up over 99 percent of the biovolume.

Guadalupe Reservoir, closest to the mercury-mining operation, had both the lowest cell densities (8,596 $\pm$ 1,771 cells per milliliter) and the lowest biovolumes (430,534 $\pm$ 99,766 cubic micrometers per milliliter), and were dominated by chlorophytes. Two taxa, a blue-green alga, *Aphanothece smithii* (41 percent) and a green algal, *Nannochloris* sp. (41 percent) were numerically dominant. However, a diatom, *Fragilaria crotonensis* (Bacillariophyta, 34.4 percent) and golden alga, *Dinobyron divergens* (Chrysophyta, 29.6 percent) made up over 64 percent of the biovolume.

Lexington Reservoir, which is outside the major drainage area of the New Almaden Mercury Mines, had the second highest cell densities among the reservoirs (87,028 $\pm$ 19606 cells per milliliter), but the second lowest biovolumes (487,471 $\pm$ 167,137 cubic micrometers per milliliter) due to the dominance of small-sized cyanophytes, dinophytes and chlorophytes. The cyanophyte *Aphanothece smithii* (75 percent) dominated numerically with a second cyanophyte, *Dactylococcopsis irregularis* (12 percent), and the chlorophyte, *Nannochloris* sp. (7 percent) making up almost 95 percent of the individuals. Just as in Almaden Reservoir, a large dinoflagellate, *Ceratium hirundinella* f *carinthiacum* represented 27 percent of the biovolume. Also contributing to the total biovolume were *D. irregularis*, *Peridiniopsis polonicum*, and *Aphanothece smithii*. The total biovolume in Lexington Reservoir was distributed over numerous species.

Lake Almaden had both the highest cell densities (16,552 $\pm$ 3,438 cells per milliliter) and the highest biovolumes (9,268,520 $\pm$ 1,420,683 cubic micrometers per milliliter) due to a visible bloom of the cyanophyte *Merismopedia glauca* and elevated densities of *Cryptomonas erosa*, a genus common to the region (Tetra Tech, 1980). *Merismopedia glauca* dominated both numerically (84 percent) and in biovolume (40 percent). *Aphanothece smithii* (8 percent) was the second most abundant taxon; however, *Cryptomonas erosa* was the next most dominant in biovolume and represented approximate 27 percent of the total algal biovolume of the lake.

Ordination is a mathematical method often used in ecological studies to aid visualizing the similarities and differences among samples that contain too many species to visually compare. Detrended Correspondence Analysis (DCA) was used to ordinate the log-base10 transformed phytoplankton density data. DCA is constrained to represent the greatest amount of variation in the species by site data along the first derived axis, and decreasing amounts of variation on subsequent axes. The axes are highly derived and have the units of mean standard deviations, such that a distance between plotted sites of 4.0 axis units represents almost a complete change in the species present in the compared samples.

Three relationships were clearly identified in the ordination (Fig. 10). First, most of the individual replicates were far more similar within, compared to between reservoirs. This indicated that the replicate samples contained extremely similar algal assemblages compared to the differences in algal assemblages among reservoirs. Second, Calero and Lexington Reservoirs differ greatly from the other three reservoirs. Both of these two reservoirs are dominated numerically by the chlorophyte, *Nannochloris* sp. and the cyanophyte *Aphanothece smithii*. Last, Lake Almaden, dominated by the cyanophyte *Merisomopedia glauca*, differs from both Guadalupe and Almaden reservoirs.

In summary, taxonomic analyses of the five water bodies reflect wide variability in phytoplankton community indices (biomass, density, structure and diversity). This work was scheduled to coincide with other bioaccumulation studies during the low-flow period when methylmercury production and transport is of seasonal importance in the watershed (Tetra Tech, 2005). This data set therefore represents the first, but only a single look, at lower trophic-level mercury transfer in these reservoirs. One might therefore expect considerable (that is, order of magnitude) temporal variability in phytoplankton community biomass, composition, spatial distribution and diversity (Tetra Tech, 1980; Kuwabara and others, 2003b).

2. Zooplankton Community: The zooplankton community represents the heterotrophic base to food web or trophic-transfer models. Unlike higher-order organisms like fish that predominantly bioaccumulate methylmercury, zooplankton can contain significant concentrations of inorganic mercury forms (Weiner and others, 2005). The zooplankton can therefore represent a significant trophic level of metabolic transitions.

The contrasts between reservoirs is exhibited by both zooplankton abundance and biomass varying over four orders of magnitude (Fig. 11). In contrast to phytoplankton, trends between reservoirs were consistent for zooplankton abundance and biomass ($r^2 = 0.99$) with Lexington Reservoir having the most sparse community, followed by Calero and Guadalupe Reservoirs, and with Almaden Reservoir and Lake Almaden having the highest densities but statistically similar averages (Table 3). Note that the ratio of biomass to abundance (both determined with respect to water-column volume) provides a coarse average of the relative mass (size) per individual in the water body. So in figure 11, zooplankton biomass in excess of the abundance for only Almaden Reservoir, Guadalupe Reservoir and Lake Almaden, in contrast to the other lentic systems, is consistent with observed sparse zooplankton populations in Calero and Lexington reservoirs. The relative differences in the average mass of individuals may also reflect grazing preferences for certain size classes of zooplankton. Within each water body, the importance of at least triplicate sampling is demonstrated here by the fact that even with triplicate sampling the standard deviation for the site was on average between 40 and 50 percent of the site mean (Table 3).

Calero Reservoir was dominated numerically by rotifers (82 percent) that could not be identified to species and the carnivorous rotifer *Asplanchna* (6 percent). Two copedods, *Cyclops* sp. (4.5 percent) and *Acanthodiaptomus siciloides* (3.7 percent) were the next most abundant taxa. Because of the dramatic difference in size between the Rotifera and Copepoda, *Cyclops* sp. and *A. siciloides* represented 32 percent and 31 percent, respectively, of the biomass even though most of the individual copepods were immature. *Asplanchna* and the other rotifers represented a total biovolume of about 13 percent each.

Almaden Reservoir was dominated numerically by *A. siciloides* (43 percent), of which most were mature. Two cladocerans, *Daphnia ambigua* (17 percent) and *Diaphanosoma* sp. (13 percent) were also very abundant. *A. siciloides* also dominated the biomass in Almaden Reservoir and represented almost 71 percent of the biomass. The two most abundant cladocerans (*D. ambigua* and *Diaphanosoma* sp.) contributed 13 percent and 6 percent of the zooplankton biomass.

Three taxa were about equally abundant in Guadalupe Reservoir. Two cladocerans *Simocephalus* (33 percent) and *Bosmina* (26 percent) and the copepod *A. siciloides*. *Cyclops* spp. represented about 7 percent of the individuals. *Simocephalus* sp. represented about 41 percent of the biomass. As in Almaden Reservoir, *A. siciloides* were generally mature and in so represented about 38 percent of the biomass.

Lexington Reservoir was numerically dominated by the rotifer *Asplanchna* (44 percent) and copepod *Cyclops* spp. (23 percent). They both also represented almost half of the biomass (*Cyclops* spp., 27 percent; *Asplanchna*, 22 percent). Most of the remainder of the biomass was represented by the three cladocerns *Simocephalus* (19 percent) and *Bosmina* (10 percent) , the non-native cladoceran *Daphnia lumholzii* (6 percent) and the copepod *A. siciloides* (10 percent).

Almaden Lake was dominated numerically and in biomass by the same 4 taxa. *Bosmina* was by far numerically dominant, representing 57 percent of the individuals but only 20 percent of the biomass. *A. siciloides* represented about 15 percent of the individuals but over 41 percent of the biomass. *Simocephalus* and *Cyclops* spp. represented 15 percent and 7 percent of the individuals and 18 percent and 17 percent of the biomass, respectively.

DCA ordination of zooplankton density data was somewhat less clear than the ordination of the phytoplankton data. Within reservoir replicates at Calero and Lexington grouped independently (Fig. 12), indicating that zooplankton assemblages were somewhat unique to each reservoir. However, differences between Lake Almaden and Almaden and Guadalupe reseroirs were less distinct. These waterbodies had high abundances of the copepod *Acanthodiaptomus siciloides* and also were dominated by the cladocerans *Bosmina* and *Simocephalus*.

As a lead into trophic-transfer discussions in later sections, it is important to note that neither zooplankton densities or biomass were significantly correlated with phytoplankton densities or biovolumes. That is, for this single sampling, the transferable energy from the existing standing stock of phytoplankton was at disequilibrium with the zooplankton standing stock. The periodicity of zooplankton biomass is typically out of phase (lags) phytoplankton biomass. How this temporal disequilibrium in energy transfer affects temporal variability in mercury transfer between these trophic levels (that is, biomagnification factors or trophic-transfer coefficients) is beyond the scope of this study, but may be important to quantify when refining water-quality management strategies.

Microscopic examination of zooplankton samples from each site indicated the presence of the invasive species *Daphnia lumholtz* (Fig. 5). The rapid spread of this species in the Great Lakes and more recently in the northern San Francisco Bay region has been tracked on the Internet (Stoeckel and Charlebois, 1999; Center for Aquatic Resources Studies, 2004). This initial sighting of the species in the southern San Francisco Bay region was reported on September 22, 2004 and later confirmed by taxonomic analyses (Table 2) for Calero, Almaden and Lexington Reservoirs. The variability in the abundance of *D. lumholtzi* and other less media-prominent species within each water body provides another example in support of at least triplicate zooplankton sampling.

Although an effort was made to collect zooplankton from the Chlorophyll-a maximum depth, the zooplankton sampling differed in many respects from the phytoplankton sampling. First, sampling at a desired depth for zooplankton was not precise because the net drifted vertically over the duration of the tow in response to changes in boat speed and direction. Therefore, the tow vertically and horizontally integrated the zooplankton sample to a much greater extent than the phytoplankton point sample at a fixed depth (Study Design and Methods). If taxonomic composition of zooplankton assemblages varied with depth as the phytoplankton assemblage did at Lake Almaden (Fig. 4), the actual pathways for trophic transfer may have been skewed by the sampling methods. In future studies, a more precise stratified sampling with depth would quantify this effect.

Chemical Data

1. **Dissolved oxygen and pH profiles**: Vertical profiles in surface waters for dissolved oxygen and pH often correspond during the day because the production of oxygen by photosynthesis is coupled to the consumption of dissolved carbon dioxide (carbonic acid) and hence an increase in pH. The deepest three reservoirs (Lexington, Guadalupe and Calero) exhibited an oxycline at approximately 10 meters (Fig. 3B) with a consistent decrease in pH below that depth. Almaden Reservoir showed multiple-step oxygen and pH profiles, with both decreasing with depth. The shallowest sampled water body, Lake Almaden, was the only one to exhibit a distinct subsurface dissolved-oxygen maximum at a depth of approximately two meters, coincident with a pH peak. Bottom-waters in all reservoirs except Almaden were oxygen depleted (less than or equal to 2 milligrams per liter).

2. **Specific Conductance profiles**: In general, specific conductivities for the sampled lentic systems were uniform with depth and similar in magnitude (0.3 to 0.4 millisiemens per centimeter) (Fig. 3C). The notable exception was Lake Almaden that exhibited elevated specific conductances relative to the four reservoirs (greater than 0.5 millisiemens per centimeter) that increased with depth.

3. **Mercury in the water column:** As one might expect, the lowest concentrations of mercury species were seen in Lexington and Calero Reservoirs, removed from historic operation of the New Almaden Mercury Mines. However, Calero Reservoir can be hydrologically connected to Almaden Reservoir because as much as 9.3 million cubic meters (7500 acre-feet) per year of water can be transport from Almaden Reservoir to Calero Reservoir (that is, 75 percent of the storage volume for Calero Reservoir) via the Almaden-Calero canal during the months of December through April. Total mercury (dissolved and particulate) ranged from 1.5 to 20.1 nanograms per liter at Lexington Reservoir and Lake Almaden, respectively (Table 4). Similarly, Lexington Reservoir and Lake Almaden exhibited the concentration extremes for dissolved total mercury that ranged from 0.5 to 2.6 nanograms per liter. Similarly for total methylmercury and dissolved methylmercury, the concentration ranges (0.1 to 1.7 and 0.04 to 0.41 nanograms per liter, respectively) was bracketed by concentrations from Lexington Reservoir at the bottom and Lake Almaden at the top. These trends between lentic systems are consistent with epilimnetic concentrations reported in collaborative studies by Tetra Tech (2004, 2005). Although the highest total-mercury concentrations in both the dissolved and particulate phases were found at Lake Almaden and Guadalupe Reservoir, the highest methylmercury concentrations were associated with Lake Almaden and Almaden Reservoir. The fraction of dissolved total mercury relative to dissolved and particulate total mercury was consistently less than 15 percent (14 $\pm$ 7 percent average), with one exception (Lexington as high as 31 percent). By contrast, the fraction of dissolved methylmercury relative to dissolved and particulate methylmercury was consistently greater than 19 percent (26 $\pm$ 4 percent average).

   It has been previously mentioned that these initial data for the lowest trophic levels must be interpreted within the constraints of the sampling design on one date. For example under these low-flow, low suspended sediment conditions, the correlation between dissolved and total methylmercury ($r^2 = 0.99$; Fig. 6C) and between dissolved and total inorganic mercury ($r^2 = 0.73$) for the five sampled water bodies may suggest a consistent partitioning. Over multiple samplings during the summer of 2004, the correlation between dissolved and total methylmercury ($r^2 = 0.92$) and between dissolved and total inorganic mercury ($r^2 = 0.47$) were lower (Tetra Tech, 2005), but estimates for the logarithm of the partitioning coefficient for methylmercury were generated (5.5 $\pm$ 0.5). Suspended sediment concentrations were not determined in this study, but if a typical range is assumed from reservoir sampling during the 2004 summer (3.5 $\pm$ 2.5 milligrams per liter; Tetra Tech, 2005), results from this study indicate a logarithmic partitioning coefficient, 6.1 $\pm$ 0.4, that is consistent with independent investigations in the watershed. On an absolute scale, however, the ratios of total to dissolved inorganic or methylmercury (8 $\pm$ 4 and 4 $\pm$ 1, respectively) were

approximately double that of ratios observed in the coincident study over the entire summer (3.1 and 1.4; Tetra Tech, 2005). This may be due to a more consistent partitioning of mercury species onto and into phytoplankton cells during our sampling relative to the summer in general, suggesting the potential for temporal variability in bioaccumulation factors.

4. **Dissolved Organic Carbon (DOC) in the water column**: Dissolved organic matter, measured as DOC, is a ligand that can compete for mercury complexation in the water, and hence affect the solubility of particulate mercury (Ravichandran, 1998). For example, Kuwabara and others (2002) noted that spatial trends in dissolved-mercury concentrations in Lahontan Reservoir, Nevada, were coincident with DOC. This is not the case for the lentic systems sampled in this study, with poor correlation between dissolved mercury and DOC ($r^2 = 0.11$). Concentrations for DOC varied from 2.01 ± 0.02 to 4.36 ± 0.02 milligrams carbon per liter at Guadalupe and Lexington Reservoirs, respectively (Table 5). It has been suggested that elevated ratios of methyl to total mercury in zooplankton may possibly be related to elevated DOC although a mechanism was not specified (Paterson and others, 1998). In the Guadalupe River watershed, data from this study do not support this hypothesis ($r^2 = 0.07$). In fact, the two highest DOC concentrations were observed in reservoirs removed from the historic mercury-mining activity (that is, Calero and Lexington Reservoirs), and having the lowest zooplankton densities (Fig. 9; Table 2). The net effect of DOC on mercury bioavailability and mercury trophic transfer is confounded by its role as a competing ligand in complexation and partitioning reactions as well as a carbon source to stimulate microbial methylation.

