

Clear Lake Report 2010

Clear Lake Report

Clear Lake Historical Data Analysis

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2010

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1. Background and Objectives

The Clear Lake watershed is currently subject to separate TMDL requirements for mercury (adopted December 2002) and nutrients (adopted June 2006). The scientific justification for these TMDLs was significant, including an extensive water quality monitoring program that has been in place to some extent since the late 1960s. Most recently (September 26, 2008) a document entitled *Monitoring and Implementation Plan – Clear Lake Mercury and Nutrient TMDL's* was published. This document includes areas of discussion including, but not limited to responsible parties and the stakeholder groups, existing efforts of stakeholders that implement the Clear Lake TMDL's, and an discussion of appropriate monitoring for evaluating conditions in the lake (vis-à-vis, determining changes in the state of Clear Lake's level of impairment).

A Clean Lake Study (Richerson et al. 1994) used available data to evaluate nuisance blue-green algal blooms in Clear Lake in preparation for the Clear Lake Nutrient TMDL. Phosphorus was targeted in that report as a major cause of the algal blooms. However, commencing in the early 1990s, LCWPD staff saw an improvement in mean, minimum and maximum water clarity as measured by Secchi depth. This improvement continues through the end of 2008 (Data from DWR provided by Tom Smythe, LCPWD). Interestingly, LCPWD analysis of the water quality data through 2002 indicates that “no major changes in lake chemistry were noted during this analysis”, including phosphorus. This lead the LCPWD to hypothesize that phosphorus reduction may not be the “only action required to improve water clarity and quality.”

Given that, among other things, (1) water quality data has continued to be collected in the 15 or so years since the 1994 Clear Lake Report, (2) the much improved clarity first seen in 1990 has been maintained for the last 18 years, (3) water quality data for new, yet vital parameters is now being collected (e.g. chlorophyll *a*), (4) phosphorus levels in the lake – as analyzed from 1992-2001 - appear not to have changed significantly relative to levels found in the 1970s and 1980s.

The goal of the present project was to undertake a review of lake data collected at Clear Lake over the last four decades in an effort to update current thinking on the cause(s) of high primary productivity and nuisance algal blooms in Clear Lake. A particular focus of the study was to assess the status and trends of available water quality parameters such as nutrient concentrations (both N and P), phytoplankton, zooplankton, fish and Secchi depth. In particular, the review will focus on the apparent change in lake condition from the early 1990s to the present, as discussed above. In essence this work will update the older Clean Lakes Report so that decision makers and managers can plan based on current information.

For the review of the available data on lake water quality, lake sediment phosphorus content and phosphorus loading from the watershed, we were aware that there are issues that go beyond a traditional limnological analysis. Due to limited funds complete

answers to all issues were not developed and the present report focuses on the following objectives:

Objectives of the present report

1. Summary of data availability and a literature review of recent relevant publications.
 - a. Describe data sets used in previous analysis of Clear Lake water quality and data sets collected since the Clear Lake Project (after 1992).
 - b. Review methodologies used over the long-term sampling period and determine if any water quality changes were due to this factor.
 - c. Review scientific papers and reports relevant to the Clear Lake TMDL for nutrients
2. Describe status and trends for all variables for which a sufficiently long data record exists.
 - a. Statistical time series analyses will be performed for each water quality parameter individually to determine current status and historic trends. Data includes physical, chemical, biological and meteorological categories.
3. The development of a conceptual model(s) to account for the long-term behavior of Clear Lake.
 - a. Based on the results of Task #2, a conceptual model that presents hypotheses as to (i) why the clarity of Clear Lake has improved since 1991-1992, (ii) criteria to determine when Clear Lake is no longer impacted with regard to nutrients and algal blooms and (iii) management decisions regarding P-load reduction or other factors found to be related to the observed improvement in clarity.
4. Assessment of the adequacy/suitability of the present nutrient TMDL and water quality monitoring program.
 - a. Based on the finding in Tasks #1-3, evaluate and make recommendations for the Clear Lake water quality monitoring program.

2. Clear Lake Site Description

Clear Lake has been described in detail in Richardson et al. (1994) and we give only a short overview of major characteristics of the lake.

Clear Lake is the largest natural lake entirely within the borders of California. Several lake sediments have been recovered, reaching back 480,000 years (Sims et al. 1988) and to the Early Pleistocene 1.8-1.6 million years ago (Heam et al. 1988). The diatom record of these cores indicate that Clear Lake has been a shallow, productive system, similar to the modern lake, since the end of the Pleistocene (R Development Core Team 1988a; Bradbury 1988b).

The lake has three major basins of modest depth (Fig. 3.1). Maximum depth in the main basin (Upper Arm) is ~12 m, and in the other basins ~ 18 m, depending on lake water level. Residence time of the lake (the time it would take to empty at the average annual outflow) is about 4.5 years (Richerson et al. 1994). The lake is usually well mixed from top to bottom and stratification may persist during periods of calm weather during the summer. An additional source of vertical water-column mixing results from gas vents and water spring (Suchanek et al. 1993).

Clear Lake is a turbid system as a result of inorganic suspended particulate matter in the winter and algal blooms in the summer (Richerson et al. 1994). The lake has frequent blooms of noxious scum forming cyanobacteria, which largely reduce water quality and have huge impact on recreational activities on the lake and causing large economic losses.

The cyanobacteria scums are typically formed by *Microcystis*, *Anabaena* and *Aphanizomenon*, and the magnitude and composition of blooms varies substantially from year to year (Horne 1975). *Aphanizomenon* and *Anabaena* have a competitive advantage in the phosphorus rich waters of Clear Lake because of their ability to fix atmospheric nitrogen. On average the dissolved ion ratio is about 1:1 in Clear Lake, but fluctuates between large excesses of nitrogen in winter to large excesses of phosphorus in summer. Under bloom conditions in the warm seasons, dissolved forms of nitrogen are often undetectable in summer, while phosphorus levels exceed 100 µg/L (Richerson et al. 1994).

It has been suggested that the algal blooms have become more of a problem in the last half of the last century. This is also supported by frequent observations of macrophytes in the 19th and early 20th Centuries, while macrophytes have been absent in most years since the late 1930s. Cyanobacteria blooms reduce water transparency, affecting growth of macrophytes that require relatively transparent water to thrive.

The main sources of excess phosphorus and iron are typically sewage and erosion, and excess nitrogen typically derive from ground-water inflow. The phosphorus loading from sewage is small in Clear Lake (Richerson et al. 1994), and groundwater inflow into the

lake is negligible (Richerson et al. 1994). The study by Richerson et al. (1994) indicates that erosion from fine sediment entering the lake during winter runoff is the most important source of phosphorus as fine sediments carry nutrients and trace elements. The increased nutrient load from erosion is likely a result of disturbances to stream channels, filling and other earthmoving activities, and the removal of the filtering capacity of marshes.

This nutrient-rich lake produces also high densities of noxious aquatic insects, particularly the gnat *Chaoborus astictopus* has received considerable attention. This invertebrate species has a benthic and zooplanktonic immature life stages. As a consequence, the lake was treated with DDD in the 1940s and 1950s to control the gnat. DDD accumulated in the food chain and led to the reproductive failure of western grebes. This has become one of the first documented example of food chain accumulation of a chlorinated hydrocarbon pesticide (Carson 1962).

The lake is also contaminated with mercury from the abandoned Sulphur Bank Mercury Mine, now a USEPA SuperFund cleanup site (Suchanek et al. 1993). The contamination problem however continuous, as the large quantity of inorganic mercury stored in the sediment, mostly in the Oaks Arm, is being released by bacterial activity. Under anoxic conditions, inorganic mercury is converted to the toxic organic form methyl mercury, that contaminates fish and other wildlife.

The native fish fauna of the lake, mainly large minnows, has been largely replaced by intentional and unintentional introductions of warm-water fishes (Moyle 1976; Moyle 2002). Introductions of Florida strain black bass continue, and threadfin shad appeared in the lake in 1985 as a result of an accidental or unapproved introduction. Whereas historically bluegill and crappie fishery were most important, largemouth bass and channel catfish fishery has been the most important in recent years. There is a commercial fishery based upon the native cyprinid black-fish, and upon carp. The lake is also heavily used by fish-eating birds and mammals, and over wintering waterfowl and has considerable value as wildlife habitat (Richerson et al. 1994).

3. Data Source and Methods for Data Collection

3.1 Data Source

Clear Lake has been monitored since the late 1960s. Long-term physical, chemical, mineral, and biological data were obtained from monitoring programs of the California Department of Water Resources (DWR) and the Lake County Vector Control monitoring. Table 3.1 gives an overview of the available abiotic and biotic data from Clear Lake that are included in the present study.

Table 3.1. Sources of datasets used in the present study. Abbreviations: DWR: California Department of Water Resources; Vector Control: Lake County Vector Control District's monitoring program.

Data	Agency / Source	Time period	Comments
Chlorophyll	DWR		measured only sporadically between 2005 and 2009; shown in appendix
Physical data	DWR	1969-2002	
Chemical data	DWR	1969-2002	
Mineral data	DWR	1977-2001	
Water quality data (physical, chemical, mineral)	DWR	2002-2008	switch in laboratory chemical analysis in 2002
Phytoplankton	DWR	1969 - 1994	data available in biovolume; identified by different personnel
Phytoplankton	DWR	1995 - 2006	count data; were converted to biovolume in the present study; identified by 2 people
Zooplankton	Vector Control	1988 - 2002	Tow nets
Zooplankton	Vector Control	1974 - 2003	Schindler trap, Upper Arm only
Water quality (Temperature, pH, Hardness, Turbidity, Secchi depth)	Vector Control	1954 - 2002	Stations: R3S5, R4S9, R5S13
Macroinvertebrates	Vector Control	1969 - 2002	
Fish	Vector Control	1987 - 2001	Beach seine sampling

3.2 Data collection

3.2.1 Abiotic variables

Physical, chemical and mineral variables were sampled at three sampling stations between February 1969 and August 2008 at about a monthly interval. The three sampling stations (CL1, CL3, CL4) are located in the major basins of the lake (see Fig. 3.1).

Samples were taken from discrete depth from the surface to the deepest depth of the station (between 10 and 15 m, depending on water level). Physical lake data include temperature, Secchi depth, dissolved oxygen (DO), electric conductivity (EC), and turbidity. Temperature, DO, EC were typically measured at 1-m depth interval once per month. Other water quality variables (chemical and mineral) were typically collected at surface and bottom depth. Methods for sampling and analysis are described in detail in Richardson et al. (1994). Chemical lake data sampled continuously since the beginning of the monitoring program include: $\text{NH}_3\text{-N}$, Nitrate and Nitrite, Ammonia (NH_3), total nitrogen (TN), orthophosphate (PO_4), and total phosphorus (TP). N to P ratio is expressed as molar TN:TP ratio.

Mineral lake data sampled continuously over the last decades include Calcium (CA), Magnesium (MG), Sodium (NA), Cadmium (K), Sulfate (SO_4), Hardness (CaCO_3), Barium (B). In addition, Chloride (Cl) was sampled sporadically and is not illustrated in this study.

In addition to the data provided by the DWR, water quality variables were sampled by the Vector Control monitoring program, using similar methods.

Flow data for Cache Creek outflow (near Lower Lake) and water level were obtained from DWR's website at <http://nwis.waterdata.usgs.gov/ca/nwis/sw>. Minimum and maximum air temperature were recorded at Lakeport.

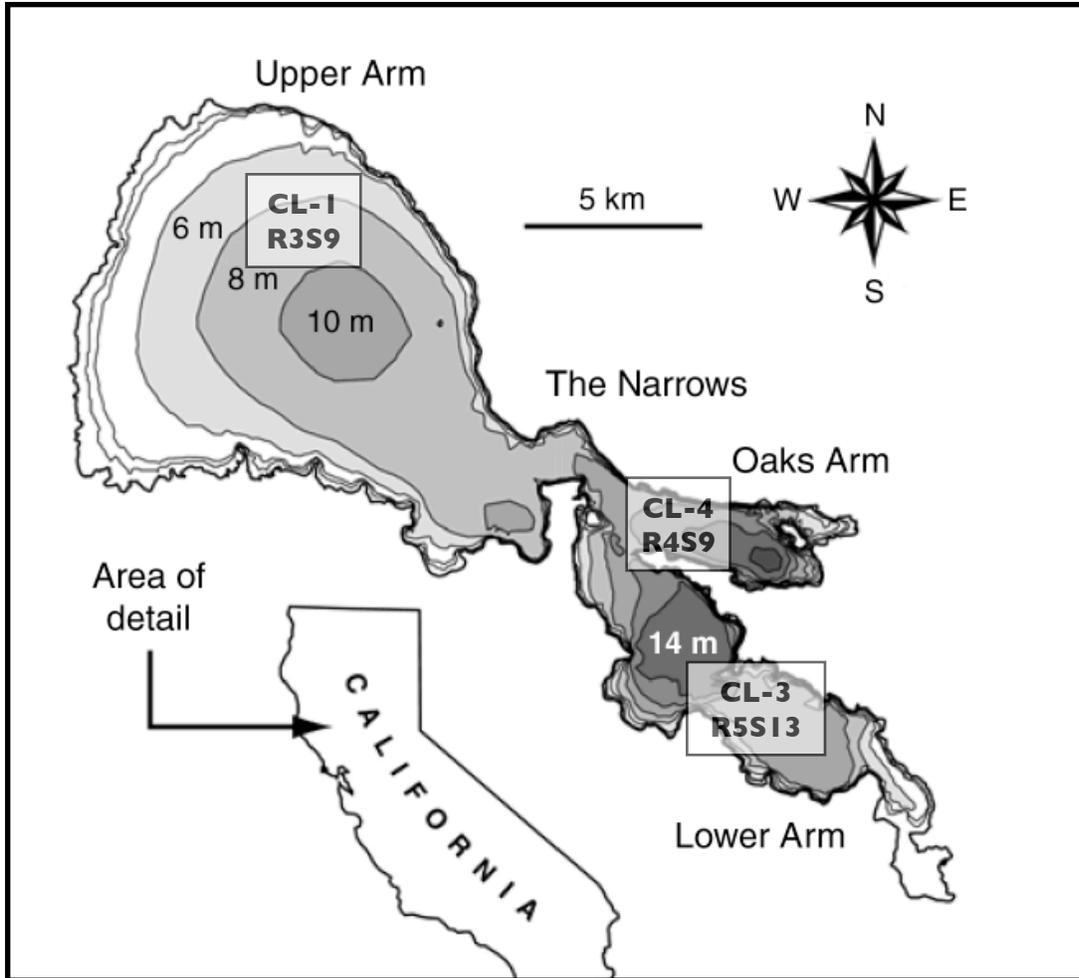


Fig. 3.1. Clear Lake sampling site locations.

3.2.2 Phytoplankton

The phytoplankton data were provided in two different datasets: biomass values from 1969 to 1994 and count values from 1995 - 2006. Phytoplankton data were counted by different personnel over the last decades: the data before the mid 1990s were identified by many different people and the most recent back to the mid 1990s primarily by 2 individuals.

Samples for phytoplankton counting and taxonomic identification were collected at different depths from the surface to the bottom of the lake at about 3-m interval at stations in the three arms of the lake (CL-1, CL-3, CL-4, see Fig. 3.1) at about a monthly interval and fixed with Lugol's solution. After sedimentation (Utermöhl technique Lund *et al.* 1958), cells were measured and counted at the species level with an inverted

microscope at 200 x magnification using a Sedgwick-Rafter cell. The sample bottles were inverted several times and a pipette of the well-mixed sample was delivered into the cell (volume =1 ml). Two transects were counted. The forms counted were identified to genus using standard reference guides (see Richerson et al. 1994). Biomass of each genus was determined by measuring several cells or colonies of all the abundant forms (remeasuring if different values were obtained), and approximating volumes by combinations of geometric shapes that were most similar to the real shape of each phytoplankton species (Hillebrand 1999). A mean cell volume was assigned for each phytoplankton species based on cell-size measurements.

In some cases, biomass per unit count (cell or colony) varied substantially, so the biomass estimates have a correspondingly large uncertainty. In addition, there were large shifts in species composition associated with shifts in personnel, thus the long-term patterns have to be treated with caution.

3.2.3 Zooplankton

Zooplankton was sampled by two methods: *i*) Schindler trap between 1974 and 2002, *ii*) Tow net between 1980 and 2008. The Schindler method yields in general higher densities compared to tow net samples, therefore the two datasets can not be merged and are shown separately.

Tow net data: samples were collected as part of the Vector Control monitoring program by vertical tow nets (80- μ m mesh size, 1 m length) from bottom to surface at stations CL1, CL3, CL4, representing the major basins of the lake (Fig. 3.1). Sampling was conducted at about monthly intervals between 1988 and 2002. Samples were preserved with Lugol's solution. A 5-ml aliquot was counted for Cladocerans, Copepods and Ostracods at 16x. A 1-ml sample was placed in a Sedwick-Rafter cell. A single pass at 200x is examined for phytoplankton and rotifers.

Schindler trap data: The zooplankton monitoring was a component of a Vector Control program focused on the Upper Arm of the lake. As a result there were no stations established in the Oaks or Lower Arms. Zooplankton were sampled monthly between 1974 and 2002 onshore and offshore stations in the Upper Arm of the lake (Cl-1) (Fig. 3.1) using a 15-L Schindler trap with an 80- μ m mesh dolphin bucket. Onshore stations were sampled by pooling surface, 1.0 m deep, and 1.5 m deep samples. Offshore stations were sampled by pooling surface, 1, 2, 3, 4, 5, and 6 m deep samples. Samples were preserved in 5% formalin and later identified and counted in the laboratory using keys by Edmondson (1959), Pennak (1989), and Thorp and Covich (1991).

3.2.4 Macroinvertebrates

Benthic Sampling was conducted once per month, year-round using an Eckman Dredge at 5 different sampling stations. Samples were rinsed in sieve-bottomed bucket over the side of the boat. Two dredges per station were collected in a single canning jar. Samples were counted in white enamel trays in the lab. The Upper Arm is examined for Tanypodinae, Chrionomidae, Chaoboridae, and Leeches. The Oaks and Lower Arms are examined for Chironomidae and Choboridae only.

3.2.5 Fish

Relative abundance of nearshore fishes was monitored biannually (summer and fall) in Clear Lake from 1986 to 2004 as part of the Lake County Vector Control District's monitoring program. A seine (9.1 m long 31.2 m high) with an ace mesh (3.2 mm apertures) was used to sample an 83-m² area of the shoreline once in June and August. On each sampling occasion three separate seine hauls were made at least 100 m apart at each of 11 fixed stations (Fig. 3.2). All captured fish were identified to species and counted, and standard lengths of up to 25 individuals of each species per capture event were measured. Additionally, five common species were selected for collection and subsequent biomass analyses. These species included: threadfin shad, inland silverside, largemouth bass, bluegill, and prickly sculpin (*Cottus asper*). to the nearest 0.1 mm and weighed to the nearest 0.001g. Mean relative biomass per unit area was estimated for each monitoring event by multiplying the number of fish captured with the estimated biomass of the mean fish size, determined using year and site-specific length–mass regressions (Eagles-Smith 2006). Biomass estimates are limited to years between 1986 and 2002 because representative size was not recorded for fish captured outside that time period.

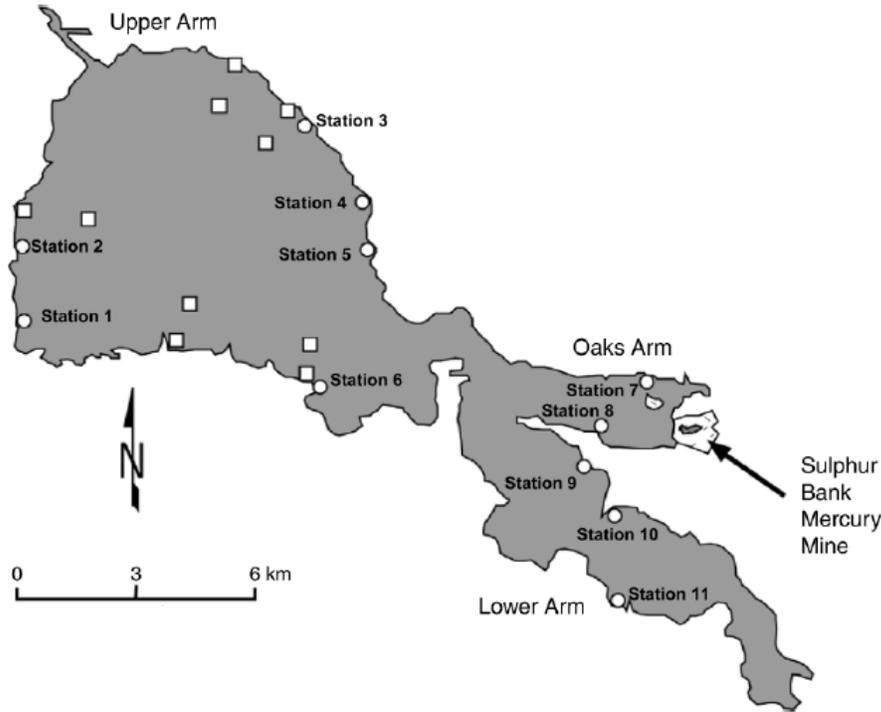


Fig. 3.2. Map of Clear Lake, California, USA. Circles are fish and squares zooplankton sampling stations as part of the Lake County Vector Control monitoring program.

3.3 Data Analysis

The significance of trends was determined by using the nonparametric Seasonal Kendall test (Hirsch & Slack 1984). To avoid *Type I* error a threshold p -value of 0.005 was considered to help compensate for serial correlation among months or among years in the time series. The overall trend slope is computed as the median of all slopes between data pairs within the same season (no cross-season slopes contribute to the overall slope estimate), known as the Theil-Sen' slope. Long-term data trajectories are illustrated using a locally weighted polynomial regression (LOESS fit \pm standard error).

Electrical conductivity data are converted to salinity using the extension of the practical salinity scale as salinities are below 2 and expressed as practical salinity unit (psu) (Fofonoff & Millard 1983; Hill et al. 1986).

Calculations and tests were carried out in the R software environment 2.10.0 (R Development Core Team 2009).

4. Status and Trends of Physical, Chemical, and Mineral Variables

Physical and some chemical lake variables were measured both by the DWR and Vector Control monitoring program. Since the DWR data is more complete, we illustrate this dataset in detail in the main text (except pH, which was measured only in the Vector Control monitoring, and turbidity, which showed a different patterns between the two datasets) and give an overview of the Vector Control data in the appendix.

4.1 Air Temperature

Maximum and minimum air temperature were continuously recorded at Lakeport between 1968 and 2009. Minimum monthly temperature ranged between 14.9 °C during the summer and -5 °C during the winter. Maximum monthly air temperature ranged between 9.1 and 37.5 °C during winter and summer period, respectively (Fig. 4.1). There was no long-term trend of the maximum and minimum monthly-averaged air temperature ($\tau < -.03$; $p > 0.38$).

Annual-averaged maximum air temperature reached 23.8 °C and decreased significantly between 1968 and 2009 ($\tau = -0.5$; $p < 0.0001$) (Fig. 4.2). Annual-averaged minimum air temperature ranged between 3.9 and 6.7 °C and showed no long-term trend ($\tau = -0.15$; $p > 0.16$).

Maximum air temperature for the month June to August showed a decreasing trend ($\tau = -0.65$, $p < 0.0001$) (Fig. 4.3). Whereas temperature for other seasons showed high interannual variability but no long-term trends.

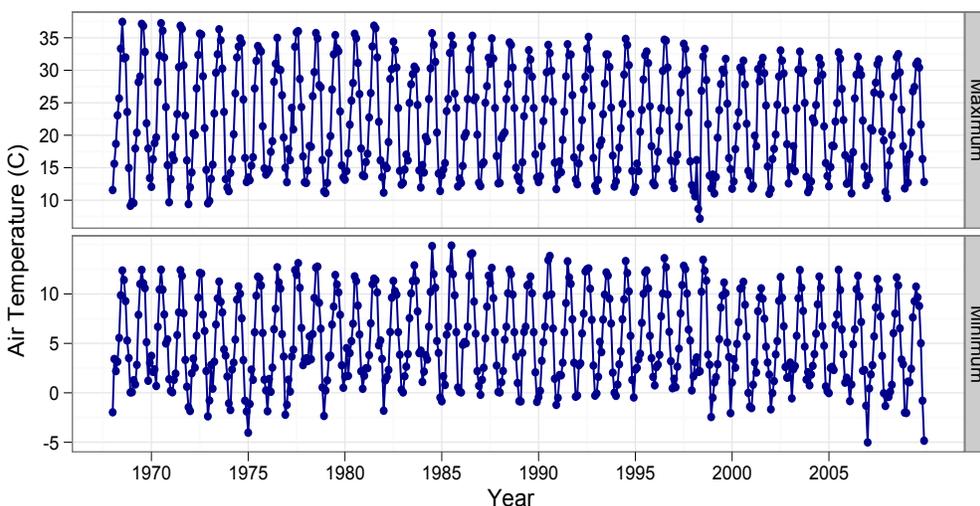


Fig. 4.1. Monthly-averaged minimum and maximum air temperature (°C) measured at Lakeport between 1968 and 2009.

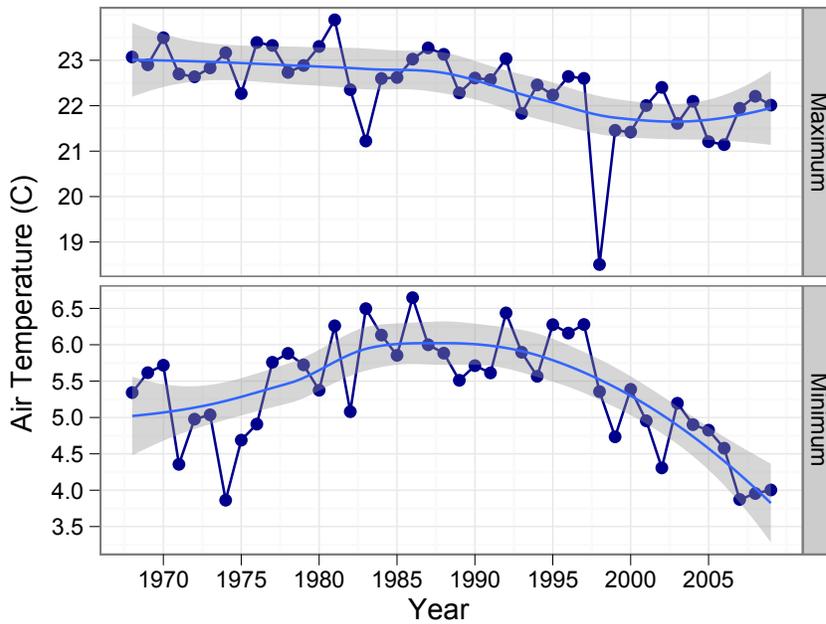


Fig. 4.2. Annual-averaged minimum and maximum air temperature (°C) measured at Lakeport between 1968 and 2009. Blue line displays a loess fit \pm standard error (grey area).

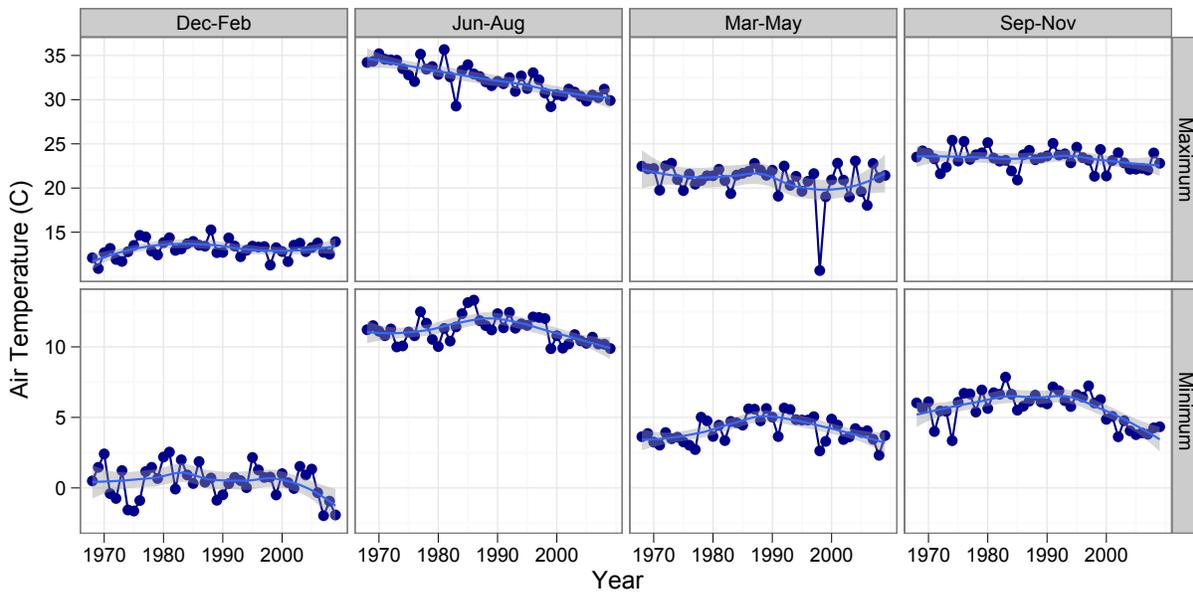


Fig. 4.3. Lakeport maximum and minimum air temperature averaged by quarters of the year. Blue line displays a loess fit \pm standard error (grey area).