5. **Dissolve trace metals in the water column**: In addition to mercury, other trace metals in the dissolved phase can compete for ligands in both dissolved and particulate phases, and hence affect mercury speciation and partitioning. With the exception of cadmium and lead, dissolved-metal concentrations were higher (sometimes by orders of magnitude) than total-dissolved mercury concentrations. Elevated concentrations for dissolved copper, nickel and lead were observed in Guadalupe Reservoir relative to the other reservoirs, but concentration trends between reservoirs were inconsistent for other metals (Table 6). Given that the lowest DOC concentrations were from Guadalupe Reservoir, the speciation of these metals (and mercury, see section above) does not appear to be dominated by organic chelation. Serpentinite formations in the region are a likely contributor to the high dissolved-nickel (11.5 micrograms per liter in Guadalupe Reservoir) and other trace-metal concentrations (Topping and Kuwabara, 2003).

6. **Mercury in phytoplankton**: Concentrations of total mercury associated with phytoplankton ranged from 22.8 to 172 nanograms per gram dry weight from Lexington and Guadalupe Reservoirs, respectively. Lake Almaden displayed the second highest total mercury concentration with 74.3 nanograms mercury per gram dry weight. Sample replicates were composited rather than independently analyzed, so a pure error estimate is not available for phytoplankton concentrations, but analytical and replicate precision were both less than 6 percent of the mean for the zooplankton analyses (Appendix 2; Table 4). The bioaccumulation factor between water and phytoplankton relative to total mercury was approximately 26,000 ($r^2 = 0.84$). In view of the magnitude of this calculated bioaccumulation factor for total mercury and the low percentage of methylmercury relative to total mercury in phytoplankton observed within this watershed (a range of less than 1 to 11 percent), it may be prudent to consider the uptake or adsorption of inorganic mercury by phytoplankton as a complementary pathway of site-specific importance for subsequent biomagnification by higher trophic levels. Mason and others (1996) found that methylmercury was assimilated about four times more efficiently than inorganic mercury from diatoms (phytoplankton) to copepods (zooplankton). Given the low ratio of methyl to total mercury in phytoplankton reported here (less than 1 to 11 percent) relative to other studies of lakes not affected by mercury mining (e.g., 13 and 31 percent; Watras and Bloom, 1992), perhaps the supply of inorganic mercury from certain phytoplankton species (adsorbed or cytoplasmic) or

from other suspended particles can significantly contribute to zooplankton assimilation in this mining-affected watershed.

Concentrations of methylmercury associated with phytoplankton ranged from less than 1.50 (the detection limit) to 8.2 nanograms per gram dry weight. Unlike total mercury concentrations, the highest methylmercury concentrations were from Lake Almaden. In fact, of the five sampled water bodies, only two, Lake Almaden and Almaden Reservoir, exhibited phytoplankton-mercury concentrations greater than the detection limit. Given that Lake Almaden and Almaden Reservoir had the highest dissolved and particulate methylmercury concentrations among the lenthic systems sampled in this study, this result is not surprising. In contrast, phytoplankton from Guadalupe Reservoir, having the highest total-mercury concentrations, had undetectable methylmercury. The fraction of methylmercury in phytoplankton (less than 1 to 11 percent of total mercury) contrasts the predominance of methylmercury in fish, typically greater than 90 percent of total mercury in fish tissue (Grieb and others, 1990; Bloom, 1992). With a very coarse approximation of 0.75 nanograms per gram for the non-detectable (less than 1.5) methylmercury concentrations in phytoplankton, the accumulation factor between water and phytoplankton relative to methylmercury is estimated at 19,000 ($r^2 = 0.91$). This estimate of the initial diffusive uptake by phytoplankton is consistent with those reported by Watras and others (1998), and approximately four orders of magnitude greater than biomagnification factors between prey and piscivorous fish in this watershed (5.4 with $r^2 = 0.90$; Tetra Tech, 2005). Furthermore, the percentage of methymercury relative to total mercury in phytoplankton is also well correlated with dissolved methylmercury in the water column ($r^2 = 0.82$; Table 4). This observation is consistent with those of Lawson and Mason (1998) who noted that cytoplasmic assimilation of methylmercury by phytoplankton was dependent on solution-phase concentration exposure. Watras and Bloom (1992) observed that the percentage of methylmercury in phytoplankton relative to total mercury was inversely correlated with pH (13 and 31 percent methylmercury in lakes at pH 6.1 and 4.7, respectively). They hypothesized that methylmercury through transfer in lower trophic levels is enriched upon acidification. The pH range observed in this study was 6.5 to 9 (Fig. 3D), routinely higher than those measured by Watras and Bloom (1992). The lower percent methylmercury in phytoplankton reported here (less than 1 to 11 percent, Table 4) relative to the lakes studied by Watras and Bloom (1992) is consistent with the hypothesis that a higher percentage of inorganic mercury is associated with phytoplankton as pH increases.

Consistent with the observation of others (Watras and others, 1998), we speculate that the lower relative concentration for methylmercury in phytoplankton (less than 1 to 11 percent) compared to fish (greater than 90 percent) is related to the greater exposure of the phytoplankton cell to mercury species in the bulk solution (that is a higher reactive surface to volume ratio relative to higher trophic level organisms for diffusive and sorptive uptake from the water column), in contrast to the dietary assimilation of methylmercury into fish tissue as it grows. There is also a possibility that the filtered phytoplankton samples may have included particulate materials not representative of the natural phytoplankton assemblage (for example, inorganic particulates). Although not observed under microscopic examination, the significant presence of inorganic particles would favor the adsorption of inorganic mercury over methylmercury onto metal-oxide surfaces (Gunneriusson and others, 1995).

In a study of 55 lakes in the United States, Chen and Folt (2005) observed that mercury concentrations in phytoplankton were negatively correlated with phytoplankton densities. They suggested that this phytoplankton "density dilution" underlies the fate of mercury and other contaminants in aquatic systems. Results presented in this report can be used to examine how well the concept of density dilution relates to reservoirs where the primary source of mercury is not atmospheric. There was no significant correlation between methylmercury in phytoplankton and phytoplankton biovolumes or densities ($r^2 = 0.08$ and 0.24, respectively), indicating an absence of

density dilution during this study, or variability in density dilution between reservoirs that could not be detected by one sampling event.

7. **Mercury in zooplankton**: Consistent with phytoplankton trends between reservoirs, total mercury associated with zooplankton ranged from 102 to 757 nanograms per gram dry weight from Lexington and Guadalupe Reservoirs, respectively. As with the phytoplankton, Lake Almaden displayed the second highest total mercury concentration with 368 nanograms mercury per gram dry weight.

   Methylmercury associated with zooplankton ranged from 84 (a single composited sample) to 764 $\pm$ 14 nanograms per gram dry weight at Lexington and Guadalupe Reservoirs, respectively. Similarly, Lexington and Guadalupe Reservoirs exhibited the lowest and highest total mercury in zooplankton (102 and 898 nanograms per gram dry weight, respectively). Specific to Almaden Reservoir, mercury concentrations for zooplankton had to be corrected for the presence of algal filaments in the zooplankton-tow (Fig. 13). The mercury concentrations from this assemblage were corrected for algal-concentration dilution based on the relative dry mass of the zooplankton (46 + 6 percent dry weight rounded to 50 percent) and phytoplankton. In contrast to trends seen for methylmercury in phytoplankton, Almaden Reservoir and Guadalupe Reservoir (notably, not Lake Almaden) showed the highest methylmercury in zooplankton. Although this shift in uptake pattern cannot currently be explained, it is important to note that this shift is propagated into the next trophic level (that is small fish) as will be discussed in the subsequent section. Perhaps the varied assimilation of methylmercury contributes to this shift because this trophic level appears to represent a transition between uptake pathways. Methylmercury represented 44 to 85 percent of total mercury in zooplankton, a range clearly between those observed for phytoplankton, its prey, and for small fish, its predator (Table 4). The shift in uptake patterns is coincident with 44 percent associated with Lake Almaden and 85 percent associated with Guadalupe Reservoir.

   As with phytoplankton, Watras and Bloom (1992) observed that the percentage of methylmercury in zooplankton relative to total mercury was negatively affected by pH (29 and 91 percent methylmercury in lakes at pH 6.1 and 4.7, respectively). Although the pH range observed in this study was 6.5 to 9 (Fig. 3D), the percent methylmercury in zooplankton reported here (44 to 85 percent) is within the range observed by Watras and Bloom (1992). That is, in the Guadalupe River watershed, a lower percentage of methylmercury in reservoir phytoplankton does not carry over to the zooplankton. Feeding rates and assimilation efficiencies for methylmercury into zooplankton may be site specific. Alternatively, the size fractioned samples that were microscopically characterized may have included particulate materials not associated with the natural phytoplankton and zooplankton assemblages. In this critical transition level of trophic transfer, it may be important to confirm and understand whether biomagnification factors are constrained to a sole source of methylmercury in phytoplankton. The importance of characterizing those uptake processes in this watershed may be reflected by the fact that methylmercury in zooplankton, in both Almaden and Guadalupe Reservoirs, already exceeded the U.S. Environmental Protection Agency (USEPA) Water Quality Criteria of 300 nanograms per gram (or 0.3 milligrams per kilogram; USEPA, 2001a) for human consumption of fish, one to three trophic transfers above zooplankton (Fig. 6A).

   Methylmercury in zooplankton correlated better with total mercury rather than methylmercury in phytoplankton (r^2 = 0.60 and 0.01, respectively), although both correlations were not significant at the 95-percent confidence level. That is, the biomagnification factors for zooplankton relative to phytoplankton were not consistent for total mercury (a range of 2 to 11; Table 4), as one might expect if only methylmercury was being transferred. But counter intuitively, that phytoplankton-to-zooplankton biomagnification factor was also inconsistent for methylmercury (a range of 20 to greater than 1000). These biomagnification factors, for both mercury species, are orders of

magnitude less than those describing the initial accumulation of mercury by phytoplankton from the water column. However, the biomagnification factors for zooplankton relative to total mercury in phytoplankton are similar in magnitude to biomagnification factors between prey and piscivorous fish in this watershed (Tetra Tech, 2005). A zooplankton tow horizontally and vertically integrates the sample to a much greater degree than a point sample for phytoplankton. This difference in collection method may contribute to the lack of correlation between mercury concentrations in zooplankton and phytoplankton in this study.

In conjunction with similar findings for phytoplankton described above, Chen and Folt (2005) also observed that mercury concentrations in zooplankton were negatively correlated with zooplankton densities. They suggested that this zooplankton "density dilution" is an important biogeochemical effect contributing to the fate of mercury and other contaminants in aquatic systems. As with phytoplankton, results from our five-reservoir study can be used to examine the applicability of the density-dilution concept when atmospheric sources of mercury do not dominate. Consistent with the phytoplankton results, no significant correlation between methylmercury in zooplankton and zooplankton biomass or densities ($r^2 = 0.08$ and 0.24, respectively) was observed. Perhaps, the density-dilution effect is less discernable when multiple bioavailable mercury sources exist (fluvial and benthic) and atmospheric sources do not dominate. Therefore, the concept of density dilution cannot be extrapolated to the biomagnification of mercury in fish. Based on a negative correlation between mercury concentrations in fish with zooplankton density, Chen and Folt (2005) concluded that the data they examined "provided persuasive evidence that high zooplankton density can reduce the biomagnification of mercury to fish of all trophic levels". As with phytoplankton and zooplankton results, the hypothesis of density dilution can be tested for fish within the reservoirs of the Guadalupe River watershed. Because a density-dilution effect for methylmercury in zooplankton was not observed in this study, it is not surprising that biomagnification of mercury in small (1-year) fish was not significantly correlated with either the biomass or density of its zooplanktonic prey ($r^2 = 0.22$ and 0.17, respectively). That is at the time of our sampling, the density dilution effect was not observed at either of the base levels in trophic transfer.

8. **Associations with mercury in small (prey) fish:** Twenty age-1 largemouth bass (50 to 100 millimeter fork length) were sampled from each of the 5 reservoirs. Total mercury associated with these prey fish, assumed to be predominantly in the form of methylmercury (Grieb and others, 1990; Bloom, 1992), ranged from 450 $\pm$ 90 to 4830 $\pm$ 1220 nanograms per gram dry weight (that is, 0.5 to 4.8 micrograms mercury per gram dry weight) from Lexington and Almaden Reservoirs, respectively. As with the zooplankton (not phytoplankton), Almaden and Guadalupe Reservoirs displayed the highest total-mercury concentrations in fish, and Lexington and Calero Reservoirs the lowest. In Calero Reservoir, mercury in fish (Table 4) was approximately 3-fold higher than in Lexington Reservoir despite similar mercury concentrations in zooplankton. This suggests either a source of mercury to fish in Calero that was not detected in this study, or that measured mercury concentrations in zooplankton in Lexington Reservoir were higher at the time of collection than during other times of the year. Mercury in small fish was highly correlated with both total and methyl mercury in zooplankton suggesting consistent biomagnification factors within the five sample water bodies (4.8 $\pm$ 0.7, $r^2 = 0.94$) and for methylmercury (5.5 $\pm$ 1.0, $r^2 = 0.90$) (Fig. 6A). These values were also consistent with those describing dietary mercury transfer between prey and piscivorous fish in this watershed (3.8 to 7.1; Tetra Tech, 2005) and others (estimated at about 0.5 log units or about 3 by Watras and others, 1998), but again about four orders of magnitude smaller than bioaccumulation factors for the initial diffusive or sorptive assimilation of mercury by phytoplankton from the water column (approximately 26,000 and 19,000 for total and methylmercury, respectively). Despite the strong correlation between mercury in small fish and in zooplankton, the temporal and spatial constraints of this data set should be carefully considered when applying these results. McGeer and others (2003) cautioned against the indiscriminate use of biomagnification factors (trophic-transfer coefficients) without an understanding of processes that regulate exposure.

Study Design and Methods

The protocol described in this section focuses on method applications in this sampling of five lentic systems within the Guadalupe River watershed. Details (for example, quality control specifications) for each analysis are available in Appendix 2 or have been previously documented (Woods and others, 1999; Praskins and others, 2001; Kuwabara and others, 2003a).

Within the Guadalupe River watershed, sampling was performed on 14 and 15 September 2004, at or in close proximity (within 100 meters) of the deepest location in Calero Reservoir, Almaden Reservoir, Guadalupe Reservoir, Lexington Reservoir, and Lake Almaden, respectively (Fig. 1; Table 1). At each site, the following samples were collected from a U. S. Environmental Protection Agency research vessel:

Water-column Sampling

After locating and logging the coordinates at each sampling site, a field submersible fluorometer (Turner Designs Self-contained Underwater Fluorescence Apparatus, SCUFA) was lowered into the water column to locate the depth of relative maximum chlorophyll-a concentration. This depth was used to set and deploy devices for subsequent sampling. When a chlorophyll maximum depth was not observed, the water column was sampled at a depth of 2 meters. Vertical profiles were then determined and logged for temperature, specific conductance, dissolved oxygen and pH (YSI Model 600XLM). A Teflon-line Niskin Bottle (General Oceanics) was then used to collect water-column samples for mercury speciation at the depth indicated by prior fluorescence measurements (Fig. 14A).

Phytoplankton Sampling

After water samples were collected, phytoplankton samples were collected from the same Niskin bottle sample and preserved with Lugol's Solution for taxonomic and biomass analyses. Phytoplankton cells from the same depth as the Niskin-bottle sample were then peristaltically pumped through an in-line 35-micrometer non-metal prefilter and collected on baked quartz-fiber filters (Fig. 14B). Flow-through water volumes were recorded for each of the seven replicate filters. After transfer to the laboratory, six samples from each site were lyophilized for subsequent mercury-speciation analysis (three for inorganic-mercury analysis, three for methylmercury analysis). The remaining sample was used for photomicroscopy.

Zooplankton Sampling

At each sampling site, after phytoplankton sampling was completed, the zooplankton community was sampled (Fig. 14C). Six successive tows were conducted using a conical plankton net having a mesh size of 150-micrometers and a diameter of 50-cm. An effort was made to collect zooplankton from the Chlorophyll-a maximum depth. However, sampling at this depth was not precise because the net drifted vertically over the duration of the tow in response to changes in boat speed and direction. Six zooplankton samples were taken from each reservoir: three replicates for taxonomic and biomass analysis, and three for mercury-speciation analysis and photomicroscopic examination. A calibrated flow meter was used to determine the water volume sampled from each tow. The taxonomic/biomass samples were preserved with Rose Bengal Solution in the field for later examination. The three remaining zooplankton samples were preserved on ice, transported US Geological Survey facilities in Menlo Park, CA and stored at 5°C to wait further processing. Samples were processed within 24 hrs of collection. To remove large extraneous items such as twigs, each mercury/photomicroscopic zooplankton sample was sieved through a 1000-micrometer Nitex screen. To separate zooplankton from smaller organisms such as algal filaments, the sample was then sieved through a 125-micrometer Nitex screen. The zooplankton sample, which was collected on the fine screen, was rinsed, a subsample was removed for photomicroscopic analysis, and the remainder was lyophilized for subsequent mercury-speciation analysis.

Small-fish Sampling

At each sampling site, large-mouth bass were collected by electroshocking in two size ranges: less than 1 year fish (small fish, 50 to 100 millimeter fork length) and adult fish of legal size, greater than 305 millimeters forklength. For this report, only the data for the smaller-size class (that is, the size class feeding on the zooplankton) will be discussed. Weiner and others (2005) have suggested that one-year-old prey fish can serve as useful bioindicators of methylmercury contamination. After length measurement, the small-sized fish were wrapped in pre-cleaned foil and placed in a plastic bag. The wrapped samples were stored in a cooler with ice until transported back to the laboratory for freezing.

After removal of the gastrointestinal tract, the whole-fish samples were homogenized and analyzed for total mercury using a Milestone DMA-80 Direct Mercury Analyzer, following USEPA Method 7473/ USEPA Region 9 SOP535 (USEPA, 1998).

Chemical Parameters

1. **Dissolved Mercury and Methylmercury**: Dissolved-mercury and methylmercury samples were processed in a Class-100 laminar-flow hood. Samples from water-column sampling were filtered through a 0.45 micrometer (µm) pore-size, 15 millimeter (mm) diameter capsule filter (Gelman Supor 12175). Samples were refrigerated in darkness until analyzed by cold-vapor atomic fluorescence spectrometry (CVAFS, Fig. 15). Methodological details for total-mercury (Method 1631E, U.S. Environmental Protection Agency (USEPA), 2002) and methylmercury (Method 1630, USEPA, 2001b) were previously reported.

2. **Dissolved organic carbon (DOC)**: Dissolved organic carbon was determined by high-temperature, non-catalytic combustion (Qian and Mopper, 1996). Potassium phthalate was used as the standard. Low-DOC water (blanks less than 40 micrograms-organic C per liter) was generated from a double-deionization unit with additional ultraviolet treatment (Milli-Q Gradient, Millipore Corporation) (Fig. 16).

3. **Dissolved Trace Metals by ICP-MS:** Water-column samples were also collected, filtered (0.2-micrometer polycarbonate membrane) and acidified to provide dissolved trace-metal information for the estuary by flow-injection inductively coupled plasma mass spectrometry (Topping and Kuwabara, 1999; Fig. 17).

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Product names are provided for identification purposes only and do not constitute endorsement by the U.S. Geological Survey.

Appendix 1: Comments on the Report Structure

A major objective of this electronic document is to provide a structure that is easily accessible to a wide range of interest groups**.** Therefore, pathways within this document have been constructed to be both logical and intuitive. In contrast to typical scientific manuscripts, this report is formatted in a pyramid-like structure to serve the needs of diverse groups who may be interested in reviewing or acquiring information at various levels of technical detail. The report enables quick transitions between the initial summary information (figuratively at the top of the pyramid) and the later details of methods or results (figuratively towards the base of the pyramid) using hyperlinks to supporting figures and tables, and an electronically linked Table of Contents. In addition to hyperlinks within the document to supporting figures and tables, links in Appendices 3 and 4 provide a quick way to directly review and examine all figures and tables.

Although hard copies of this report are available on request, the advantages of the electronic version relative to the hard copy are substantial in many respects, but particularly in the rapid access of information at multiple levels of detail.

Your comments about how this type of Web-based product may be improved to better serve readers are most welcome and may be directed to the major author (kuwabara@usgs.gov) so that they may be compiled for future revisions and reports.

Appendix 2: Quality control data for mercury speciation analyses

QA/QC data for water column samples

Mercury Speciation Results for USGS-Brent Topping

Reported October 13, 2004

Frontier Geosciences Inc., 414 Pontius Ave. N, Seattle WA 98109

Quality Control Data - Matrix Duplicate Report

Analyte (ng/L)	Sample QC'd	Rep. 1	Rep. 2	Mean	RPD
Total Hg	Res #1 Rep B	4.04	4.08	4.06	0.9
Methyl Hg	Res #1 Rep A	0.239	0.237	0.238	0.8

Quality Control Data - Matrix Spike / Matrix Spike Duplicate Report

Analyte (ng/L)	Sample QC'd	Sample Mean	Spike Level	MS	% Rec.	Spike Dup Level	MSD	% Rec.	RPD
Total Hg	Res #2 Rep A	6.45	24.24	30.03	97.3		29.92	96.8	0.5
Methyl Hg	Res #1 Rep A	0.238	6.024	6.384	102.0	6.012	6.371	102.0	0.0

MS = Matrix Spike

MSD = Matrix Spike Duplicate

RPD = Relative Percent Difference

Quality Control Data - Preparation Blank Report

Analyte (ng/L)	PBW1	PBWZ	PBW3	Mean	St. Dev.	R.L.
Total Hg	0.06	0.06	0.06	0.06	0.00	0.15
Methyl Hg	0.019	0.013	0.013	0.015	0.003	0.025

St. Dev. = Standard Deviation

R.L. = Reporting Limit

Quality Control Data - Certified Reference Materials Report

Analyte (ng/L)	CRM Identity	Cert. Value	Obs. Value	% Rec.
Total Hg	NIST 1641d	1601000	1574000	98.3
Methyl Hg	DORM-2	4470	4597	102.8

CRM Identity = Certified reference material identity

Cert. Value = Certified value

Obs. Value = Experimental result

% Rec. = Percent recovery

QA/QC data for phytoplankton and zooplankton analyses

Mercury Speciation Results for USGS-James S. Kuwabara

Reported November 10, 2004

Frontier Geosciences Inc., 414 Pontius Ave. N, Seattle WA 98109

Quality Control Data - Matrix Duplicate Report

Analyte (ng/g)	Sample QC'd	Rep. 1	Rep. 2	Mean	RPD
Total Hg	Almaden Reservoir	279.4	296.0	287.7	5.8
Methyl Hg	Almaden Reservoir	278.4	266.3	272.4	4.4

Quality Control Data - Matrix Spike / Matrix Spike Duplicate Report

Analyte (ng/g)	Sample QC'd	Sample Mean	Spike Level	MS	% Rec.	Spilke Dup Level	MSD	% Rec.	RPD
Total Hg	Guadalupe Reservoir	757.0	2151	2831	96.3	1923	2522	91.8	4.9
Methyl Hg	Lake Almaden	160.4	571.5	721.2	98.1	569.2	696.6	94.2	4.1

MS = Matrix Spike

MSD = Matrix Spike Duplicate

RPD = Relative Percent Difference

Quality Control Data - Preparation Blank Report

Analyte (ng/g)	PBW1	PBW2	PBW3	Mean	St. Dev.	R.L.
Total Hg	0.49	0.39	0.45	0.50	0.05	0.45
Methyl Hg	2.06	-0.18	0.09	0.80	1.22	1.50

St. Dev. = Standard Deviation

R.L. = Reporting Limit

Quality Control Data - Certified Reference Materials Report

Analyte (ng/g)	CRM Identity	Cert. Value	Obs. Value	% Rec.
Total Hg	DOLT-S	3370	3529	104.7
Methyl Hg	DORM-2	4470	4429	99.1

CRM Identity = Certified reference material identity

Cert. Value = Certified value

Obs. Value = Experimental result

% Rec. = Percent recovery

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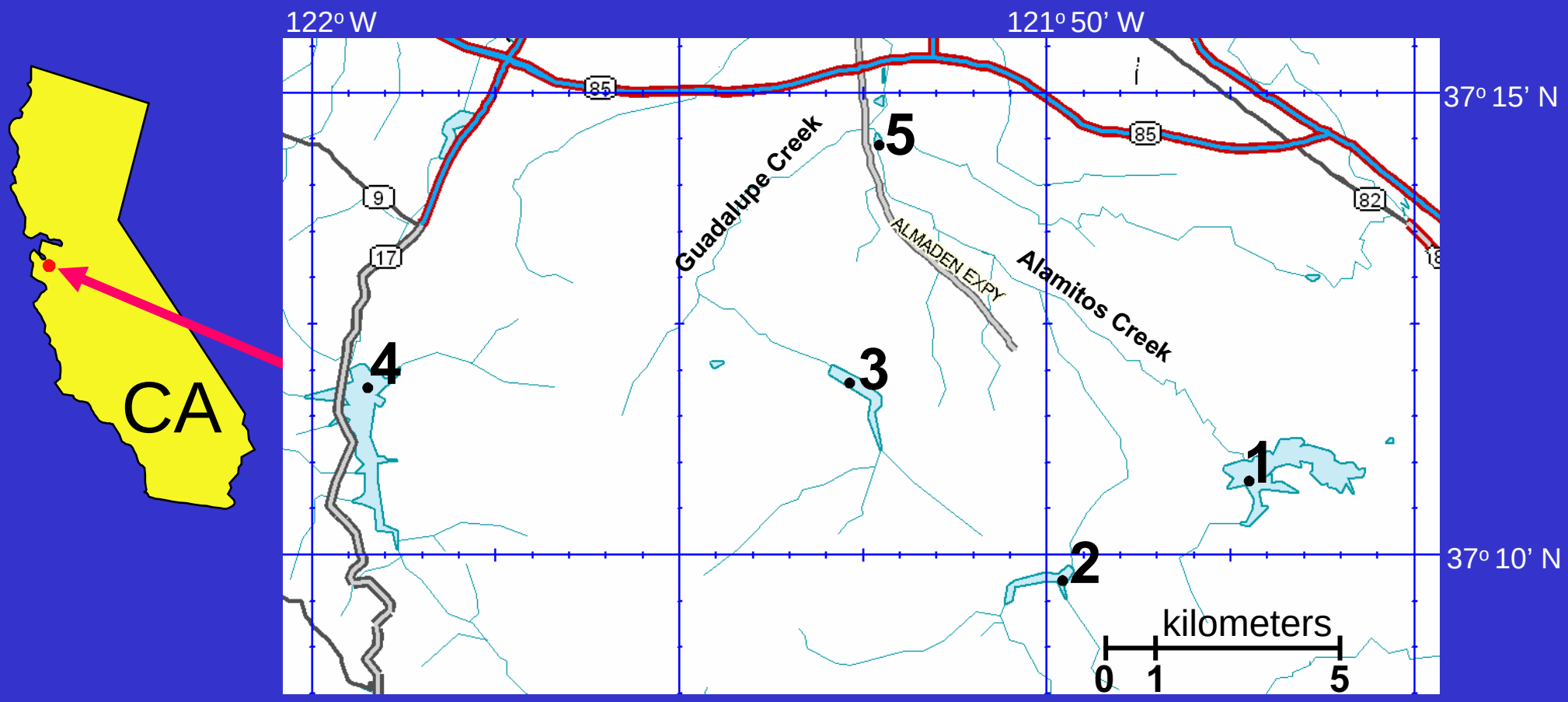
Table 6 – Dissolved trace-metal concentrations (micrograms per liter) at the chlorophyll-*a* maximum depth.

Figure 1. Sampling sites (Numbered as sampled)



1 - Calero Reservoir
2 - Almaden Reservoir
3 - Guadalupe Reservoir
4 - Lexington Reservoir
5 - Lake Almaden

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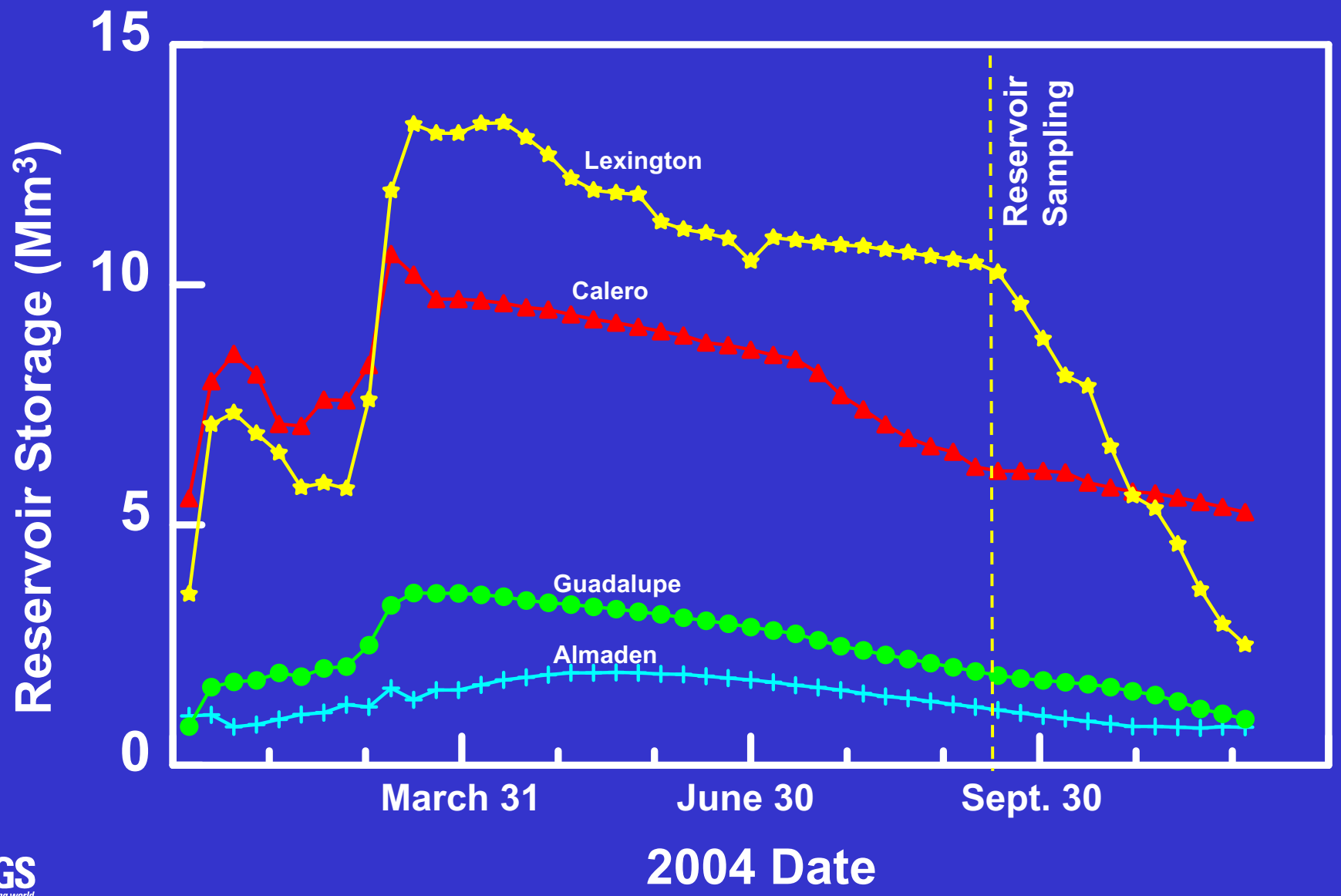
Figure 2. Variation in storage for sampled reservoirs in water year 2004.