4.2 Flow and Water Level

Clear Lake water level height and outflow are highly seasonal (Fig. 4.4) and peak during the spring months (Fig. 4.5). There was no long-term trend in water height and outflow

between 1969 and 2007, based on monthly-averaged data ($p > 0.2$) and seasonal averages ($p > 0.1$) (Fig. 4.6). However, flow and water level height show high interannual variability, ranging from annual average outflow of $0.02 \text{ m}^3 \text{ s}^{-1}$ to up to $44.4 \text{ m}^3 \text{ s}^{-1}$ and water level of 0.42 to 1.8 m during dry and wet years, respectively. An extended drought period occurred during 1987 - 1994 with low water outflow and low water level and a shorter drought between 1976 - 1978.

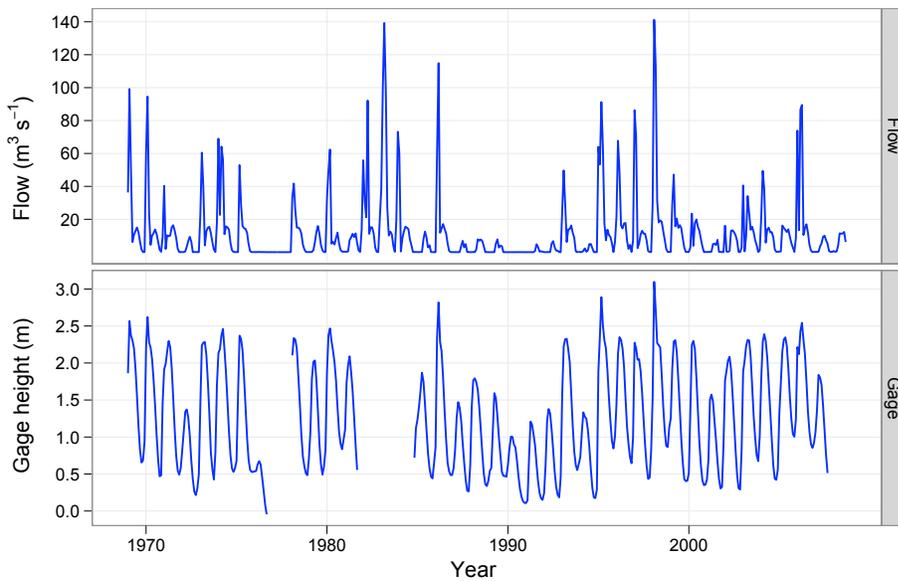


Fig. 4.5. Outflow of Cache Creek near Lower Lake and lake surface level (Gage height) from Clear Lake during the monitoring sampling program (1968 - 2008). Flow data during the 1976-77 drought have to be treated with caution.

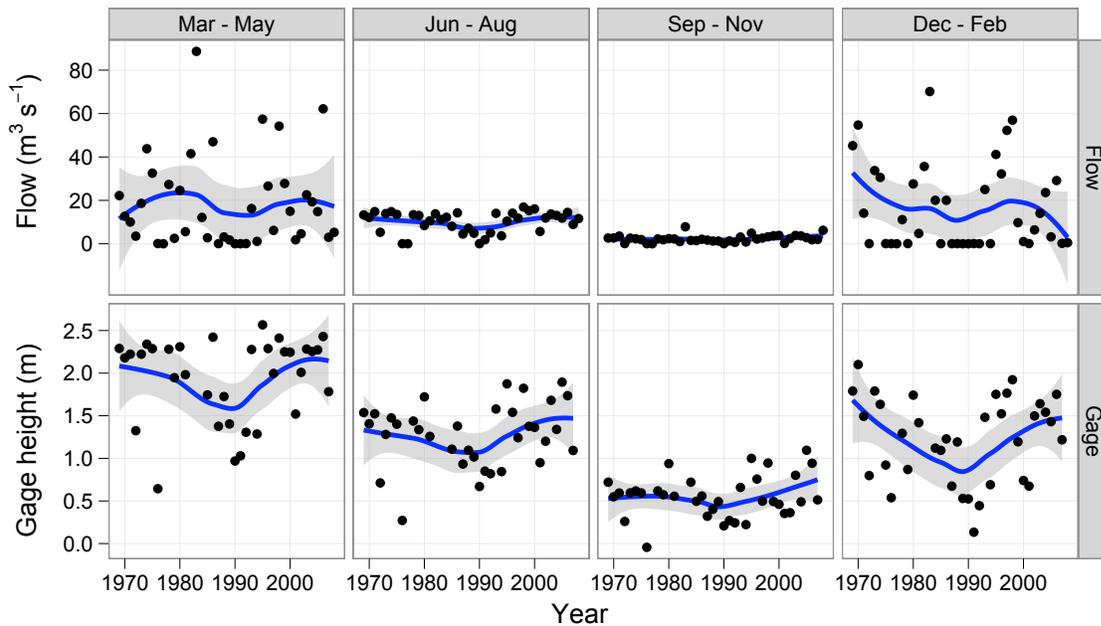


Fig. 4.6. Outflow of Cache Creek near Lower Lake and lake surface level (Gage height) from Clear Lake during the monitoring sampling program (1968 - 2008) by seasons. The blue line displays a loess fit \pm standard error (shaded area).

4.3. Lake Temperature

Vertical temperature profiles

Lake temperature vary between 7 °C in winter and reach maxima of about 27 °C in summer. The water column of Clear Lake is typically relatively well mixed from top to bottom due to its modest depth and stratifies during summer due to solar heating of the top few meters of water (Fig. 4.7). Summer stratification usually breaks down each night and the lake circulates, except during calm weather, when stratification persists for some days (Richerson et al. 1994).

Figure 4.7 highlights typical vertical temperature profiles over the season measured at daytime in 2001. This shows that the lake is vertically stratified during daytime between June and August and well-mixed the rest of the season. Detailed vertical temperature profiles over the last decades are shows in Fig. 4.8.

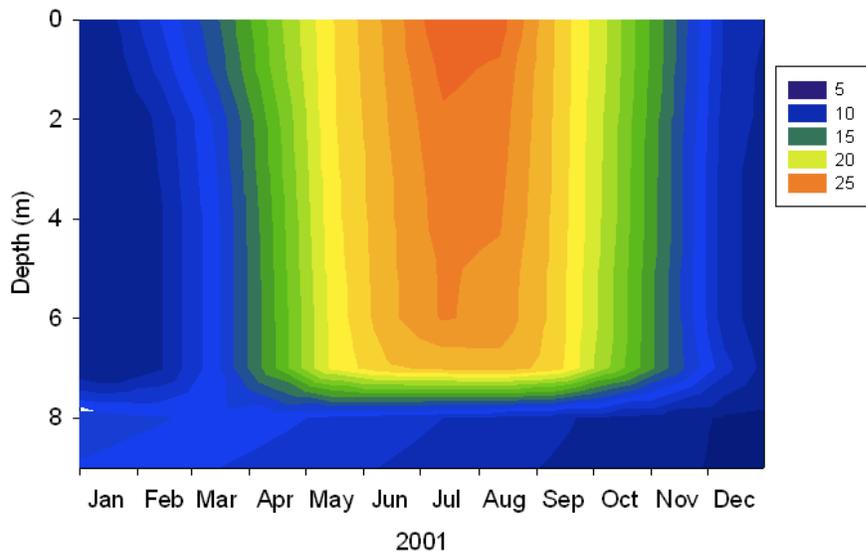


Fig. 4.7. Contour plot of temperature measurement (°C) in Clear Lake at the Upper Arm sampling station (CL-1) in 2001.

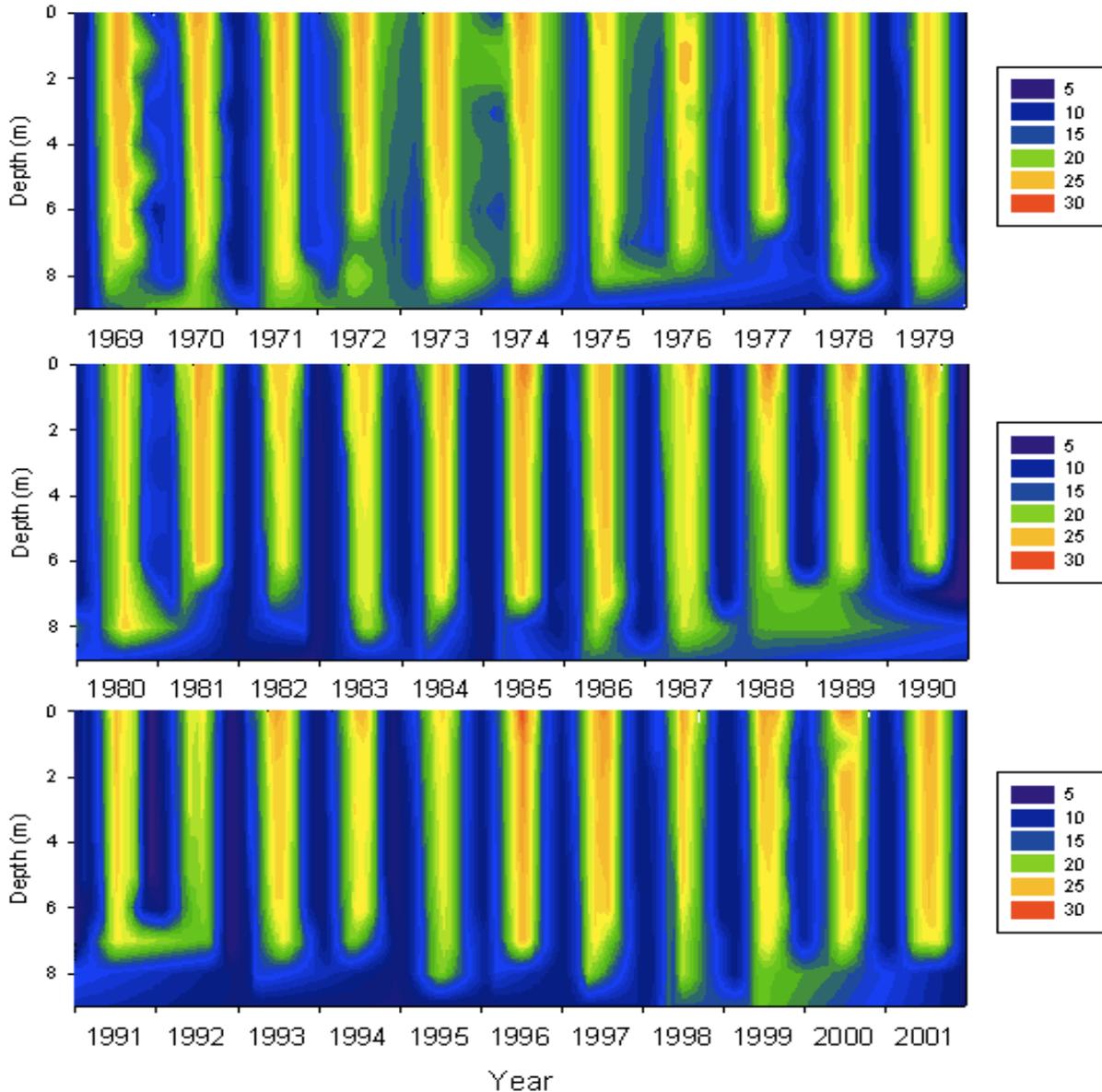


Fig. 4.8. Temperature contour plots (in °C) in Clear Lake at the Upper Arm sampling station (CL-1) between 1969 and 2001.

Depth-averaged temperature

Lake depth-averaged temperature showed high interannual variability but no significant trend over the sampling period ($\tau = 0.05$, $p = 0.17$). Lake temperature were elevated in the early 1970s, decreased in the mid 1980s to early 1990s and increased again since the late 1990s (Fig. 4.9). Average temperature were relatively low in 1991 and 1992. Discrete depths showed similar patterns and no significant trends within depth and

stations ($\tau < 0.3$, $p > 0.01$) (Fig. 4.10). Surface temperature were elevated since the year of 2000, but the long-term trend was not significant.

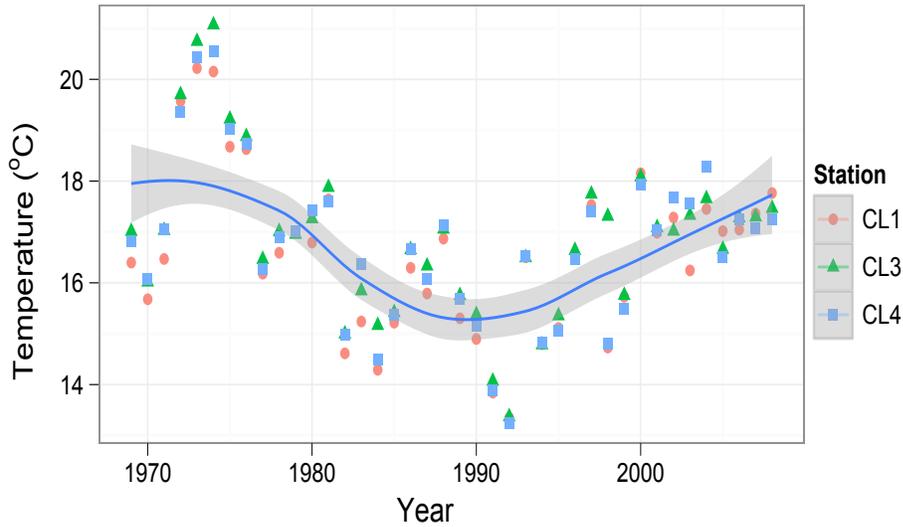


Fig. 4.9. Annual-averaged temperature over depth for each arm in Clear Lake between 1969 and 2008. Blue line displays a loess fit \pm standard error (grey area) across all sampling station.