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From: http://www.valleywater.org/water/technical_information/Measures_and_Readings/_Past_Rainfall_&_Reservoir_Reports.shtm

Figure 3. Depth profiles in sampled water bodies for: A) Temperature, B) Dissolved oxygen, C) Specific Conductance, and D) pH.

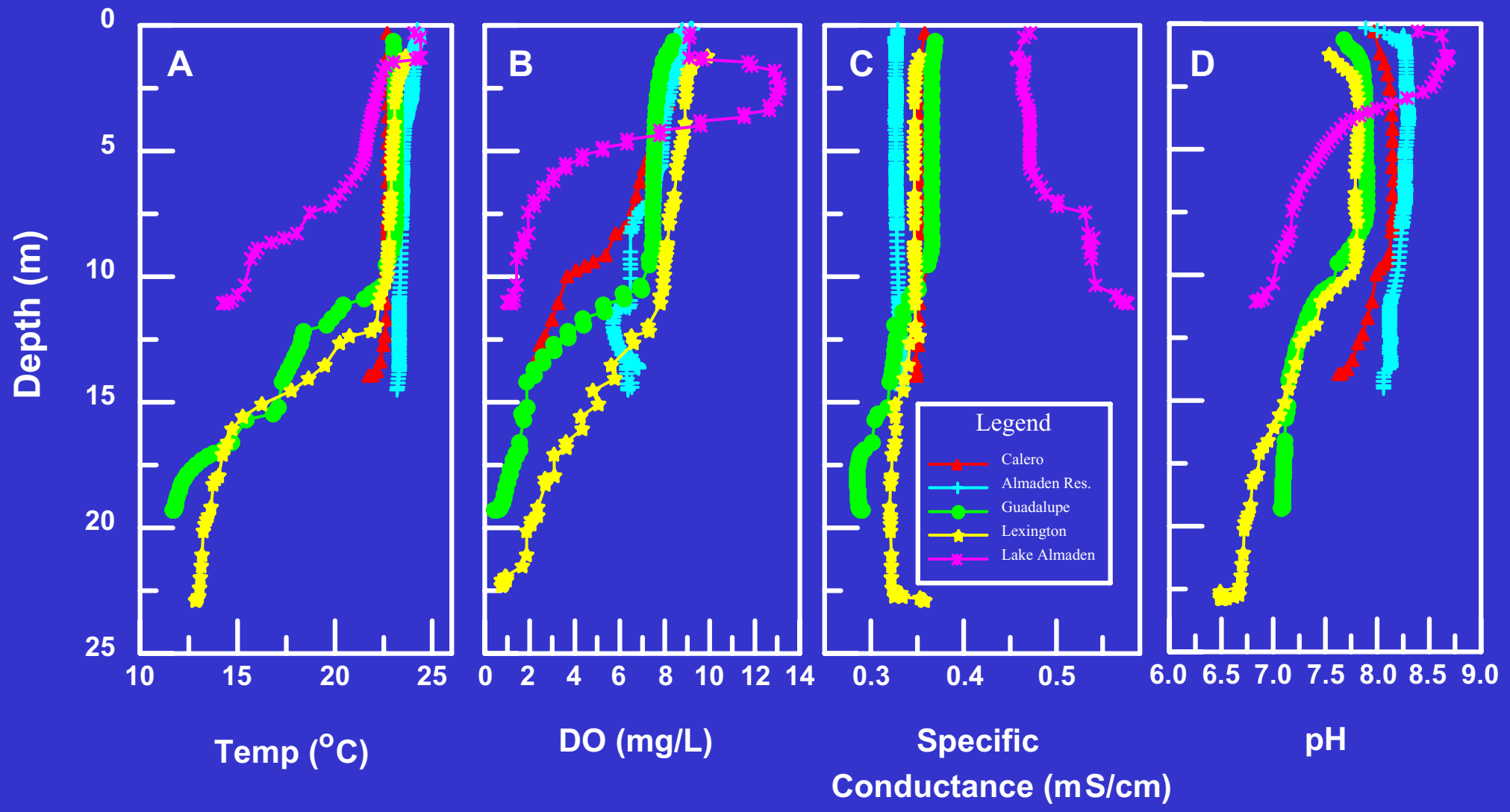

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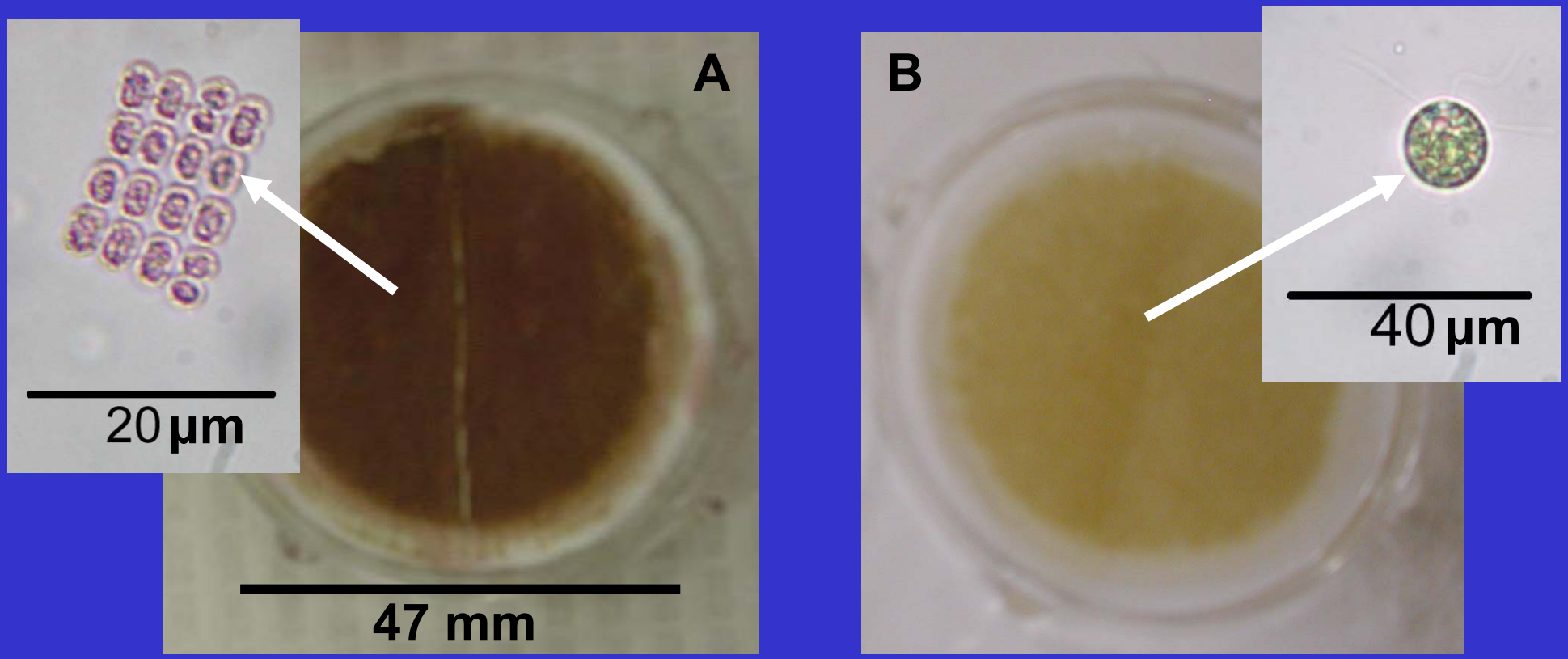
Figure 4. Photographs and photomicrographs of a stratified bloom of *Merismopedia glauca* in Lake Almaden: A) Cyanophyte-dominated community at 6 meters depth and B) Diatom-dominated community at 2 meters depth.



Photographs by F. Colich and S. Fend

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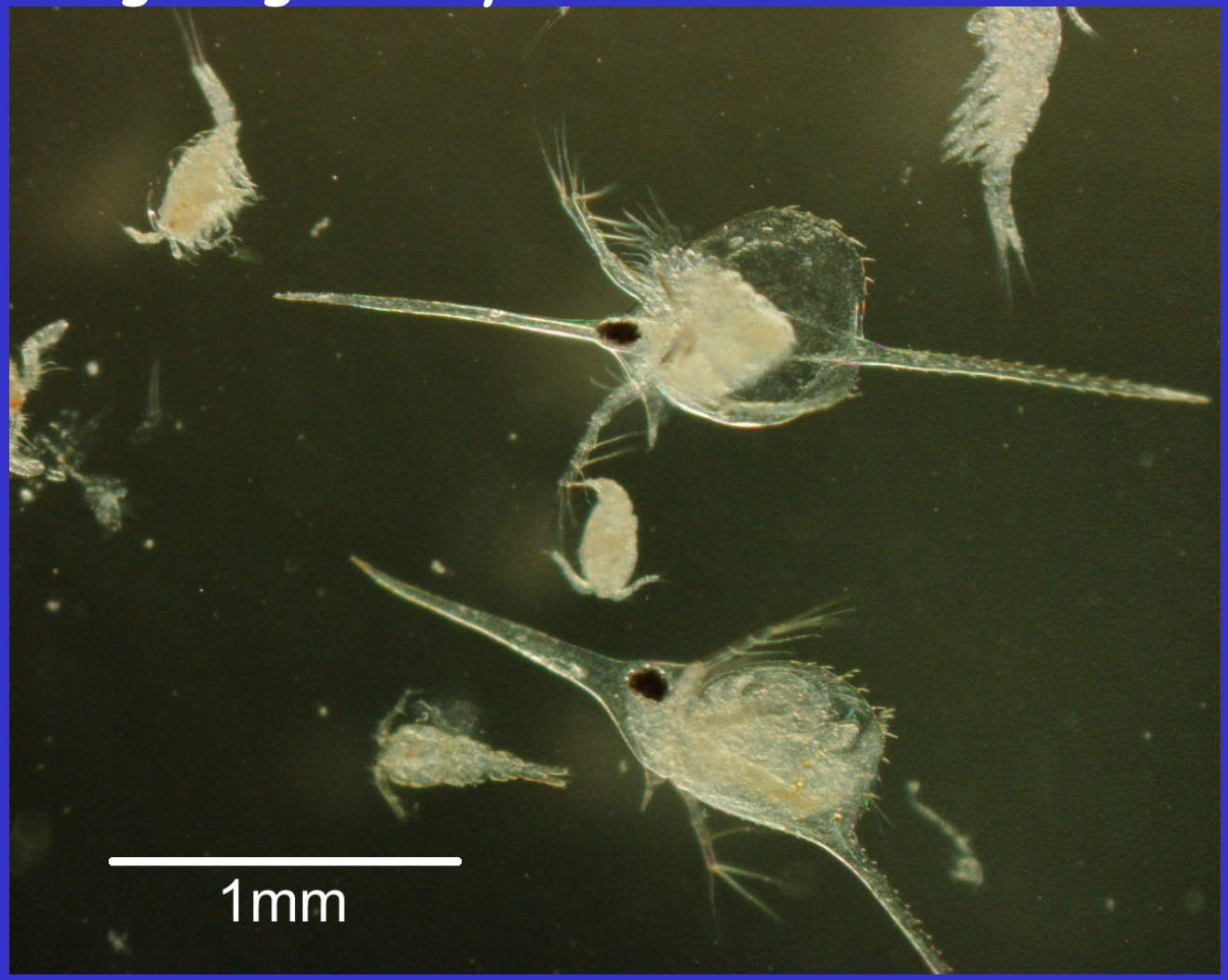
Figure 5. Photomicrograph of the initial South Bay sighting of *Daphnia lumholtzi*.



Photomicrograph by S.V. Fend

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Figure 6. Mercury trophic-transport matrix

For P less than 0.05, orange numerals in cells represent coefficients of determination (r-squared). Green numerals denote calculated bioaccumulation or biomagnification factors.

Highlighted regression lines are shown for those parameters correlated with P less than 0.05.

	Site #	Hg (ng/L)	Hg (ng/L)	% Dissolved	MeHg (ng/L)	MeHg (ng/L)	% Dissolved	% Methyl: Tot.	% Methyl: Diss.	Hg (ng/g)	MeHg (ng/g)	% Methyl	cells/ mL	um^3/ mL	Hg (ng/g)	MeHg (ng/g)	% Methy	count/ m^3	um^3/ m^3	Hg (ng/g)
Site #	Site																			Site #
Hg (ng/L)		Total Hg in water								6400*										Hg (ng/L)
Hg (ng/L)			Dissolved Hg in water							26000*	.844							.785		Hg (ng/L)
% Dissolved				% Diss. Hg in water																% Dissolved
MeHg (ng/L)					Total MeHg in water	.998					.901 4800*	.826						.985	.976	MeHg (ng/L)
MeHg (ng/L)						Diss. MeHg in water					.910 18600*	.841						.986	.977	MeHg (ng/L)
% Dissolved							% Diss. MeHg													% Dissolved
% Methyl: Tot.								MeHg/Hg % Total	.941					.888						% Methyl: Tot.
% Methyl: Diss.									MeHg/Hg % Diss.					.897						% Methyl: Diss.
Hg (ng/g)										Total Hg in phyto-plankton					4.7					Hg (ng/g)
MeHg (ng/g)											MeHg in phyto-plankton	.917				**		.881	.824	MeHg (ng/g)
% Methyl												% MeHg in phyto-plankton								% Methyl
cells/ mL													Phyto-plankton density							cells/ mL
um^3/ mL														Phyto-plankton Biovolume						um^3/ mL
Hg (ng/g)															Total Hg in zoo-plankton	.956				.942 4.8	Hg (ng/g)
MeHg (ng/g)																MeHg in zoo-plankton				.901 5.5	MeHg (ng/g)
% Methy																	% MeHg in zoo-plankton				% Methy
count/ m^3																		Zoo-plankton density	.992		count/ m^3
um^3/ m^3																			Zoo-plankton Biomass		um^3/ m^3
Hg (ng/g)																				Hg in Fish	Hg (ng/g)

* Slopes account for 1000-fold difference between the units ug/L and ug/g. These are listed as such for consistency with standard respective units (for example, ug/L for aqueous samples).

** Slope not given because negative correlation misrepresents BMF

Figure 6A. Empirical relationship between methylmercury concentrations in zooplankton and in small fish.

- The animation begins with the overview matrix (Fig. 6), then zooms in on the highlighted cell describing the biomagnification of methylmercury between zooplankton and age-1 largemouth bass in the five sampled water bodies. In the final graphic of the animation, a light blue rectangle is shown at the bottom left corner of the plot within which the EPA Water Quality Criterion for methylmercury in fish and organisms is met.
- To replay, pause, or resume the animation, use the buttons below. To print, right-click on the desired frame, select "Print".

Play/Replay | Pause | Resume

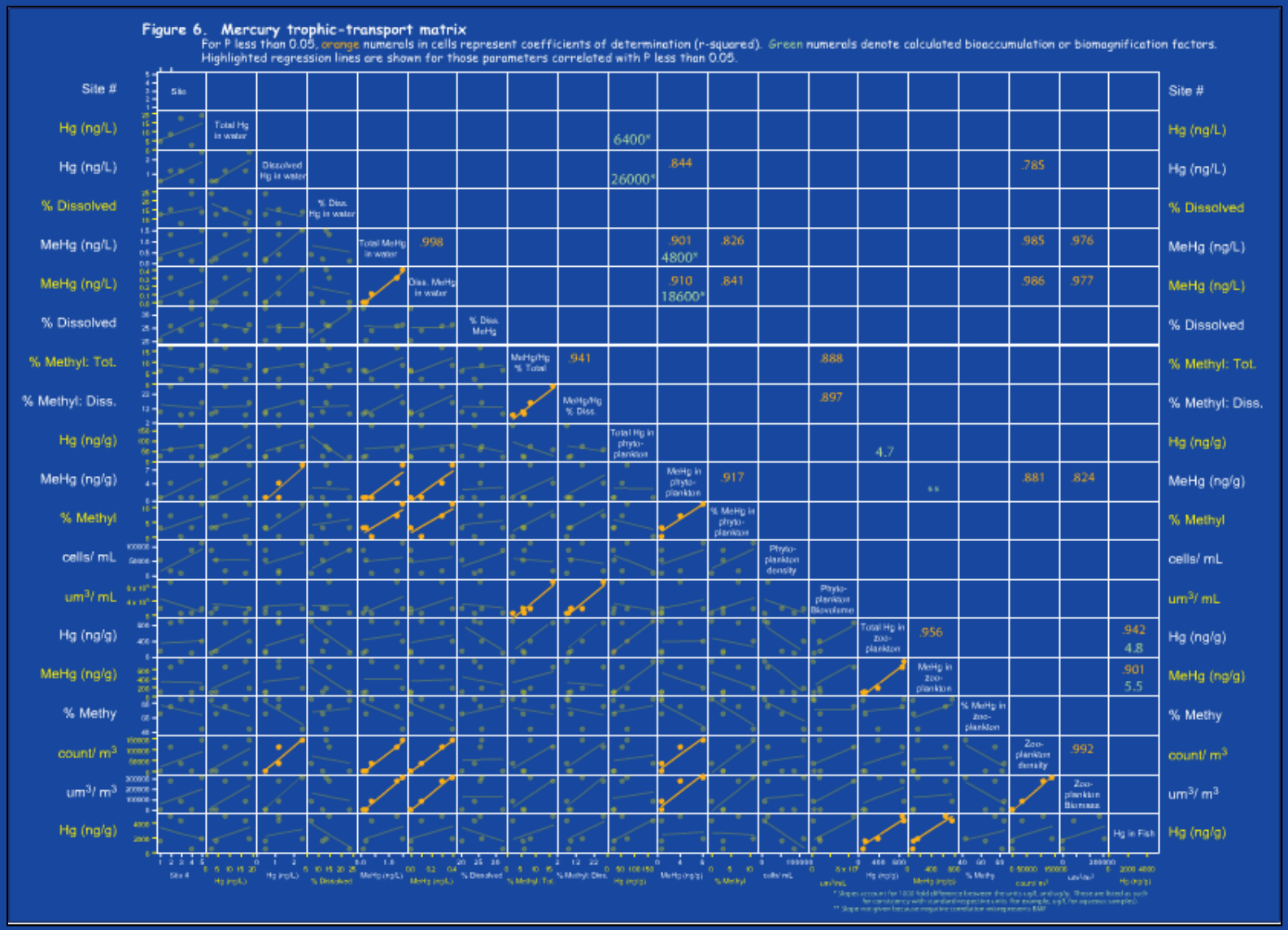


Figure 6B. Empirical relationship between total mercury concentrations in zooplankton and in small fish.

- The animation begins with the overview matrix (Fig. 6), then zooms in on the highlighted cell describing the biomagnification of total mercury between zooplankton and age-1 largemouth bass in the five sampled water bodies.
- To replay, pause, or resume the animation, use the buttons below. To print, right-click on the desired frame, select "Print".

Play/Replay | **Pause** | **Resume**

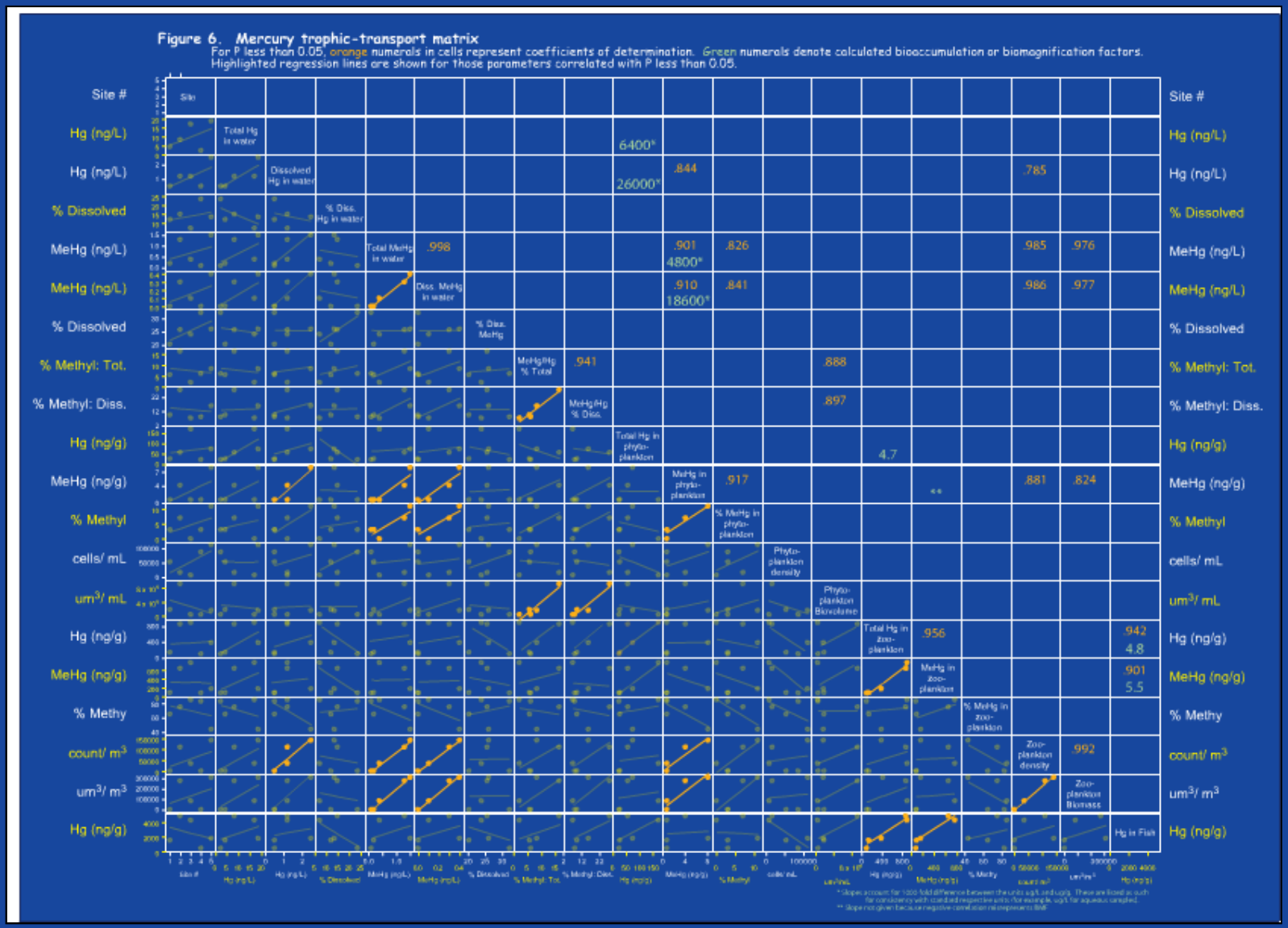


Figure 6C. Methylmercury in dissolved and particulate phases.

The animation begins with the overview matrix (Fig. 6), then zooms in to focus on the consistent relationship between dissolved and total (that is dissolved and particulate) methymercury in the water column of the five sampled water bodies.

To replay, pause, or resume the animation, use the buttons below. To print, right-click on the desired frame, select "Print".

Play/Replay | Pause | Resume

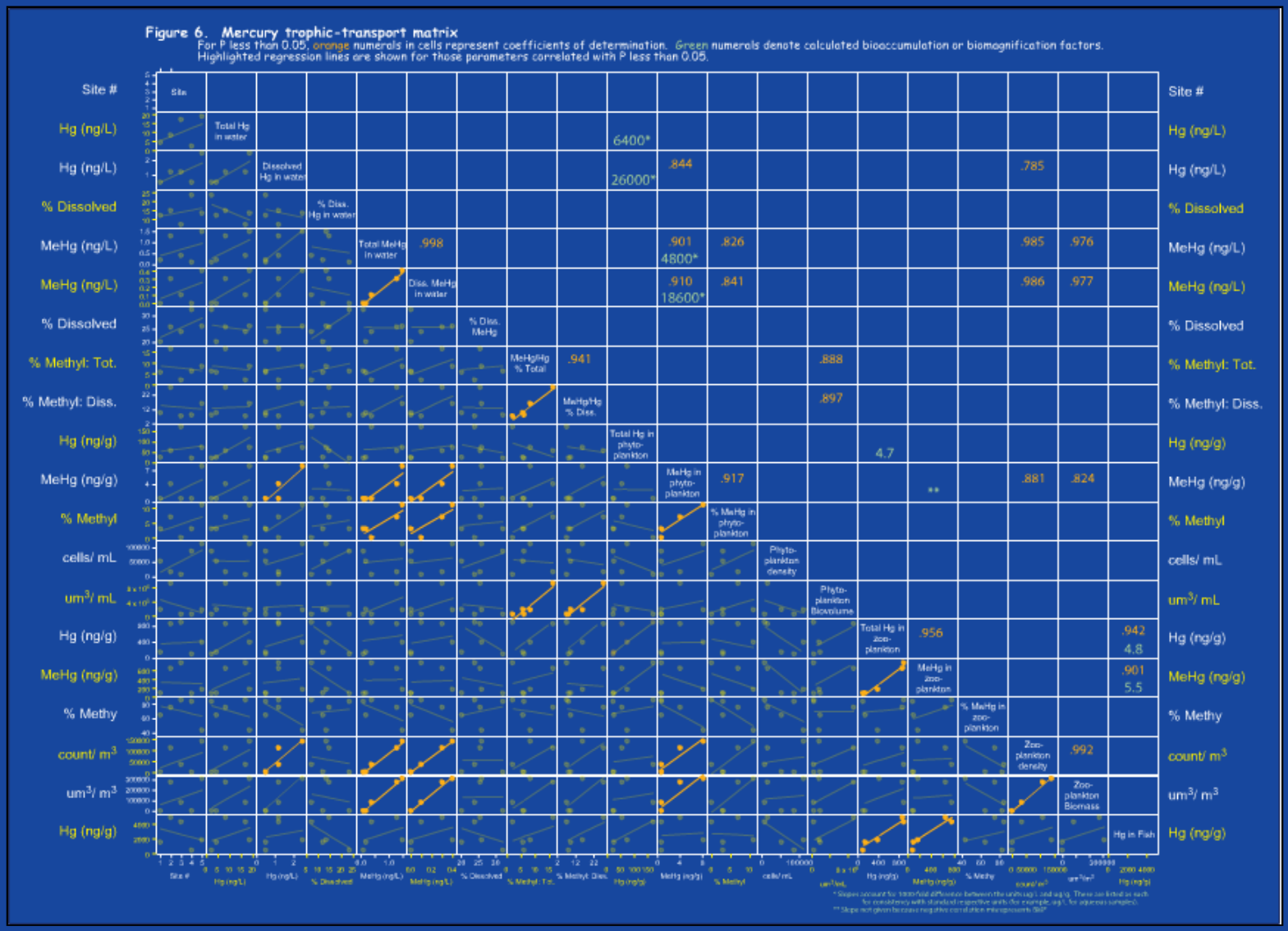


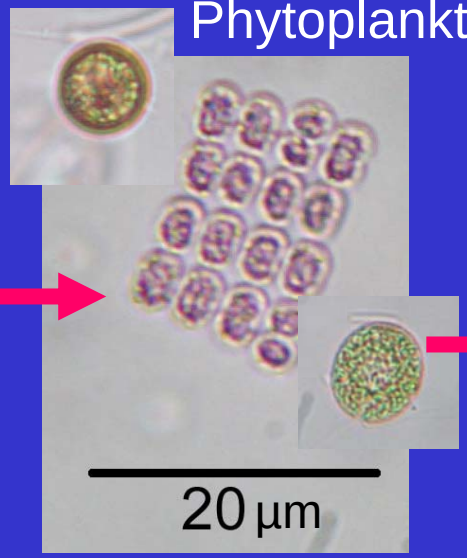
Figure 7. The pelagic pathway examined for mercury trophic transfer*

Water Column

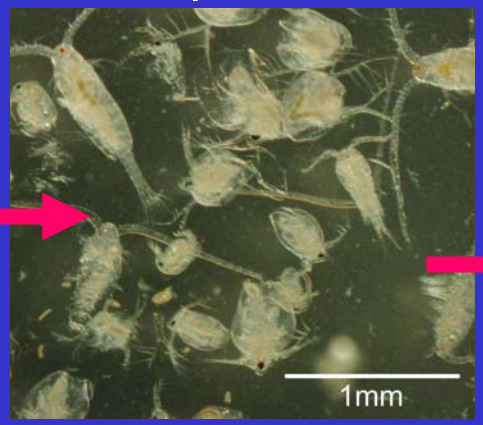
Mercury in particulate and dissolved forms

Inorganic and methymercury

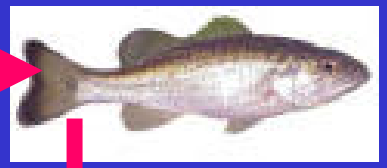
Phytoplankton



Zooplankton



Small Fish



10 cm

Piscivorous Fish

40 cm

* Note that pathways for benthic trophic transfer also exist, but are not the focus of this study.

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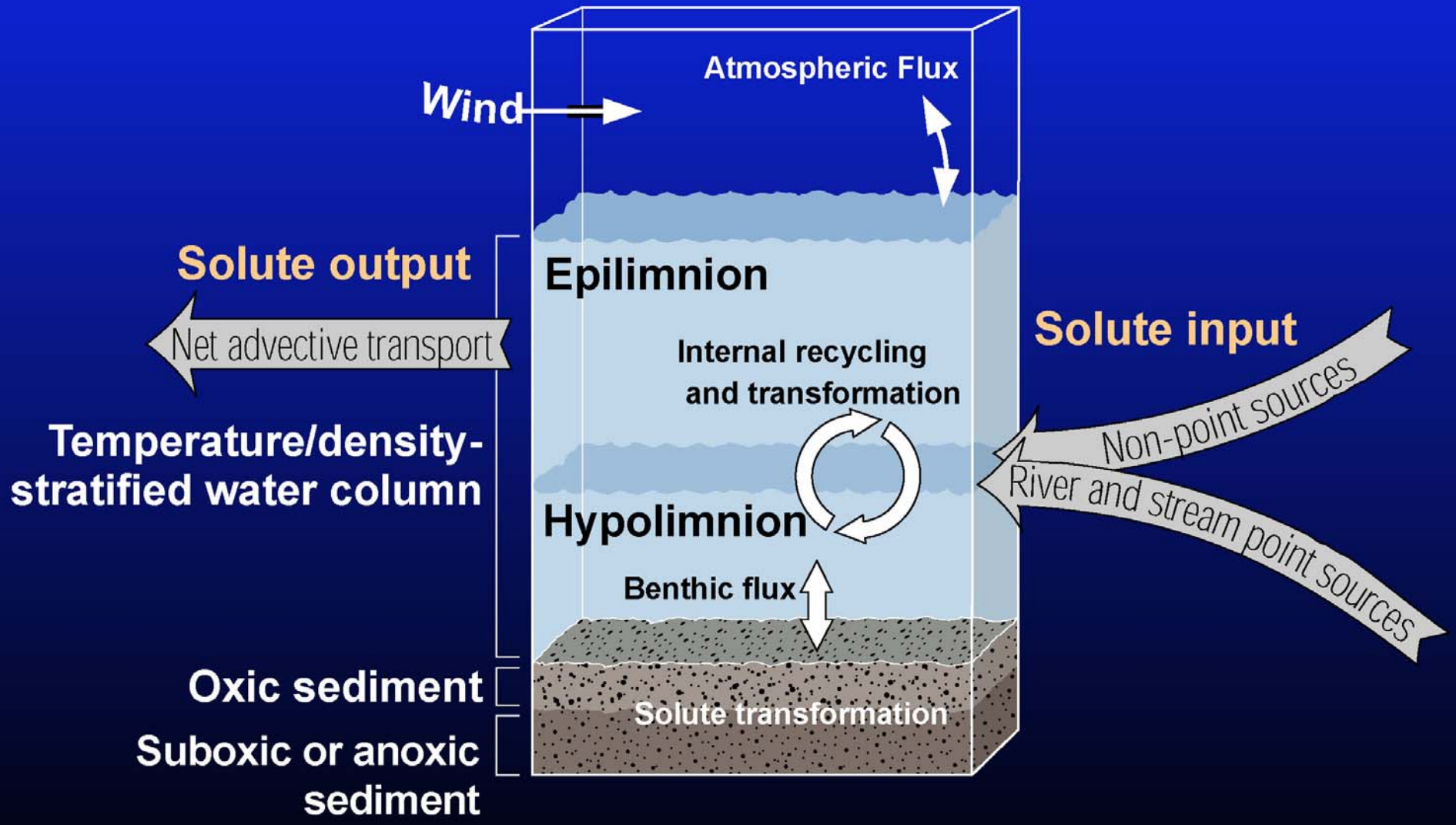
Figure 8. Conceptual Model of Solute Transport



Kuwabara et al. (2002)

Figure 9. Trends in the phytoplankton communities between lentic systems.