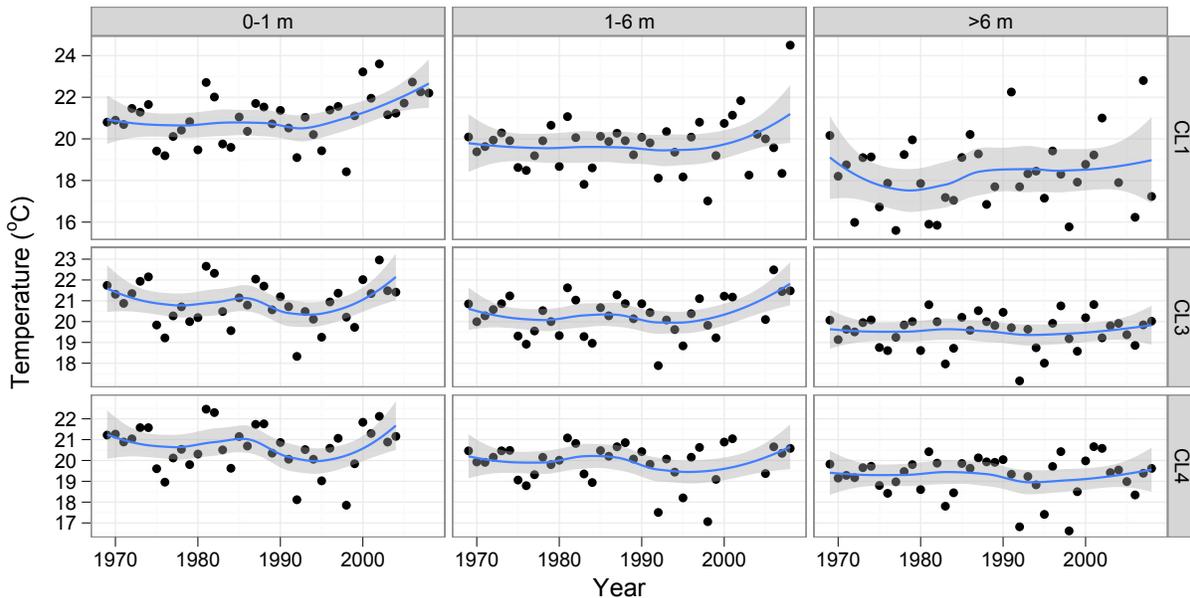


Fig. 4.10. Annual-averaged temperature by depth strata and stations in Clear Lake between 1969 and 2008. Blue line displays a loess fit \pm standard error (grey area).

4.4 Secchi depth and Turbidity

Secchi depth increased rapidly in 1990 from an annual average (April - October) of 1.1 ± 0.31 m from 1969 - 1989 to 2.2 ± 0.52 m afterwards (1990 - 2008). The positive trend ($\tau = 0.37$, $p < 0.001$) was consistent across all 3 sampling locations (Fig. 4.11). Secchi depth increased significantly in all months except July and August (Fig. 4.12). Figure 4.13 shows a comparison of annual averaged Secchi depth in May and August, illustrating the increase in spring and consistent Secchi depth in August. Detailed monthly Secchi depth readings are shown in the Appendix.

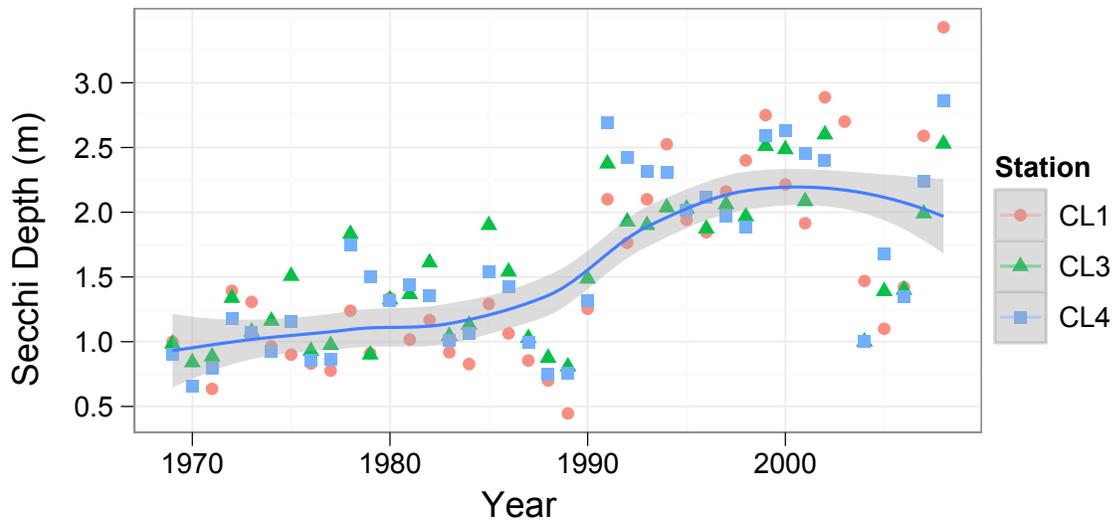


Fig. 4.11. Annual average Secchi depth (April - October) for each sampling station in Clear Lake from 1969 - 2008. Blue line displays a loess fit \pm standard error (grey area) across all sampling station. See Appendix for detailed monthly Secchi depth readings.

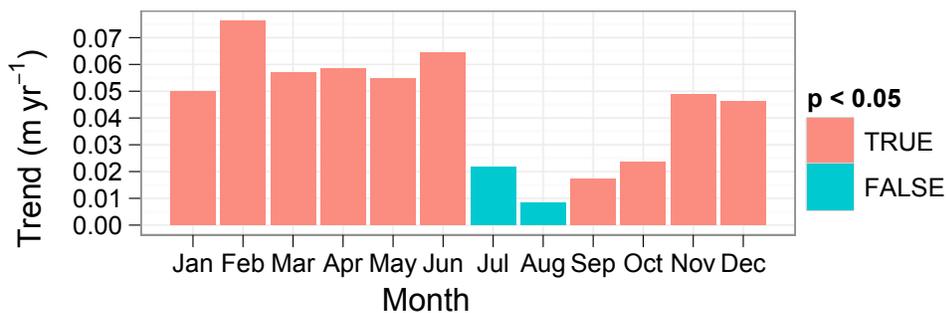


Fig. 4.12. Trend statistics for Secchi depth for each month representing the Sen's slope.

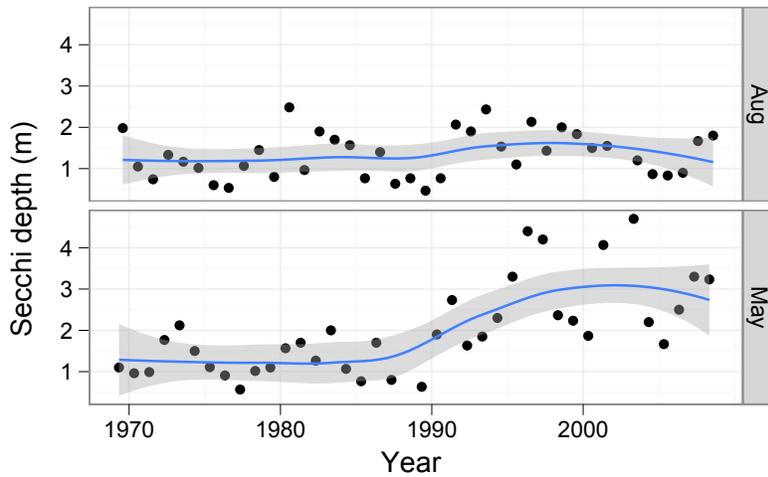


Fig. 4.13. Secchi depth in May and August across all 3 sampling stations illustrating the increasing trend in spring, whereas Secchi depth did not show a significant change in August throughout the sampling period.

Clear Lake is a turbid system due to inorganic suspended particulate matter in the winter and algal blooms in the summer. Turbidity decreased significantly ($\tau = -0.45$, $p < 0.001$) over the last 40 years (Fig. 14). The downward trend is largely due to high turbidity in the early 1970s according to the DWR data record.

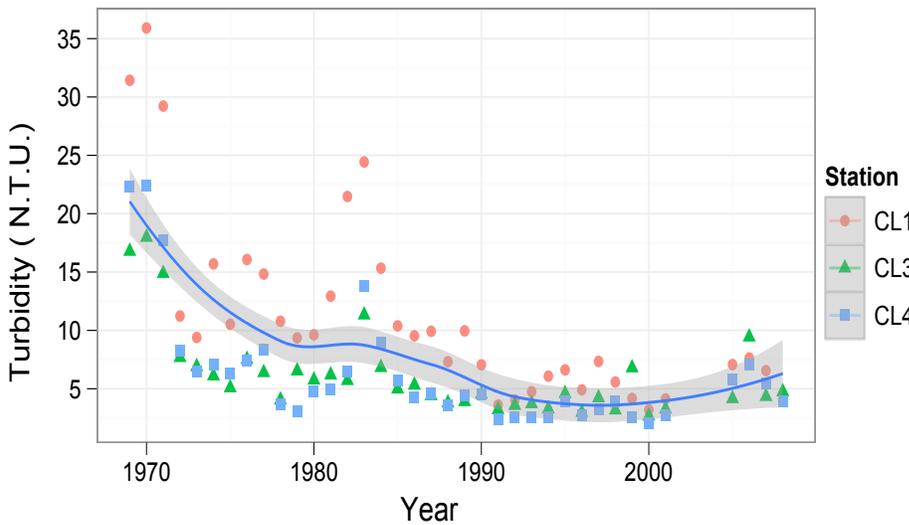


Fig. 4.14. Annual averaged (April - October) turbidity for all 3 sampling stations in Clear Lake from 1969 - 2008 (DWR data).

Turbidity measured by the Vector Control Data show a decline in the early 1980s and turbidity remained at a low level since 1990s (Fig. 4.15). Overall turbidity decreased significantly at both depth (surface: $\tau = -0.62$, $p < 0.0001$; bottom: $\tau = -0.64$, $p < 0.0001$)

and in all months of the year (Fig. 4.16), contrary to Secchi depth, with did not increase in July and August. See Appendix for long-term seasonal turbidity values.

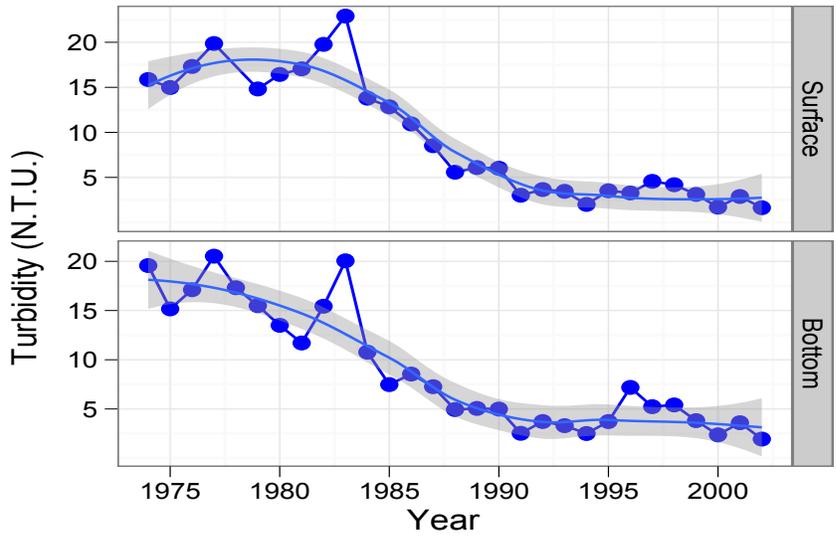


Fig. 4.15. Vector Control Data: Annual averaged turbidity for all 3 sampling stations (R3S5, R4S9, R5S13) in Clear Lake from 1969 - 2002.

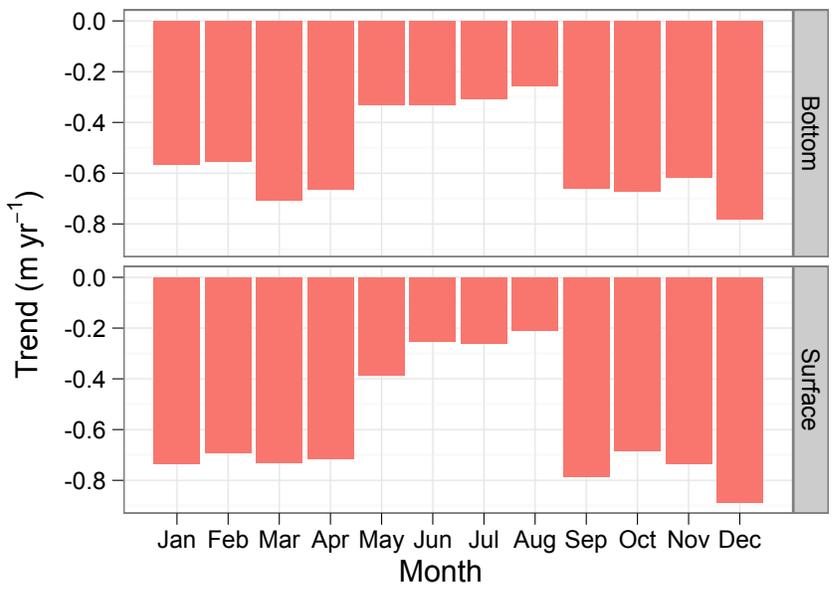


Fig. 4.16. Vector Control Data: Trend statistics of monthly-averaged turbidity across all 3 sampling stations (R3S5, R4S9, R5S13) in Clear Lake from 1969 - 2002.

4.5 Dissolved Oxygen and Salinity

Depth-averaged dissolved oxygen (DO) showed high interannual variability and no consistent trend ($\tau = -0.07$, $p = 0.05$) (Fig. 4.17). DO did not show a significant trend within the discrete depth strata and stations ($\tau < 0.15$, $p > 0.01$) (Fig. 4.18). The Upper Arm (CL1) showed lower DO and increasing frequencies of hypoxia since 2000, whereas DO was elevated in Oaks arm (CL4) after 2003 (Figs. 4.17 and 4.18).

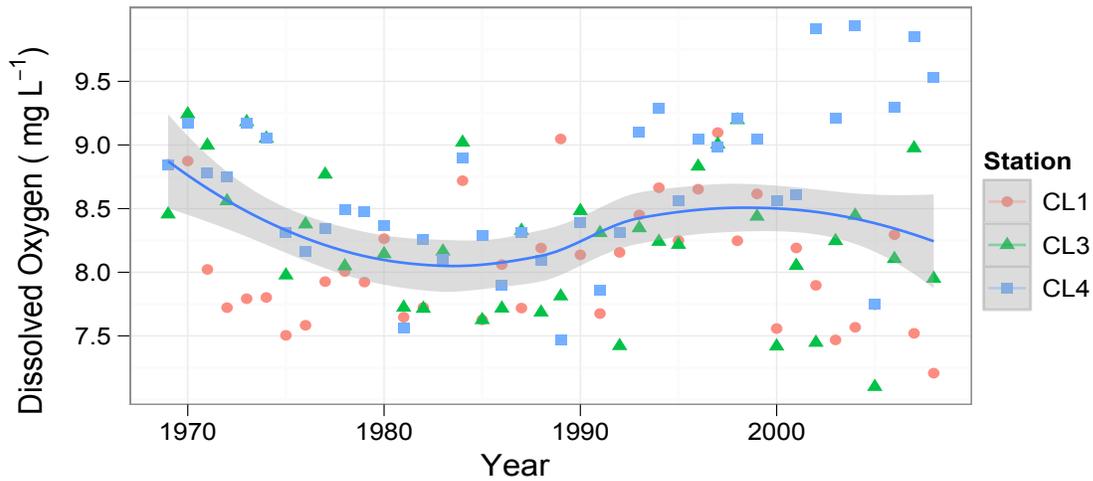
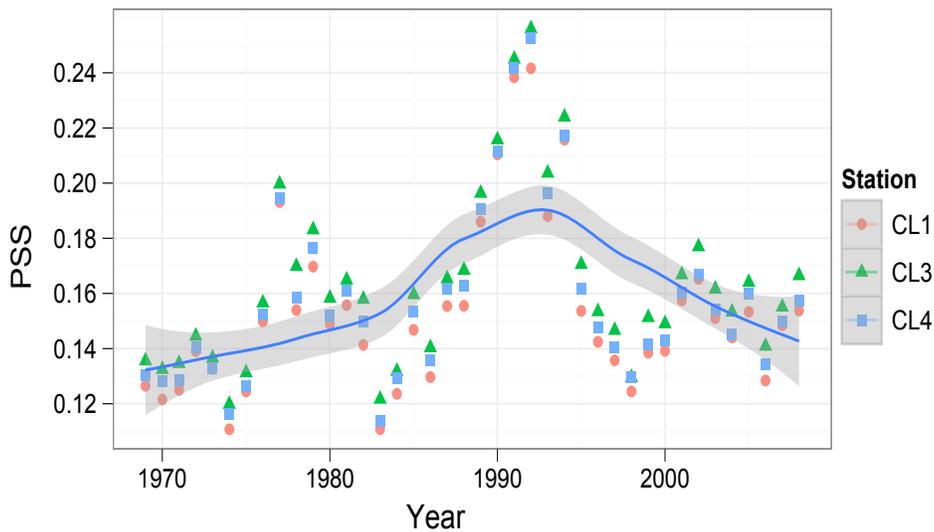


Fig. 4.17. Annual averaged (April - October) dissolved oxygen for each sampling station in Clear Lake from 1969 - 2008. Blue line displays a loess fit \pm standard error across all sampling station. See Appendix for detail trends in the different lake basins.



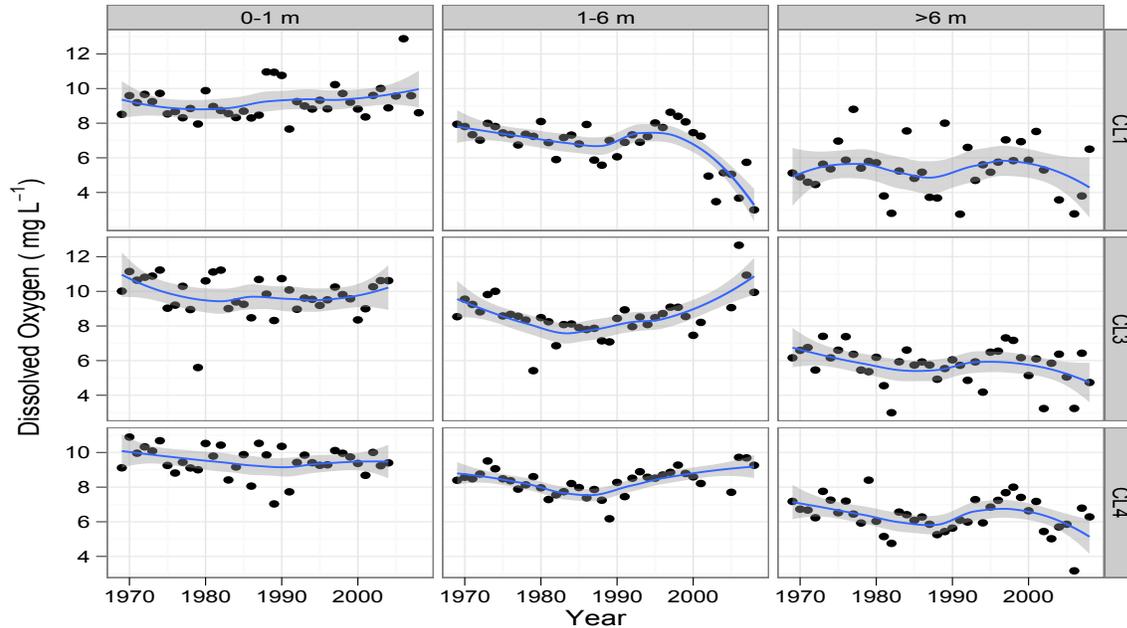


Fig. 4.18. Annual-averaged dissolved oxygen at different depth layers between April and October.

Clear Lake is a moderate hard-water system and salts are further concentrated by evaporation. Salinity fluctuates strongly from year to year and cycles with freshwater inflow and drought periods (Fig. 4.19). Overall, salinity increased significantly ($\tau = 0.17$, $p < 0.001$) over the sampling period. Salinity was highly elevated during the extended drought period from 1989 to 1993 due to a high evaporation rate and reduced inflow. Conversely, large freshwater inflow dilute the late such as flows in 1983 or 1998.

Fig. 4.19. Annual averaged (April - October) salinity for each sampling station in Clear Lake from 1969 - 2008. Blue line displays a loess fit \pm standard error across all sampling stations.

4.6 Nitrogen

Nitrogen concentration showed high interannual variability and concentrations were elevated between 1989 and 1992, corresponding to the dry water years (Fig. 4.20). Nitrate and nitrite decreased significantly across all stations ($\tau < -0.26$, $p < 0.001$), this was due to the decrease in the Upper Arm ($\tau < -0.52$, $p < 0.001$), whereas other stations did not show a long-term trend ($p < 0.01$). Ammonia concentration remained consistent

over the sampling period with no trend across the stations and within each basin ($p < 0.01$). Total nitrogen concentration did not show a significant trend in any sampling station over the sampling period ($p < 0.01$), however lake-averaged concentration increased significantly, which is however masked by different absolute concentrations within each basins ($\tau = 0.17$, $p < 0.001$).

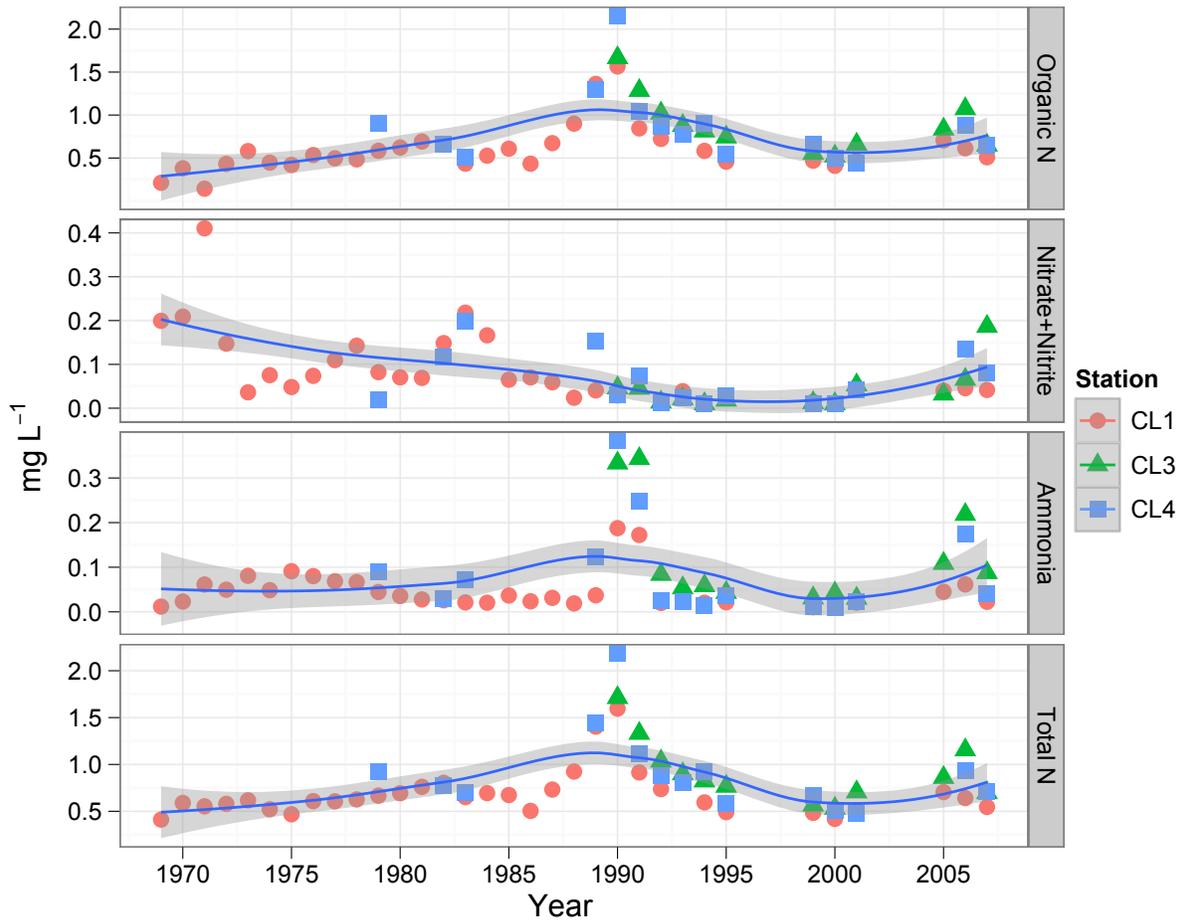


Fig. 4.20. Annual averages of nitrogen measurements for the 3 sampling station in Clear Lake from 1969 - 2008. Blue line displays a loess fit \pm standard error across all stations. See Appendix for detail trends in the different lake basins. Nitrogen showed high seasonal variability and peaks between October and April (Fig. 4.21), suggesting that phytoplankton production is limited by nitrogen during the summer months.

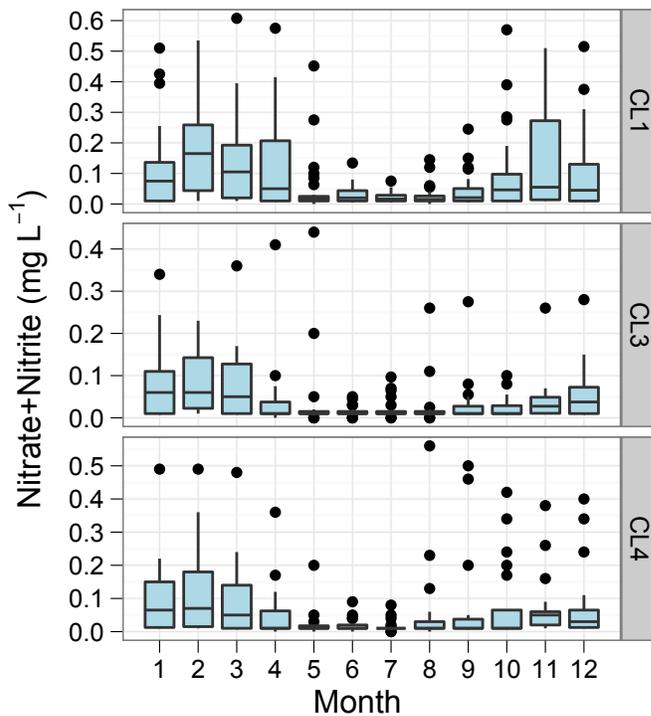


Fig. 4.21. Boxplots of monthly-averaged nitrate and nitrite for each months and station in Clear Lake between 1969 and 2008.

4.7 Phosphorus

Similar to nitrogen concentrations, phosphorus concentrations showed high interannual variability (Fig. 4.22). PO_4 and total phosphorus decreased between 1970s towards the mid 1980s and increased again during the dry water years between 1989 and 1993 (Fig. 4.22). Afterwards, total phosphorus concentrations dropped again, whereas PO_4 increased over the last years. Over the duration of the sampling period, both phosphorus variables did not show a significant change according to lake-averaged concentrations ($p > 0.01$) and within individual stations ($p > 0.01$). The recent increase of some nitrogen and phosphorus variables has to be taken with caution since the increase overlaps with a switch in laboratory analysis in 2002 (see Table 4.1).

Phosphorus showed high seasonal variability and peaks between July and November (Fig. 4.23). Increasing nutrient concentrations during summer and fall are typically a result of internal phosphorus loading from the sediment as the external phosphorus load arrives with the winter flood. Phosphorus concentrations from July through November were typically lower in Oaks Arm and Lower Arm compared to the Upper Arm (Fig. 4.23).