Error bars depict standard deviations about the mean, centered at the marker.

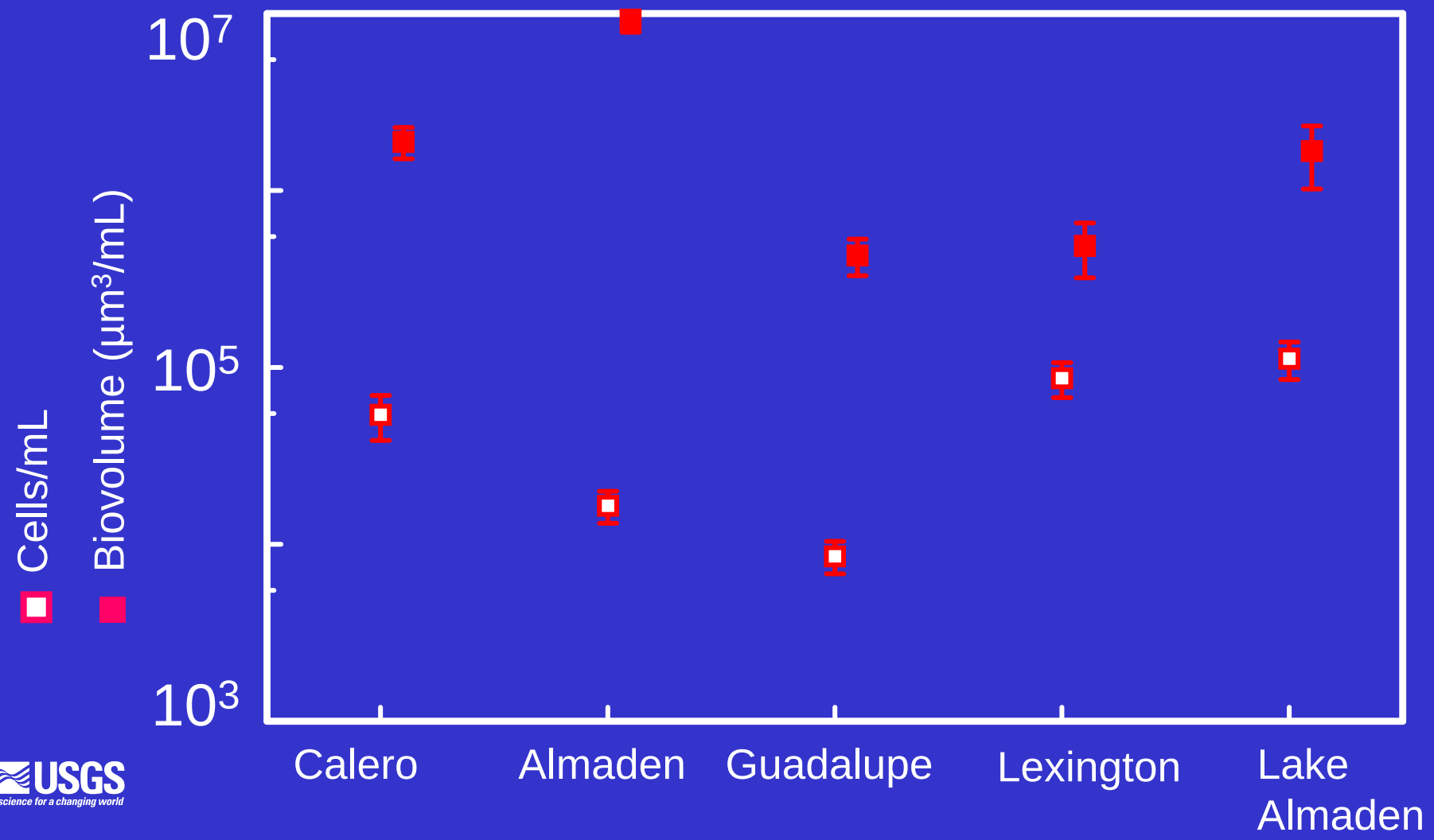


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Figure 10. Graph showing detrended correspondence analysis (DCA) of phytoplankton taxonomic data.

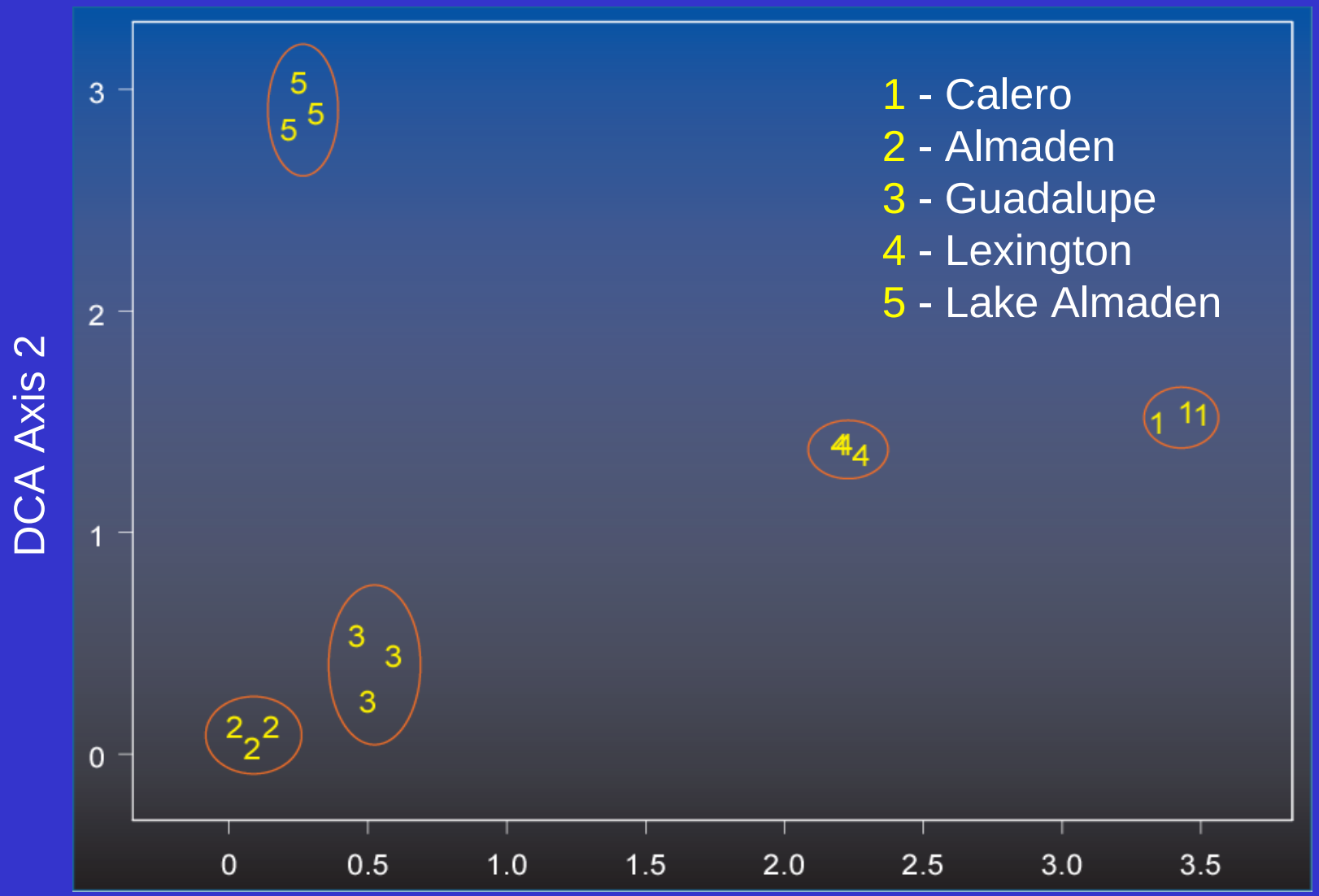

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Figure 11. Trends in the zooplankton communities between lentic systems.

Error bars depict standard deviations about the mean, centered at the marker.

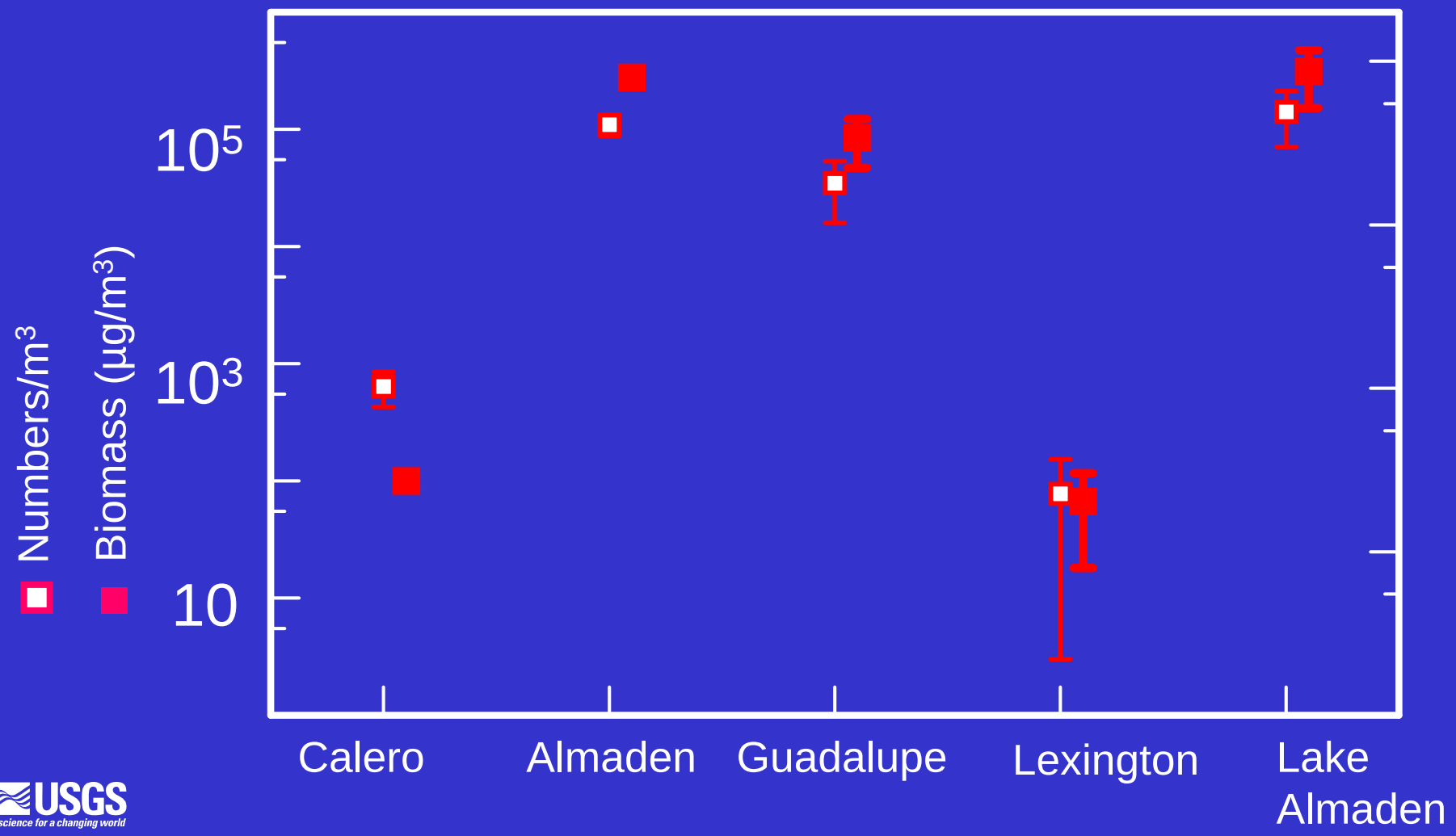

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Figure 12. Graph showing detrended correspondence analysis (DCA) of zooplankton taxonomic data.