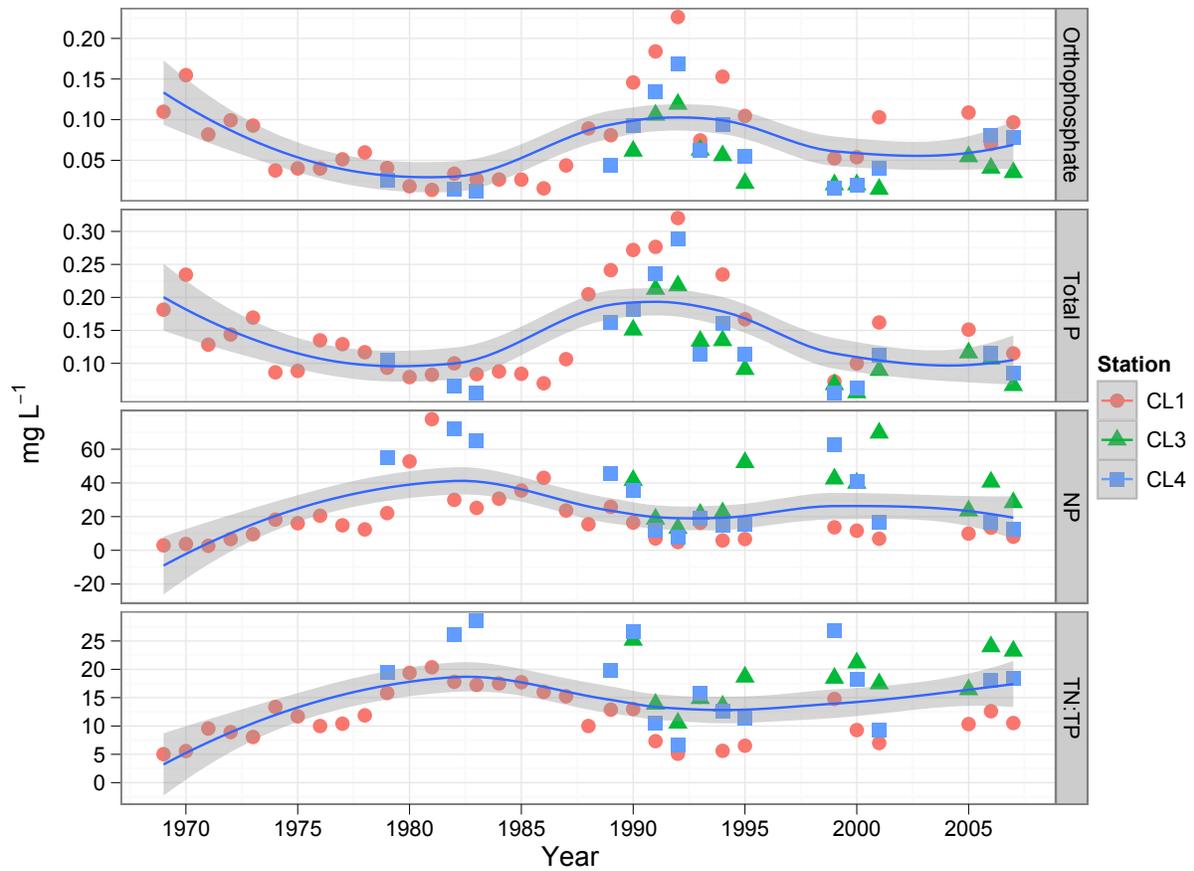


Fig. 4.22. Annual averages of phosphorus measurements and N:P ratios across 3 sampling station in Clear Lake from 1969 - 2008. See appendix for details in different lake basins.

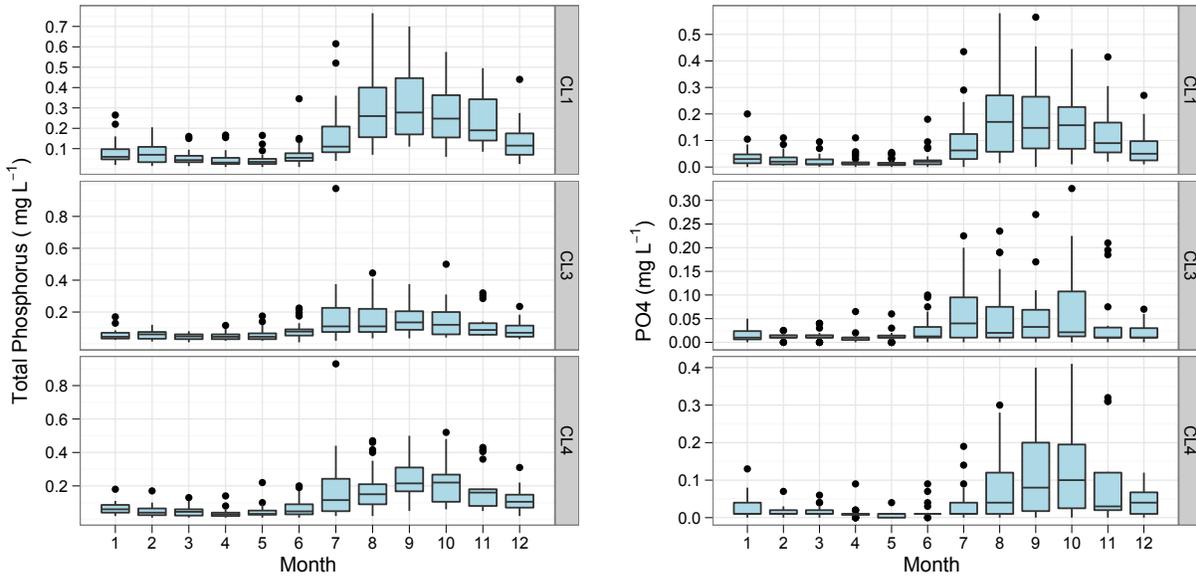


Fig. 4.23. Boxplots of monthly-averaged total phosphorus (left) and PO₄ (right) for each months and station in Clear Lake between 1969 and 2008.

4.8 pH

pH was measured through the vector control monitoring program at 3 different sampling sites, representing the main basins between 1954 and 2002. pH showed high interannual variability and increased during drought years. pH was elevated in the early 1970s and early 1990s (Fig. 4.24). Bottom and surface pH across all stations increased significantly over the sampling period according to the seasonal Mann Kendall test (bottom: $\tau = 0.22$, $p < 0.0001$; surface: $\tau = 0.20$, $p < 0.0001$). pH values showed similar trends over the seasons and stations, except the increase in the early 1970s was not obvious in all stations during Sep-Nov (Fig. 4.25).

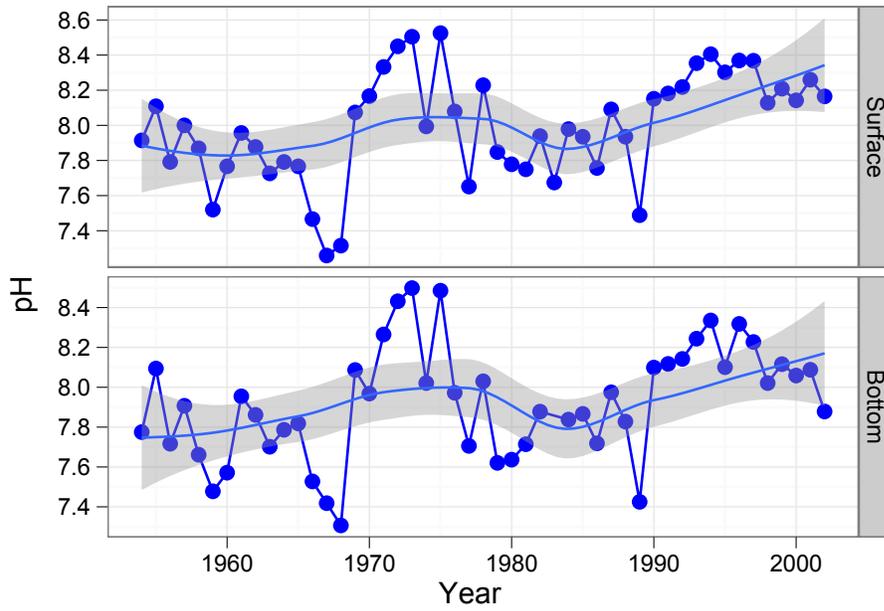


Fig. 4.24. Annual-averaged pH across all stations (R3S5, R4S9, R5S13) in Clear Lake between 1954 and 2002

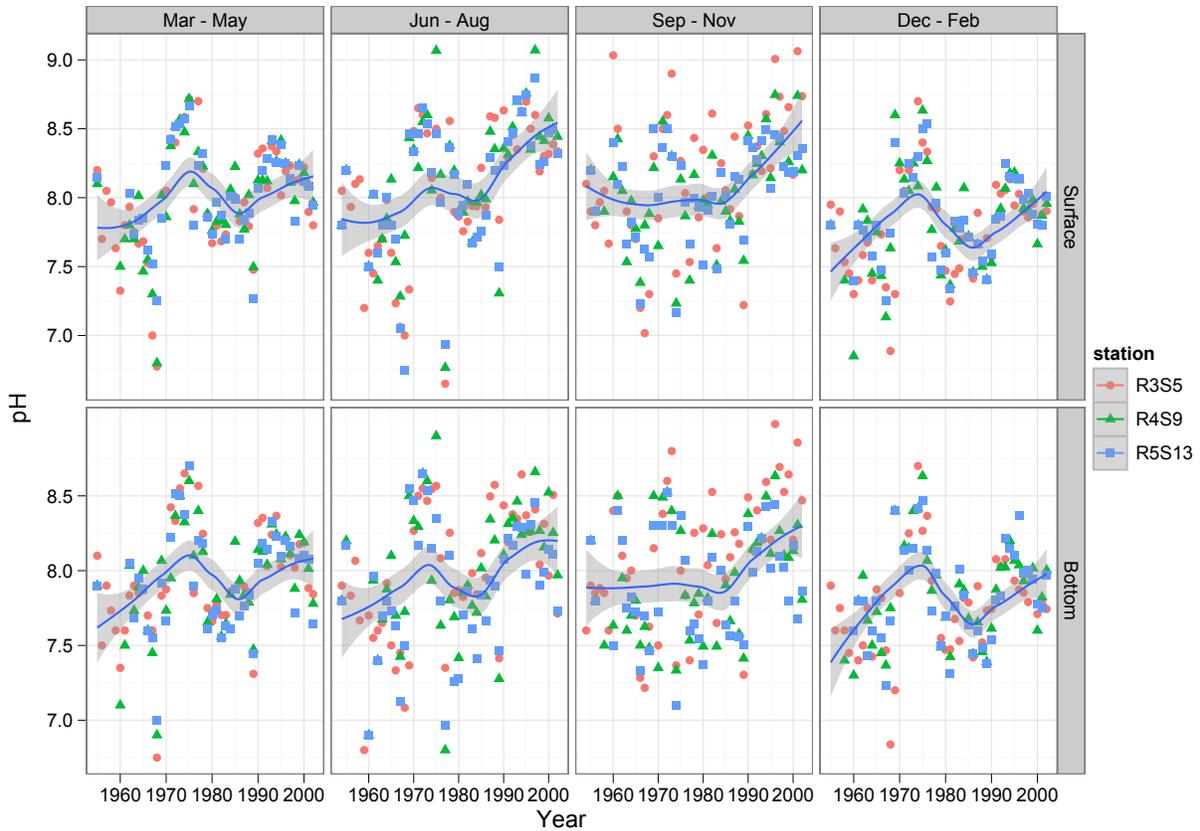


Fig. 4.25. Annual-averaged pH by season and depth (surface and bottom) in Clear Lake between 1956 and 2002.

4.9 Mineral Variables

Similar to chemical variables, mineral concentrations showed high interannual variability but no significant long-term trends (Figs. 4.26 and 4.27) and values were similar among the different basins of the lake. Concentrations increased during the 1987 - 1994 drought period and decreased to pre-drought levels afterwards.

Sulfate appears to have declined over the sampling period, however the trend was not significant, which likely results from sporadic measurements and high variability before 1987. Sulfate concentrations are of importance because they regulate the magnitude of P release from sediments and increase the availability of P released from sediments into anoxic bottom waters (Caraco 1993). Thus, a decrease in sulfate concentration may have reduced internal P loadings, although a decrease in TP is not apparent in the lake after 1987 (Fig. 4.22).

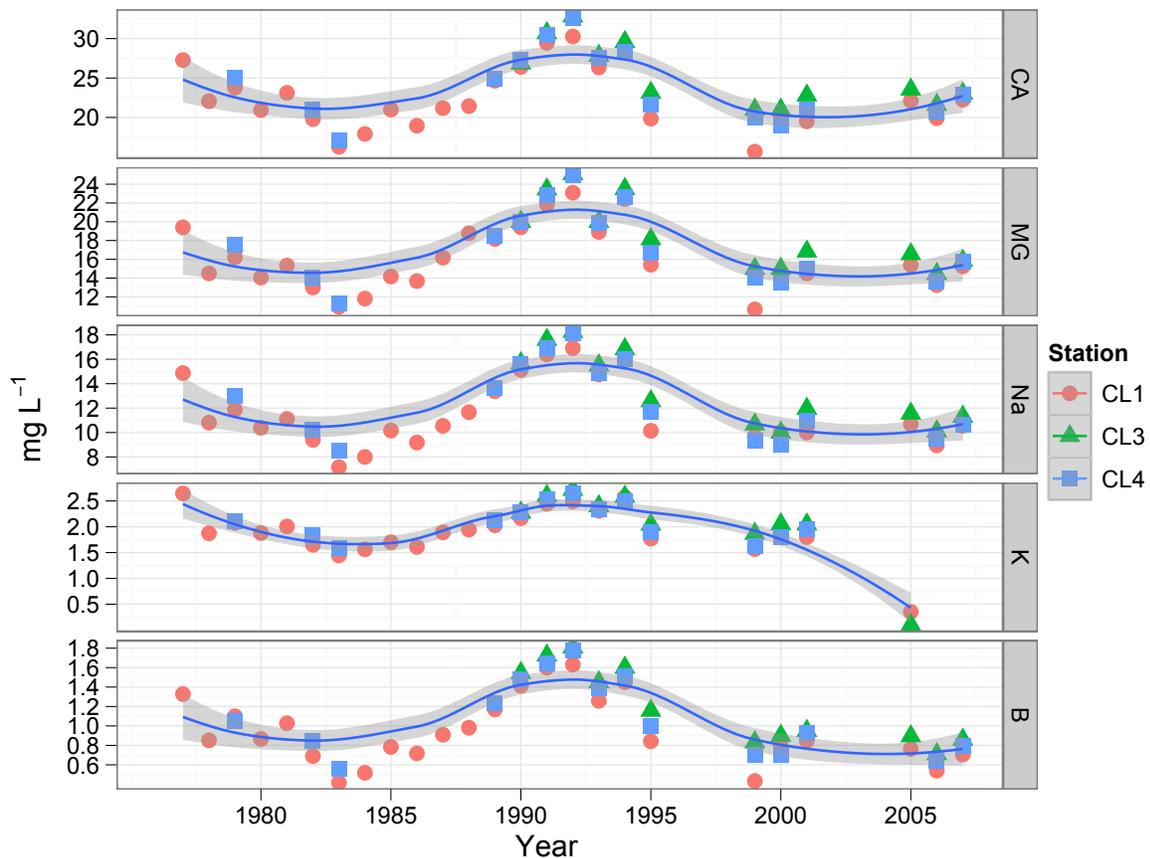


Fig. 4.26. Annual averages of mineral measurements across all 3 sampling station in Clear Lake from 1976 - 2007. Blue line displays a loess fit \pm standard error across all stations. See Appendix for detail trends in the different lake basins.

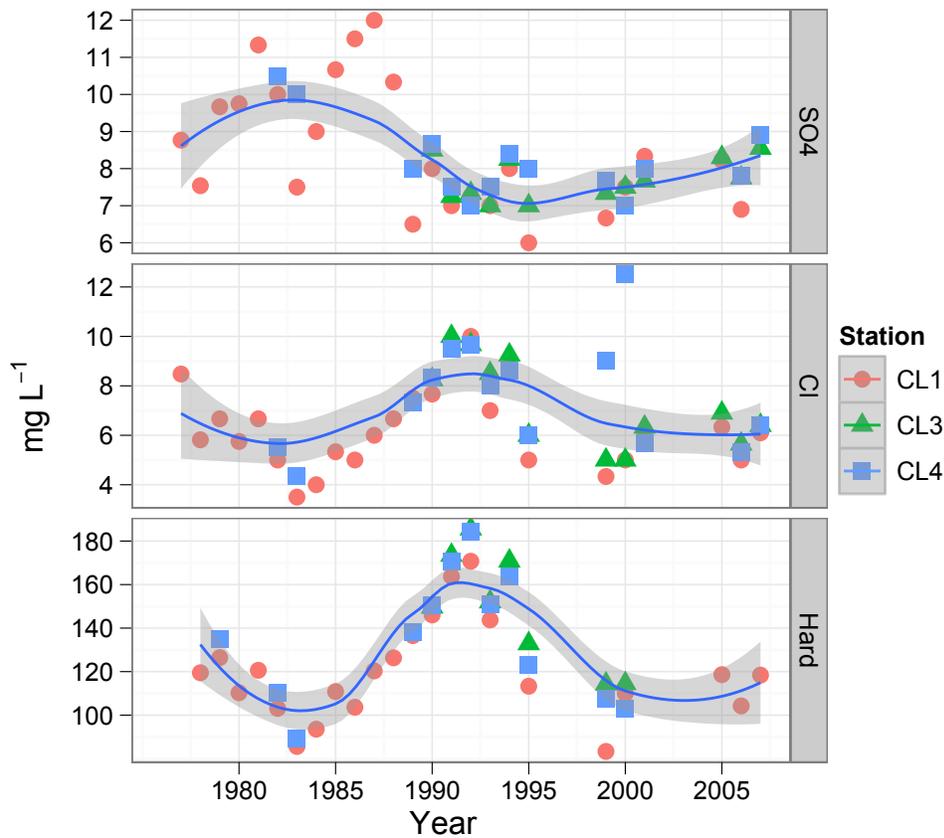


Fig. 4.27. Annual averages of Sulfate (SO₄), Chloride (Cl), and hardness (CaCO₃) across all 3 sampling station in Clear Lake from 1976 - 2007.

Table 4.1. Trend statistic of chemical and mineral variables from Clear Lake between 1972 and 2008 by stations. Mineral variable statistics for station CL3 are not shown because no measurements were taken before 1990.

Variable	CL1			CL3			CL4		
	Trend mg L ⁻¹ y ⁻¹	Trend % y ⁻¹	P	Trend mg L ⁻¹ y ⁻¹	Trend % y ⁻¹	P	Trend mg L ⁻¹ y ⁻¹	Trend % y ⁻¹	P
NH ₃ -N	0.01	1.31	0.011	-0.04	-4.74	0.034	-0.02	-2.10	0.075
NO ₂ +NO ₃	0.00	-3.84	0.000	0.00	3.21	0.409	0.00	-1.02	0.428
NH ₃	0.00	-1.68	0.042	0.00	-3.26	0.304	0.00	-2.24	0.198
Total N	0.00	0.55	0.168	-0.04	-4.68	0.034	-0.02	-1.80	0.075
PO ₄	0.00	0.93	0.329	0.00	-8.24	0.028	0.00	2.13	0.488
Total P	0.00	0.21	0.852	-0.01	-5.06	0.016	0.00	-0.15	0.767
N:P (total)	0.00	-0.01	1.000	0.49	2.72	0.193	-0.27	-1.54	0.322
CA	0.00	0.01	0.981	-	-	-	-0.10	-0.40	0.519
MG	0.02	0.14	0.708	-	-	-	-0.10	-0.59	0.457
Na	-0.01	-0.05	0.926	-	-	-	-0.12	-0.95	0.428
K	0.00	0.00	1.000	-	-	-	0.00	0.01	1.000
SO ₄	-0.08	-0.91	0.076	-	-	-	-0.06	-0.68	0.294
Cl	0.00	0.00	0.869	-	-	-	0.04	0.51	0.743
B	0.00	-0.45	0.624	-	-	-	-0.02	-1.40	0.298
Hardness	0.38	0.32	0.561	-	-	-	-0.04	-0.03	1.000

5. Status and Trends of Biological Variables

5.1 Phytoplankton

The long-term dynamic of phytoplankton is strongly driven by bloom formations of different species, mainly belonging to cyanobacteria and diatoms (Richerson et al. 1994), which masks the long-term dynamics of the overall pattern. Thus, to better highlight the long-term pattern, an upper threshold level was set for better illustration. In addition, since phytoplankton identification were performed by different personnel, data quality is questionable and long-term patterns of major taxonomic groups and major algal species have to be treated with caution.

Overall, no long-term pattern of phytoplankton biovolume emerged. Diatoms typically dominated the spring bloom and reached highest values in fall (Fig. 5.1). During the summer, cyanobacteria become abundant, whereas and chlorophytes and flagellates typically bloom in fall (Fig. 5.2). These patterns were similar across the three arms of the lake. In addition, there was no discernible long-term pattern for specific quarters of the year (Fig. 5.3). Overall, the long-term phytoplankton data do not reflect the shift in Secchi depth around 1990s. However, since the data need to be treated with caution, we cannot rule out the hypothesis that there was no reduction in phytoplankton biovolume around that time.

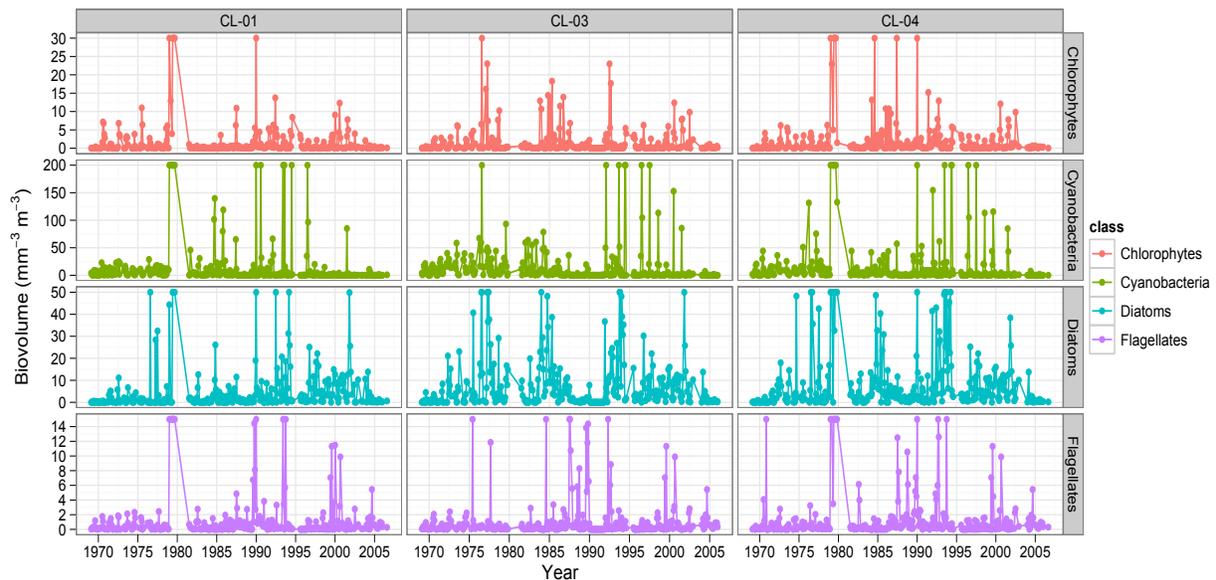


Fig. 5.1. Phytoplankton biovolume of major taxonomic groups by basins in Clear Lake between 1969 and 2006. Notice that an upper threshold value was set for better illustration of the data.

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Fig. 5.2. Monthly-averaged boxplots of phytoplankton biovolume of major taxonomic groups by station in Clear Lake between 1969 and 2006. Notice that an upper threshold value was set for better illustration of the data.

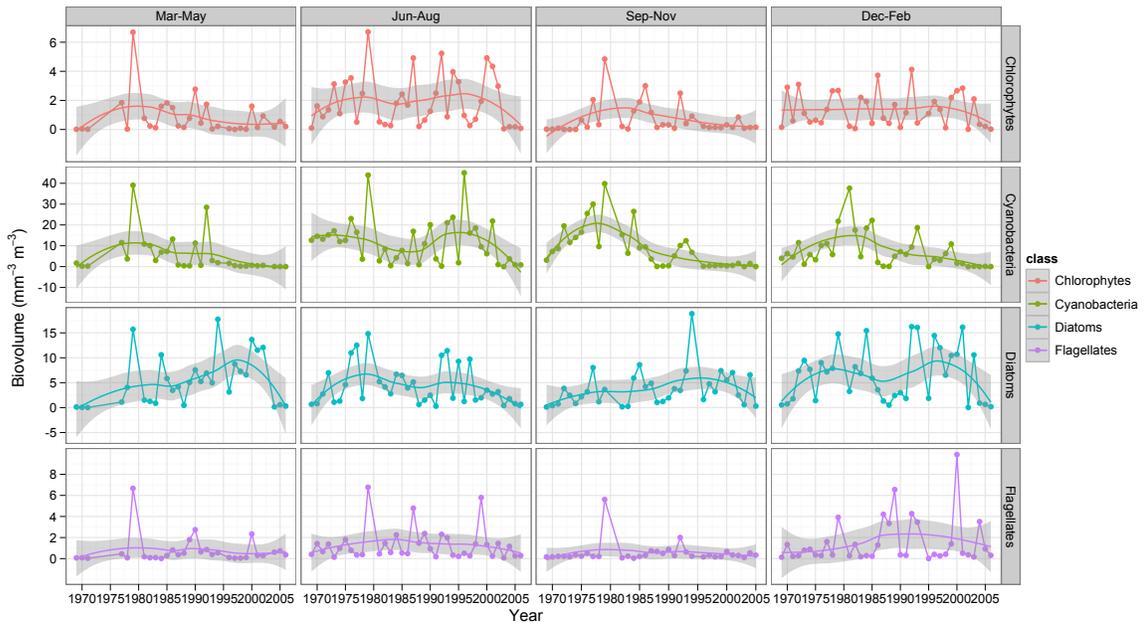


Fig. 5.3. Monthly-averaged phytoplankton biovolume of major taxonomic groups by basins across all sampling stations in Clear Lake between 1969 and 2006. Lines are a loess smooth.

Phytoplankton genera

The dominant genera according to the long-term mean are highlighted. The diatom community was dominated by *Coscinodiscus* spp. and *Stephanodiscus* spp. and *Melosira* spp. (Fig. 5.4). *Pediastrum* spp. and *Oocystis* spp. dominated biovolume of chlorophytes (Fig. 5.5), and *Ceratium* spp. was the most dominant flagellate genus (Fig. 5.6.)

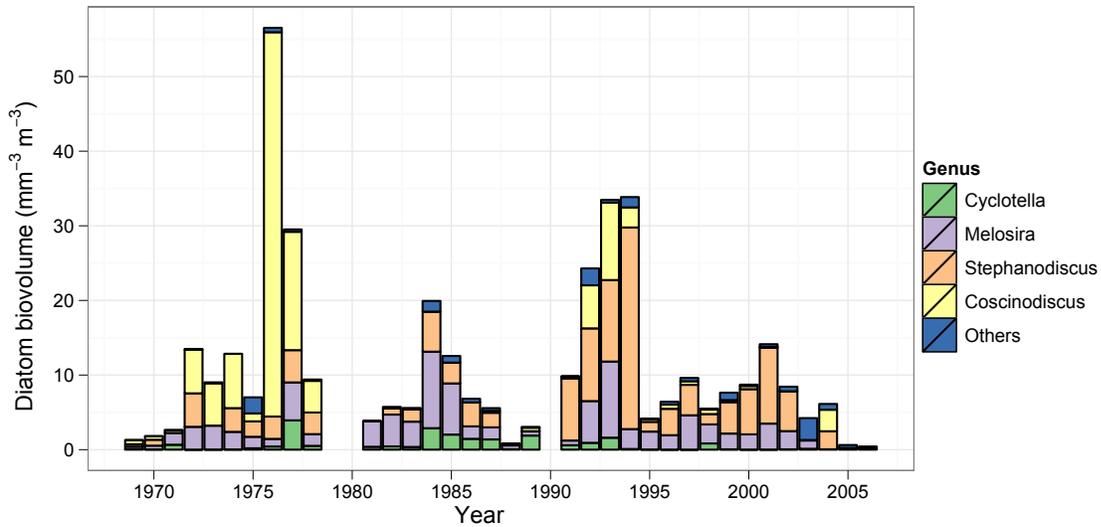


Fig. 5.4. Annual-averaged diatom biovolume of the different across stations between 1969 and 2006.

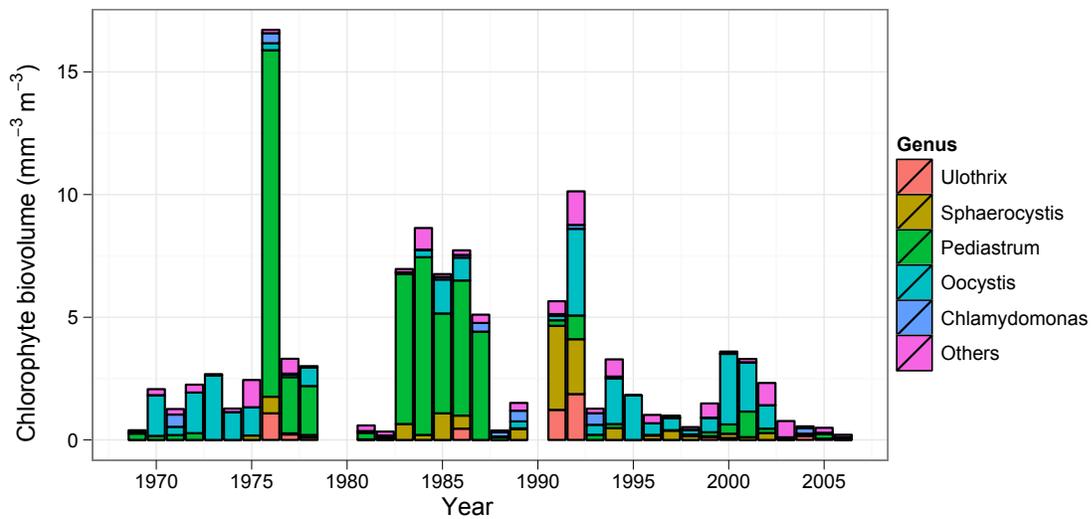


Fig. 5.5. Annual-averaged chlorophyte biovolume of the different across stations between 1969 and 2006.