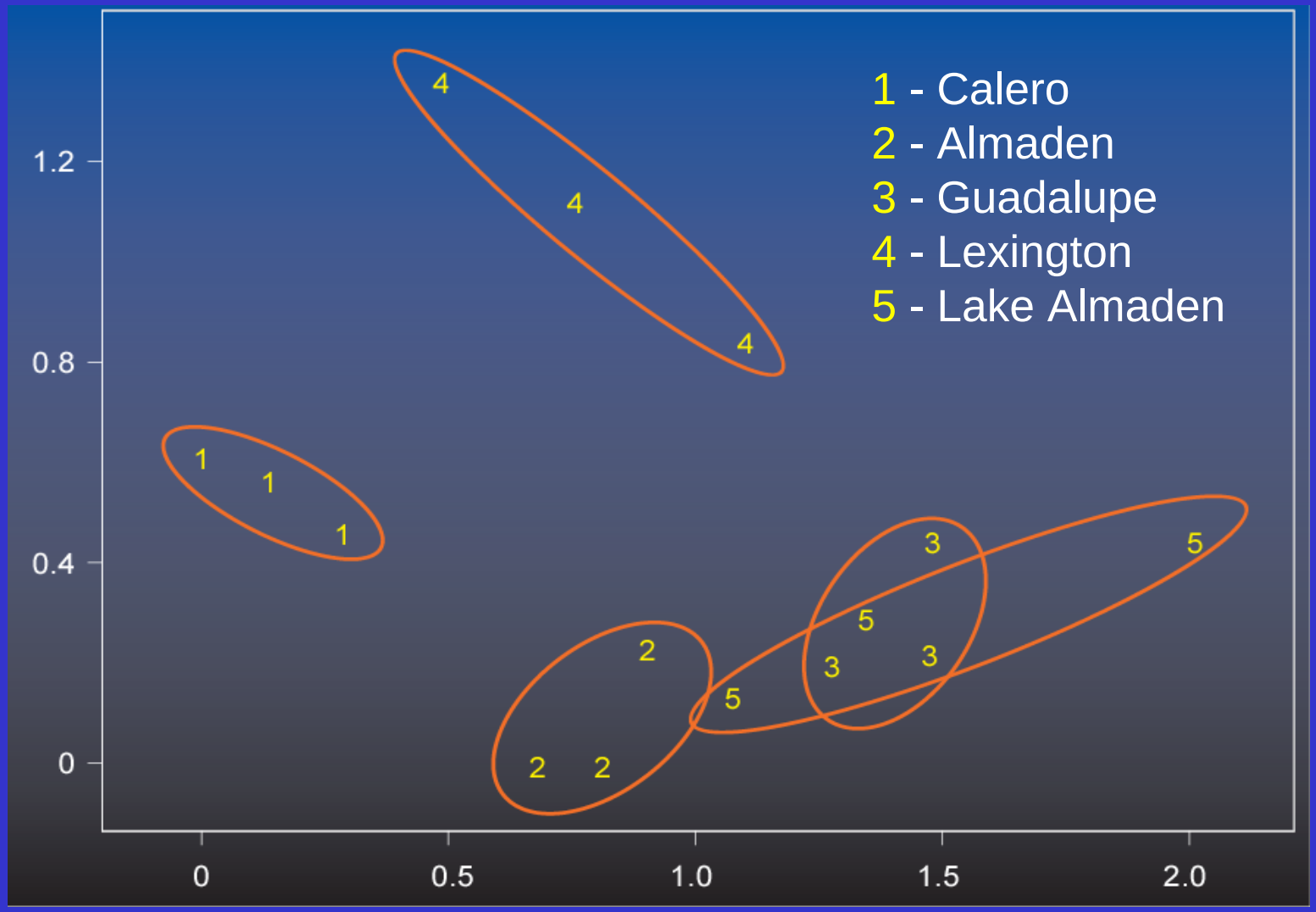

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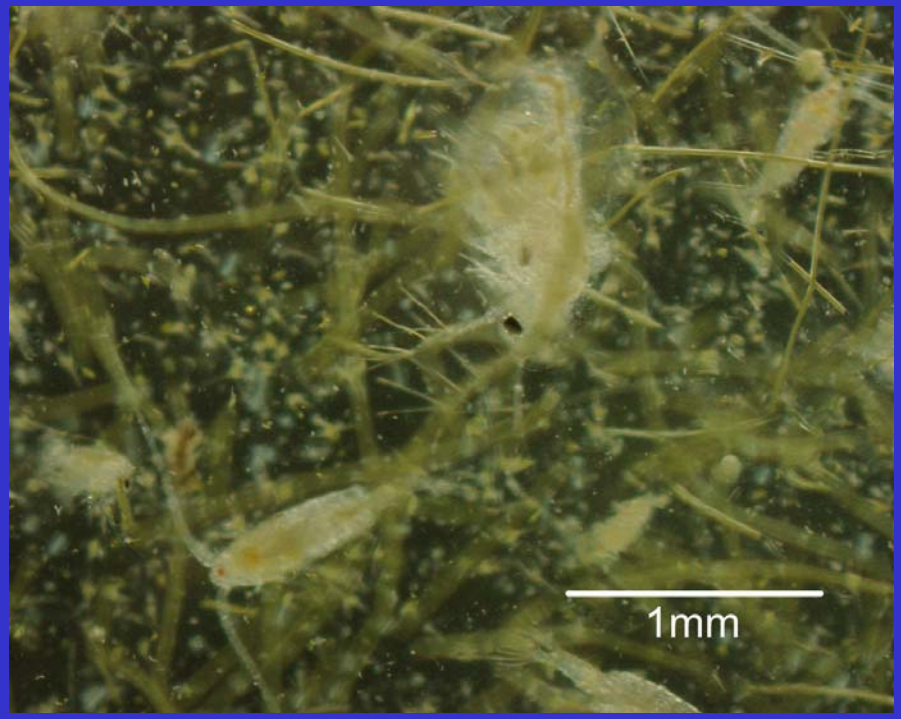
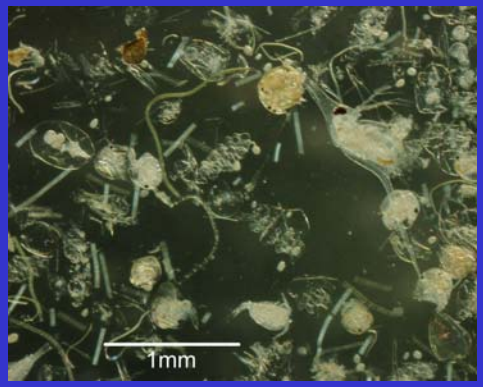
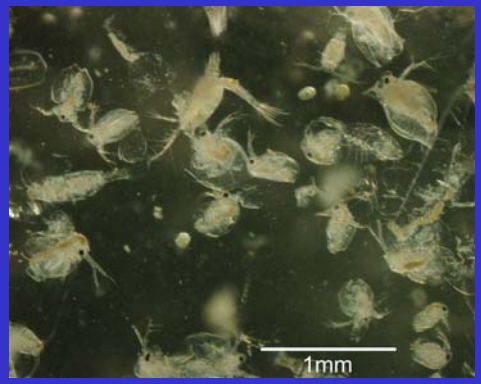
Figure 13. Photomicrographs showing a contrast in zooplankton-sample composition at Almaden Reservoir relative to other sampling sites.



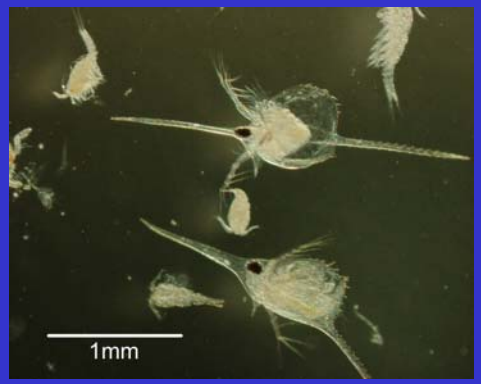
Almaden Reservoir
(Abundance of algal filaments)



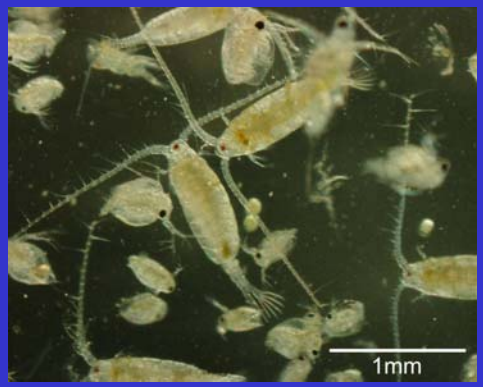
Calero Reservoir



Guadalupe Reservoir



Lexington Reservoir



Lake Almaden

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Photomicrographs by S.V. Fend

Figure 14. Field methods used in this study for sampling: A) the water column, B) phytoplankton, and C) zooplankton.

Figure 15. Photograph showing mercury analysis by cold-vapor atomic fluorescence spectroscopy (CVAFS).

Figures of merit for mercury analysis

Typical method detection limit

0.2 pM

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Figure 16. Photograph showing equipment used for dissolved organic carbon (DOC) analysis by high-temperature, non-catalytic oxidation.

Figures of merit for DOC analysis

Detection limit

0.1 mg/L

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Figure 17. Photograph showing equipment used for dissolved-metal analysis by inductively coupled plasma mass spectrometry (ICP-MS)

Figures of merit
for metal analyses

Detection limit

Cu 0.01 ug/L

Ni 0.05 ug/L

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Table 1. Specifications for size and location of five lentic systems sampled in the Guadalupe River watershed for this study, September, 2004.

Reservoir	Date Sampled	Starting Time (hr) Sampled	Location Latitude (N)	Location Longitude (W)	Surface Area (acre)	Storage Volume (acre-feet)	Surface Area (km^2)	Storage Volume (Mm^3)
Calero	9/14/2004	0900	37° 10.874'	121° 47.250'	349	9934	1.4	12.3
Almaden	9/14/2004	1400	37° 09.816'	121° 49.756'	57	1586	0.2	2.0
Guadalupe	9/15/2004	0800	37° 11.884'	121° 52.657'	74	3415	0.3	4.2
Lexington	9/15/2004	1400	37° 11.952'	121° 59.198'	412	19044	1.7	23.5
Lake Almaden[1]	9/15/2004	1630	37° 14.493'	121° 52.286'	NA	NA	NA	NA

[1] Dimensions were not available, but Lake Almaden, an abandoned quarry pit along Alamitos Creek that currently serves as a recreational area, was visibly the smallest, shallowest (Fig. 3) water body sampled.

Table 2. Phytoplankton taxonomy in five water bodies within the Guadalupe River watershed.
Density and biovolumes presented in units of cells per milliliter, and cubic micrometers per milliliter, respectively.

Water Body	Calero Reservoir						Almaden Reservoir						Guadalupe Reservoir						Lexington Reservoir						Lake Almaden					
Replicate	A	A	B	B	C	C	A	A	B	B	C	C	A	A	B	B	C	C	A	A	B	B	C	C	A	A	B	B	C	C
	Density	Biovolume	Density	Biovolume	Density	Biovolume	Density	Biovolume	Density	Biovolume	Density	Biovolume	Density	Biovolume	Density	Biovolume	Density	Biovolume	Density	Biovolume	Density	Biovolume	Density	Biovolume	Density	Biovolume	Density	Biovolume	Density	Biovolume
CYANOPHYTA																														
Anabaena catenula var. *affinis*	180	45234	80	20104	85	21360.5															80	20105.6								
Anabaena flos-aquae	630	99225	925	145687.5	1027.5	161831.3																								
Anabaena spiroides							54	19008	32	10777.6															28	7036.4			12	2413.2
Anabaenopsis elenkinii	180	24732	85	11679	117.5	16144.5															10	1005.3								
Aphanizomenon flos-aquae							338	47793.2					373.5	24950	263.3	17588.4	141.8	9472.2												
Aphanizomenon gracile	980	35574	677.5	24593.3	637.5	23141.3													65	1917.5	20	590	102	3009					28	1195.6
Aphanizomenon issatchenkoi	100	1963.4	115	2254	80	1568					80	7856													20	908	18	817.2	12	544.8
Aphanocapsa delicatissima																					750	1350								
Aphanocapsa planctonica	250	1050	1750	7350																										
Aphanothece minutissima							10687.5	8550	8160	6528	8500	6800																		
Aphanothece smithii	15000	10500	11250	7875	12000	8400							2270.4	3632.6	5676	9081.6	2683.2	4293.1	60250	42175	78750	63000	56250	39375	10500	7350	4375	3062.5	11500	8050
Chroococcus sp.							125	2575	62.5	1287.5	375	7725					51.6	216.7									500	575	250	287.5
Cyanotetras sp.																									250	2450	5625	55125	3000	29400
Cylindrospermopsis raciborskii																			612.5	3858.8	1515	9544.5	887.5	5591.3						
Dactylococcopsis irregularis	1280	10240	1080	8640	920	7360	20	560	40	1120	20	560							8000	64000	12960	103680	10000	80000						
Lyngbya birgei							261	194366.7	212	157876.4	342.5	255060																		
Merismopedia glauca																									83500	592850	78500	557350	120500	855550
Microcystis wesenbergii																									88	5764				
Phormidium splendens	720	2880	720	7632	1600	16960																								
Planktothrix agardhii																									132	8817.6	382	25517.6	345	23046
Snowella lacustris															81	3288.6														
Synechococcus sigmoideus	250	600	750	3150	2250	9450													125	337.5	250	625	250	625	500	2425	3750	13125	3000	16500
CHRYSOPHYTA																														
Chrysocapsella sp.															63	9922.5														
Chrysolykos skujae	5	940																												
Dinobryon bavaricum	2	513.2																												
Dinobryon divergens							26	13941.2	7.5	4021.5	12.5	6702.5	450	115470	515.3	132213.2	526.5	135100												
Dinobyron sociale var. *americanum*	5	1410			10	2820															1	282								
Kephyrion sp.																	4.5	92.7	20	412										
Uroglena sp.																			18	756										
XANTHOPHYTA																														
Goniochloris fallax			5	421	1	84.2																								
BACILLARIOPHYTA																														
Acanthoceras zachariasii																			1	26605	1	25764.2	1	26605						
Achnanthes sp.	120	12816	40	4272	40	4272																								
Asterionella formosa							8	1873.6	15	3513	30	7020	6.8	2652	5.6	2184	7.9	3081												
Aulacoseira granulata var. *angustissima*	50	26600	10	5320	40	21280	29	6583	2	2256.4																				
Cyclotella meneghiniana	280	394856	120	135720	40	56408																								
Cyclotella ocellata													49.5	17652	94.5	29971.4	41.6	17946.7												
Cyclotella pseudostelligera	920	34684	2680	295500	560	21112													80	24160	10	3015.8	240	18840						
Fragilaria crotonensis							2670	3343908	2075	2598730	2220	2780328	168.8	150991.6	220.5	197237.3	106.9	95622.1							40	25920			20	12960
Navicula viridula			1	8419.2																										
Nitzschia acicularis	280	7504	80	3520	440	12960															2.5	100	10	400						
Nitzschia closterium																	9	666												
Nitzschia gracilis	200	58800	400	150280	120	45084																								
Nitzschia paleacea	240	21312	880	78144	400	24000																								
Nitzschia sp.	80	8752																												
Nitzschia tubicola					120	30780															1	810								
Stephanodiscus sp.													1.1	6272																
Stephanodiscus tenuis	800	201040	840	527772	800	201040																								
Synedra delicatissima	10	20027	12.5	25033.8	10	20027.1																								
Synedra rumpens var. *familiaris*																			230	28520	175	21700	185	22940						
Synedra sp.							1	7488																						
CRYPTOPHYTA																														
Campylomonas marsonii							2	837.7																						
Campylomonas reflexa							1	3552																						
Cryptomonas erosa							2	4126.4									13.5	5428.4	1	1664					920	413080	590	264910	1500	673500
Cryptomonas ovata							2	8504.7																						
Cryptomonas sp.	200	67020	240	80424	480	160848									1.1	57321	1.1	3500												
Komma caudata							1240	138012	700	77910	770	85701	22.5	688.5	81	2478.6	45	1377	20	896	120	6036	40	2012						
Plagioselmis nannoplanctica	120	11784	120	11784	40	3928																								
DINOPHYTA																														
Ceratium hirundinella f. *carinthiacum*	1	42338.3	5	163761															1	26177	10	261770	4	104708						
Ceratium hirundinella f. *hirundinella*							135	7034850	102.5	5341275	105	5471550	1.1	57321	1.1	57321	1.1	57321												
Glenodinium sp.	1	42338.3																												
Peridiniopsis cunningtonii	10	68422	15	102633	17.5	119738.5													2	21859.6	7.5	42410.3	2	18587.2						
Peridiniopsis polonicum	30	562956	17.5	328391	15	281478													3	70092	2.5	66302.5	1	23364						
EUGLENOPHYTA																														
Euglena clara	1	1832.5																												
Euglena caudata																			4	28788	1	7197	3	34084						
Euglena elongata																									1	1172.8				
Euglena sp.																									1	4136.6				
Phacus longicauda																									1	69113	2	138226	5	345565
Phacus tortus																											2	96208.4	1	48104.2
Trachelomonas hispida var. *coronata*																			1	6283	1	6283								
Trachelomonas hispida																					1	2356.1								
Trachelomonas volvocina	10	5700.4			5	7850							1.1	2682.5	2.3	5608.8	1.1	2682.5												
PRASINOPHYTA																														
Tetraselmis cordiformis	5	5655			10	11309.4	2	3534.2	5	10053																				
CHLOROPHYTA																														
Ankyra judayi																	2.3	33.8												
Chlamydocapsa sp.																									6	21903.6	2	16218.6		
Chlorella minutissima							1687.5	4387.5	7062.5	8121.9	62.5	162.5	180.5	207.6	206.4	237.4	51.6	216.7	1312.5	5512.5	3250	13650	1625	6825	500	900	250	450	250	450
Chlorella sp.							187.5	1931.2							45	1507.5														
Closterium aciculare							3	18861.6	5	22093.5	5	22093.5													47	38403.7	36	29415.6	32	26147.2
Closterium acutum var. *variabile*																									4	2618			9	5890.5
Coelastrum pulchrum																									390	104559	198	53063.8	1300	348530
Coenococcus sp.																									8	524	68	4454	70	4585
Coenochloris fottii																	18	253.8												
Crucigenia tetrapedia													180	7074	198	7781.4	126	4951.8	80	2680	80	2680	160	5360						
Dimorphococcus lunatus													144	5846.4	31.5	1279			120	4872	1000	8400	250	2100						
Eudorina elegans							14	15794.8																						
Lagerheima genevensis			5	65.5															120	1968	10	302.6	100	2540						
Monoraphidium minutum							20	606			10	302.6	31.5	1622.3	9	463.5	4.5	231.8							40	944				
Mougeotia sp.															3.4	1759.5	2.3	1190.3												
Nannochloris sp.	41750	48012.5	12500	14375	36250	41687.5	750	525	62.5	43.8			2658	1860.6	2193	1535.1	5701.8	4269.9	1500	1050	10125	8100	7875	5512.5	1750	3150	250	450	1500	2700
Oocystis apiculata					2	898	2	898			2	898	13.5	2544.8			2.3	581												
Pediastrum simplex																									12	5262	15	6577.5	10	4385
Pediastrum tetras			4	282.7																										
Raphidocelis microscopica	360	1872	800	4160	480	2496													480	3024	320	2016	440	2772						
Scenedesmus armatus			160	10720																										
Scenedesmus communis	640	18112	240	67680	560	157920																								
Scenedesmus denticulatus			4	242																										
Scenedesmus ecornis	240	2016																												
Scenedesmus sp.					80	840																								
Schroederia setigera			40	504	20	252	160	9680	100	6050	50	3025																		
Staurastrum sp. 1									1	5370					0.5	2826														
Staurastrum sp. 2																									1	854.5	2	1709	6	5127
Tetraedron minimum	40	2620	40	2620	80	5240													140	9170	10	655	10	655						
TOTAL DENSITY	65970	1901931.6	36691.5	2261009	59338	1500568.3	18427.5	10892748	18644.5	8257027.6	12584.5	8655784.1	6552.3	401467.9	9691.5	541605.8	9543.6	348528.5	73186	376777.9	109463.5	679730.9	78435.5	405905	98739	1320142.2	94565	1267255.2	143350	2414931
Percent living algae	57		51		51		40		63		25		43		18		18		67		70		73		82		54		61	
					density	biovolume					density	biovolume					density	biovolume					density	biovolume					density	biovolume
			avg		**54000**	**1887836**			avg		**16552**	**9268520**			avg		**8596**	**430534**			avg		**87028**	**487471**			avg		**112218**	**1667443**
			stdev		15352	380416			stdev		3438	1420683			stdev		1771	99766			stdev		19606	167137			stdev		27042	647884

Table 3. Characterization of zooplankton assemblages in five water bodies within the Guadalupe River watershed.

Water Body	Calero Reservoir						Almaden Reservoir						Guadalupe Reservoir						Lexington Reservoir						Lake Almaden					
Replicate	A	A	B	B	C	C	A	A	B	B	C	C	A	A	B	B	C	C	A	A	B	B	C	C	A	A	B	B	C	C
Density\Biomass	No./m3	BM/m3	No./m3	BM/m3	No./m3	BM/m3	No./m3	BM/m3	No./m3	BM/m3	No./m3	BM/m3	No./m3	BM/m3	No./m3	BM/m3	No./m3	BM/m3	No./m3	BM/m3	No./m3	BM/m3	No./m3	BM/m3	No./m3	BM/m3	No./m3	BM/m3	No./m3	BM/m3
Copepods																														
Acanthodiaptomus siciloides males	0	0	0	0	0	0	9213	80153	7663	66668	7308	63580	376	3346	723	6435	1048	9327	0	0	0.3	2.3	0	0	2475	25968	4872	51156	2015	21158
Acanthodiaptomus siciloides females	0	0	0	0	0	0	10077	85655	10421	88579	8404	71434	1094	11815	434	4687	2018	21794	0	0	0.9	10	0	0	4332	65846	7308	111082	1727	26250
Acanthodiaptomus siciloides copepodids	32.8	59	11.9	21.4	0	0	28214	45142	32183	51493	24482	39171	3762	6395	8815	14986	10437	17743	3.4	7.5	1.4	3	0.9	1.7	11448	24041	23548	49451	6334	13301
Acanthodiaptomus siciloides N1-2	0	0	0	0	0	0	1152	na	3985	na	1096	na	0	0	0	0	116	na	0	0	0	0	0	0	309	na	0	0	0	0
Acanthodiaptomus siciloides N3-6	17	8.5	13.5	6.8	0	0	4606	1842	5211	2084	3289	1316	68	27	578	231	543	217	0	0	0	0	0	0	309	139	812	365	0	0
Cyclops spp. Males	0	0	1.6	5.8	1.9	5.7	0	0	307	706	0	0	376	1241	578	1907	854	2818	0	0	0.9	2.23	0	0	2166	11263	6496	33779	0	0
Cyclops spp. females	0	0	0.8	2	0	0	0	0	0	0	0	0	34	731	289	6214	233	5010	0	0	0	0	0	0	3713	60151	1624	26309	576	9331
Cyclops spp. Copepodids	3.4	3.4	41	41	39	39	6910	5528	10421	8337	7673	6138	340	255	1879	1409	2988	2204	76	53.2	8.3	5.8	12.9	9	4332	5198	7308	8770	2015	2418
Cyclops spp. N1-2	0	0	0	0	0	0	576	na	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cyclops spp. N3-6	3.4	1.4	0	0	1.1	0.4	1727	691	0	0	0	0	34	14	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cladocerans																														
Alona	2.3	2.5	0.8	0.9	1.1	1.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Bosmina	3.4	1.4	25	10	7.6	3.1	864	432	1226	613	1827	914	1471	1103	8092	6069	18430	13823	28	16.8	11	7	9	5	71781	53836	125860	94395	47216	35412
Chydorus	10.2	3.1	5.6	1.7	9.5	31	864	259	1533	460	365	110	0	0	0	0	0	0	38	11.4	1.7	0.5	4.2	1.3	0	0	0	0	0	0
Daphnia ambigua	0	0	0	0	0	0	29942	52399	22375	39156	10962	19184	410	1066	2457	6388	1280	3328	0	0	0.3	0	0	0	928	1763	6496	12342	1440	2736
Daphnia lumholzii	0	0	3.2	4.8	3	4.5	0	0	307	2610	0	0	0	0	0	0	0	0	7	12.6	0.13	0.5	1.5	2.7	0	0	0	0	0	0
Daphnia parvula	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5569	7825	0	0	0	0
Daphnia sp.	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2166	15162	0	0	0	0
Diaphanosoma	0	0	0	0	0	0	21593	23572	15325	16858	10962	12058	34	17	0	0	78	39	0	0	0	0	0	0	0	0	812	731	0	0
Simocephalus	0	0	0	0	0	0	6046	12092	8889	17778	7308	14616	5062	15186	20664	61992	8730	26190	10	20	9.7	19.4	4.5	9	21040	55540	30856	76328	12092	34549
Herbivorous Rotifers																														
Brachnionus	0	0	0	0	0	0	288	6.9	307	7.4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Keratella	0	0	0	0	0	0	0	0	307	7.4	0	0	0	0	0	0	39	1	0	0	0.3	0	0	0	0	0	0	0	288	6.9
Polyarthra	1.1	0.03	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.3	0.08	0.3	0	0.3	0.01	0	0	0	0	0	0
Other rotifers	322	7.8	635	15.2	726	17.5	864	20.7	613	30.7	1192	98	0	0	0	0	0	0	0.9	0.18	0	0	0	0	0	0	0	0	2879	83
Carnivorous Rotifers																														
Asplanchna [2]	62	18.6	12	3.6	53	16.9	7198	2159	17471	5241	11693	3508	2	0.6	434	130	1009	303	155	46.5	6.3	1.9	25	7.5	1237	385	812	359	2591	777
Benthos																														
Ostracods	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3.4	na	0	0	na	na	0	0	0	0	0	0
Site totals	**396**	**87**	**738**	**110**	**789**	**102**	**122936**	**307793**	**121073**	**295388**	**84868**	**228619**	**13061**	**41196**	**44509**	**110318**	**46794**	**102494**	**165**	**122**	**35**	**51**	**33**	**29**	**130568**	**326732**	**215992**	**464708**	**76582**	**145245**
Site averages	**641**	**100**					**109626**	**277266**					**34788**	**84669**					**78**	**67**					**141047**	**312228**				
Site STD	**214**	**11**					**21461**	**42584**					**18851**	**37852**					**75**	**49**					**70293**	**160225**				
Site STD/average	**0.33**	**0.12**					**0.20**	**0.15**					**0.54**	**0.45**					**0.97**	**0.73**					**0.50**	**0.51**				
Overall STD/average	0.51	0.39																												

[1] Taxonomic analyses by James Orsi.

[2] *Asplanchna* biomass not calculated because it is carnivorous. Ostracods are benthic animals and hence no biomass was calculated.
Biomass was not calculated for the N1-2 naupliar stages because they do not feed.

Table 4. Mercury speciation in the water column and biota.

Results from Frontier for Guadalupe Watershed sampling on 9/14/04 and 9/15/04

Water-column Samples

			Inorganic and Methyl Hg				Methyl Mercury				Percent	
			Total Hg (ng/L)		Percent	Ratio	Methyl Hg (ng/L)		Percent	Ratio	Methyl / Total	
Reservoir	Site #	Rep.	Total	Dissolved	Dissolved	Total:Diss.	Total	Dissolved	Dissolved	Total:Diss.	Total	Dissolved
Calero	**1**	A	4.57	0.52	11	9	0.239	0.051	21	5	5	10
		B	4.04	0.52	13	8	0.248	0.048	19	5	6	9
Almaden	**2**	A	6.45	1.17	18	6	1.430	0.367	26	4	22	31
		B	10.10	1.18	12	9	1.070	0.275	26	4	11	23
Guadalupe	**3**	A	17.50	1.11	6	16	0.360	0.087	24	4	2	8
		B	16.40	1.28	8	13	0.365	0.087	24	4	2	7
Lexington	**4**	A	1.54	0.47	31	3	0.123	0.040	33	3	8	9
		B	2.96	0.49	17	6	0.122	0.039	32	3	4	8
Lake Almaden	**5**	A	20.10	2.62	13	8	1.670	0.410	25	4	8	16
		B	17.20	2.40	14	7	1.410	0.390	28	4	8	16
		Average =	10.09	1.18	14	8	0.70	0.18	26	4	8	14
		Standard Deviation =	7.07	0.78	7	4	0.62	0.16	4	1	6	8

Mean Concentrations for Summer, 2003 (Tetra Tech, 2003)

Total Hg (ng/L)		Methyl Hg (ng/L)			
Total	Dissolved	Total	Dissolved		Reservoir
2.0	0.25	0.8	0.14	epilimnion	Calero
3.4	2.02	3.1	1.25	hypolimnion	
5.6	1.36	2.3	0.61	epilimnion	Almaden
5.9	1.05	2.3	0.56	hypolimnion	
10.6	1.05	3.3	0.49	epilimnion	Guadalupe
7.6	1.63	2.9	0.74	hypolimnion	
1.4	0.20	0.6	0.07	epilimnion	Lexington
2.2	0.69	1.3	0.74	hypolimnion	
25.4	4.4	17.9	1.72	epilimnion	Lake Almaden
n/a	n/a	n/a	n/a	hypolimnion	

Biological Samples (All biological concentrations relative to dry weight.)

			Phytoplankton			Zooplankton			Small Fish		
Reservoir	Site #	Rep.	Total-Hg (ng/g)	Methyl-Hg (ng/g)	% Methyl	Total-Hg (ng/g)	Methyl-Hg (ng/g)	% Methyl	Total-Hg (ng/g)	STD (ng/g)	Replicates (n)
Calero	**1**	A	25.2	<1.50	<6	146.0	95.1	65	1520	1790	20
		B	NA	NA		NA	NA				
		C	NA	NA		NA	NA				
Almaden[1]	**2**	A	56.6	4.11	7	861.9	647.9	75	4830	1220	20
		B	NA	NA		859.9	639.9				
		C	NA	NA		NA	NA				
Guadalupe	**3**	A	172.0	<1.50	<1	885.0	756.0	85	4240	560	20
		B	NA	NA		890.0	755.0				
		C	NA	NA		918.0	780.0				
Lexington	**4**	A	22.8	<1.50	<7	102.0	84.2	83	450	90	20
		B	NA	NA		NA	NA				
		C	NA	NA		NA	NA				
Lake Almaden	**5**	A	74.3	8.20	11	383.0	179.0	44	1820	370	20
		B	NA	NA		391.0	178.0				
		C	NA	NA		405.0	162.0				
		Average =	70			631	492	70	2572	806	
		Standard Deviation =	61			358	314	17	1875	690	

[1] The netted zooplankton sample from Almaden Reservoir was an assemblage of both zooplankton and significant amounts of algal filaments (Fig. 13). The mercury concentrations from this assemblage were corrected for algal-concentration dilution based on the relative dry mass of the zooplankton (46 ± 6 % dry weight rounded to 50%) and phytoplankton.

Table 5. Dissolved organic carbon (DOC) concentrations at the chlorophyll-a maximum depth[1].

Water Body	Sampling Depth (meters)	DOC (uM) mean	DOC (uM) 95% ci	DOC (mg-C/L) mean	DOC (mg-C/L) 95% ci
Calero Reservoir	**2**	363	2	**4.36**	**0.02**
Almaden Reservoir	**2**	182	4	**2.18**	**0.04**
Guadalupe Reservoir	**2**	168	2	**2.01**	**0.02**
Lexington Reservoir	**2**	256	1	**3.07**	**0.01**
Lake Almaden	**6**	224	3	**2.69**	**0.03**

[1] When a discernable peak in chlorophyll-a concentration was not observed in the depth profile, the water column was sampled at a depth of 2 meters.

Table 6. Dissolved trace-metal concentrations (micrograms per liter) at the chlorophyll-a maximum depth[1].

	Copper		Cadmium		Zinc		Nickel		Iron		Lead		Manganese		Cobalt		Vanadium	
Water Body	mean	95%ci	mean	95%ci	mean	95%ci	mean	95%ci	mean	95%ci	mean	95%ci	mean	95%ci	mean	95%ci	mean	95%ci
Calero Reservoir	**1.210**	0.027	**0.002**	0.000	**0.85**	0.06	**2.00**	0.01	**41.5**	1.4	**0.006**	0.000	**0.341**	0.006	**0.069**	0.000	**6.674**	0.000
Almaden Reservoir	**0.392**	0.004	**0.000**	0.001	**0.60**	0.00	**1.15**	0.01	**48.6**	0.7	**0.008**	0.000	**0.775**	0.005	**0.079**	0.000	**2.376**	0.000
Guadalupe Reservoir	**0.740**	0.001	**0.002**	0.000	**0.73**	0.01	**11.46**	0.04	**65.5**	1.5	**0.015**	0.000	**0.348**	0.003	**0.049**	0.001	**3.168**	0.001
Lexington Reservoir	**0.725**	0.002	**0.002**	0.000	**1.32**	0.01	**1.12**	0.02	**58.7**	0.9	**0.004**	0.000	**0.381**	0.002	**0.047**	0.001	**1.456**	0.001
Lake Almaden	**0.680**	0.002	**0.000**	0.000	**1.08**	0.02	**1.94**	0.03	**48.2**	0.4	**0.005**	0.001	**1.822**	0.009	**0.052**	0.000	**1.988**	0.000

[1] When a discernable peak in chlorophyll-a concentration was not observed in the depth profile, the water column was sampled at a depth of 2 meters.