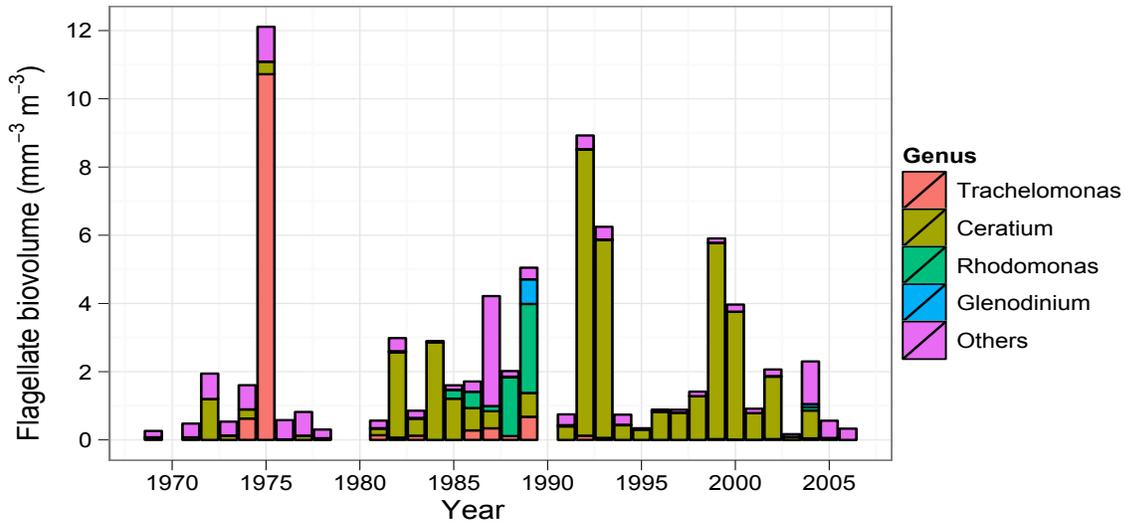


Fig. 5.6. Annual-averaged flagellate biovolume of the different genera across stations between 1969 and 2006.

Cyanobacteria are shown separately for the periods 1969-1989 and 1996-2002 because of difference in abundant species, which may be a result of identification problems related to shifts in personnel. The years 1989-1994 are excluded due to abnormal high values. *Aphanizomenon* spp. dominated the early time period (Fig. 5.7), while *Gloeotrichia* spp. was the most abundant genus after 1995 (Fig. 5.8).

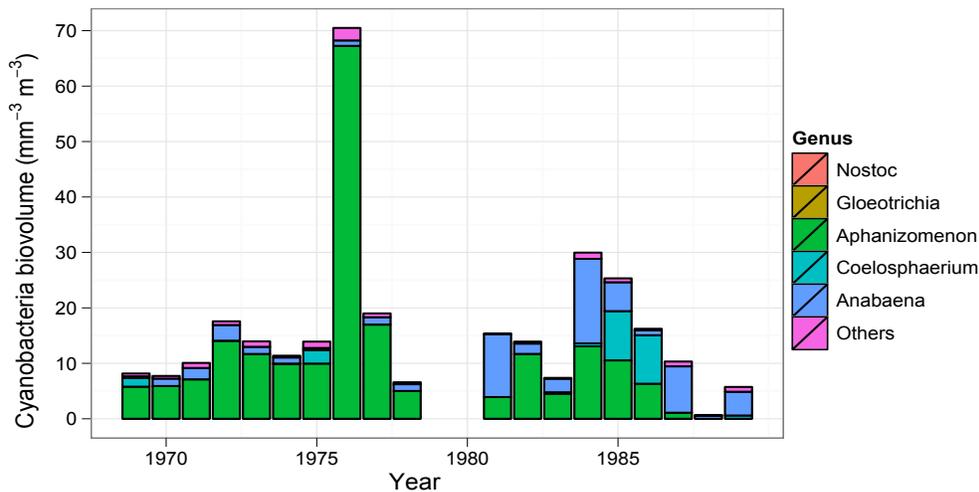


Fig. 5.7. Annual-averaged cyanobacteria biovolume of the different genera across stations between 1969 and 1989.

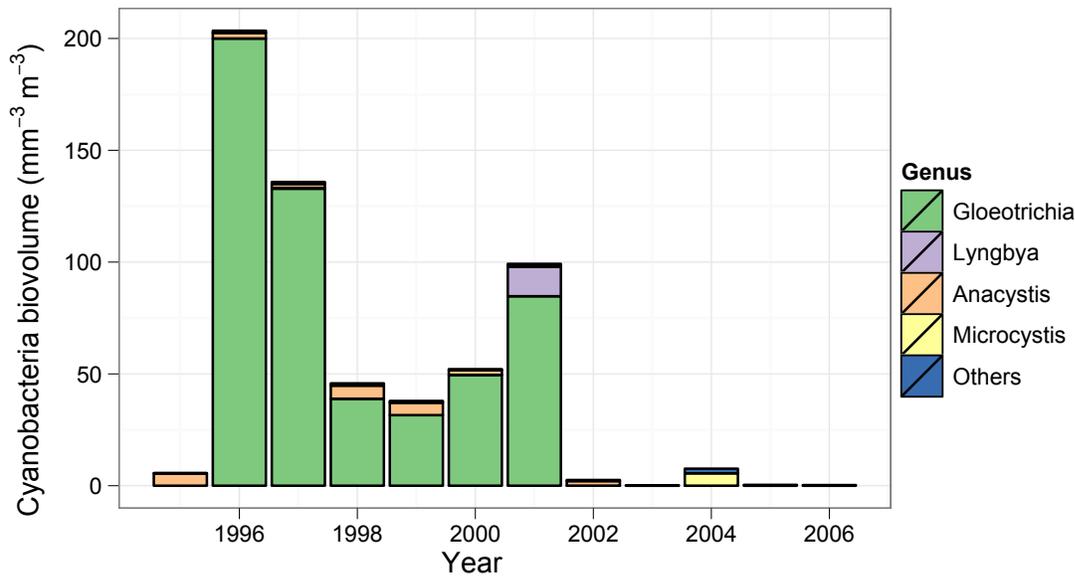


Fig. 5.8. Annual-averaged cyanobacteria biovolume of the different genera across stations between 1995 and 2006.

5.2 Zooplankton

Zooplankton was sampled by vertical tow nets and Schindler trap. Because the two methods yield different densities values (see appendix), the dataset was not merged and is illustrated separately. Overall, Schindler trap data between 1974 and 2002 yielded higher densities compared to tow net data.

Schindler trap data: 1974 - 2002

Rotifer (4.8 % yr⁻¹; $p = 0.001$), immature cladocerans (3.4 % yr⁻¹; $p = 0.002$), and chydoridae (4.0 % yr⁻¹; $p = 0.002$) showed a significant increasing trend, and copepods a decreasing trend (-3.2 % yr⁻¹; $p < 0.003$), whereas other taxa did not show significant changes (Table 5.1) (Fig. 5.9).

Cladoceran species showed high interannual variability, but no significant trend (Fig. 5.10). Within copepods, *Tropocyclops* spp. and *Cyclops* spp. decreased abruptly in 1980s, however this may be due to species identification (Fig. 5.11). Rotifer species increased around 1990s (Fig. 5.12); *Polyarthra* spp. (4.9 % yr⁻¹; $p = 0.001$), *Brachionus* spp. (5.8 % yr⁻¹; $p = 0.001$), *Trichocerca* spp. (12.4 % yr⁻¹; $p = 0.001$), and *Lecane* spp. (11.8 % yr⁻¹; $p = 0.001$) showed a significant increase.

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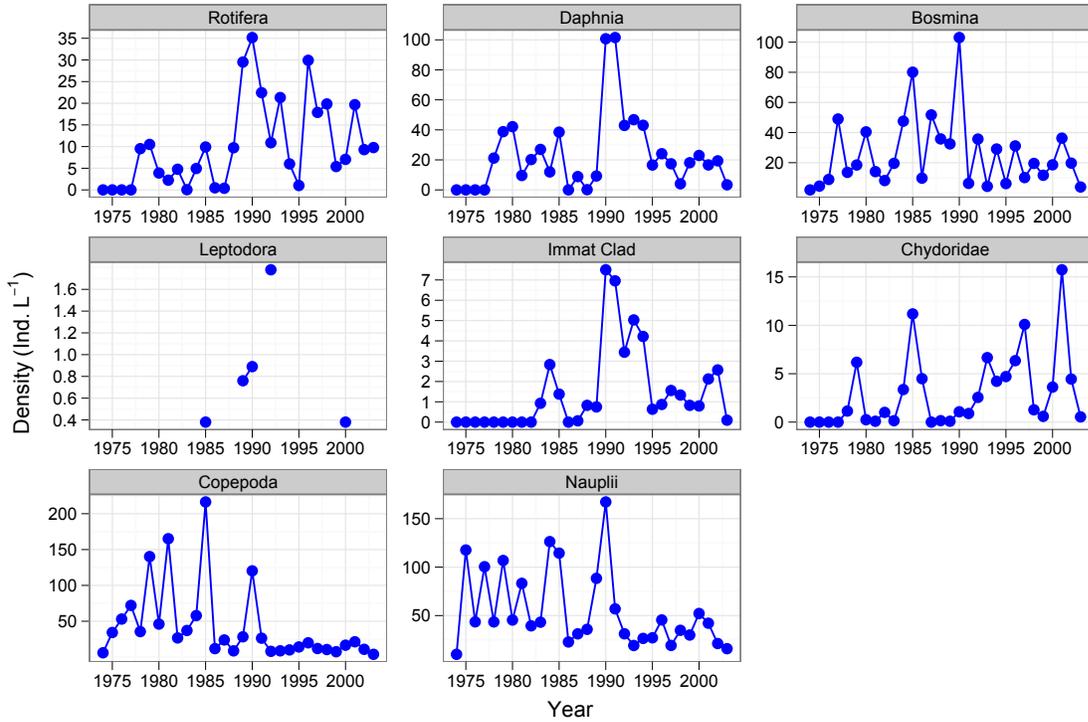


Fig. 5.9. Schindler trap data: Annual-averaged density of major zooplankton taxonomic groups between 1974 and 2002.

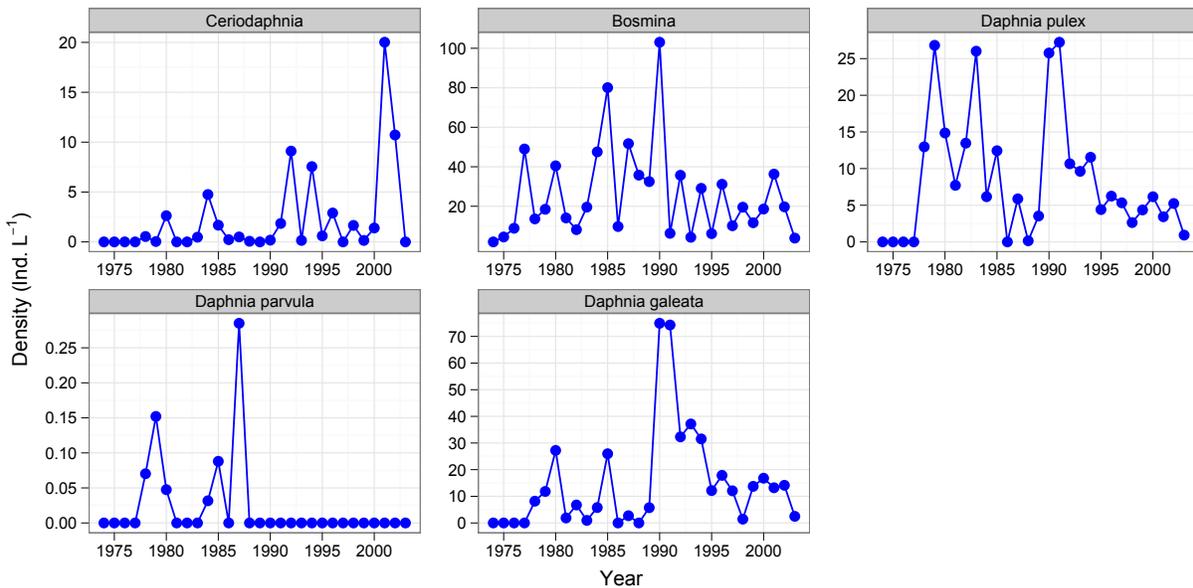


Fig. 5.10. Schindler trap data: Annual-averaged density of dominant cladoceran species between 1974 and 2002.

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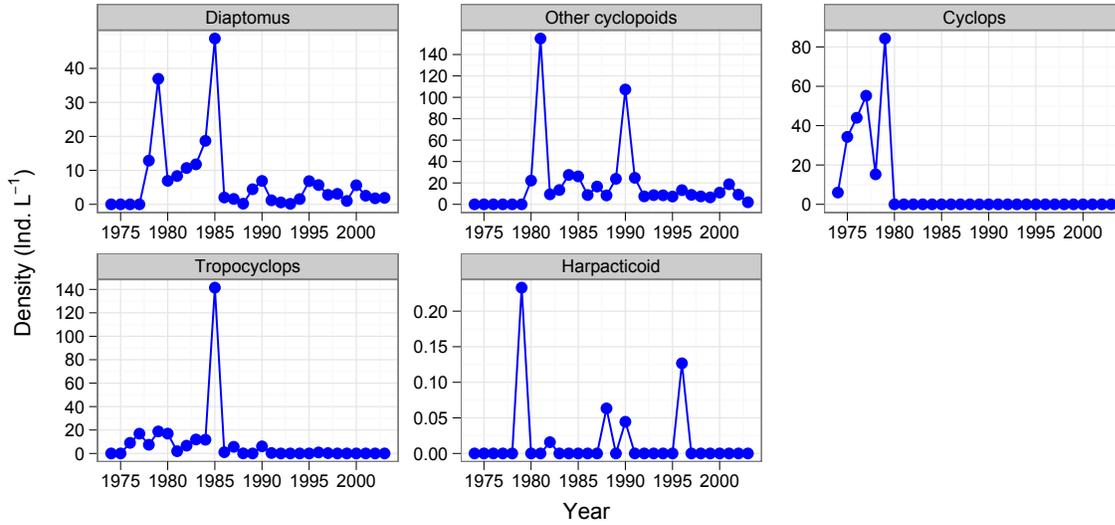


Fig. 5.11. Schindler trap data: Annual-averaged density of dominant copepod species between 1974 and 2002.

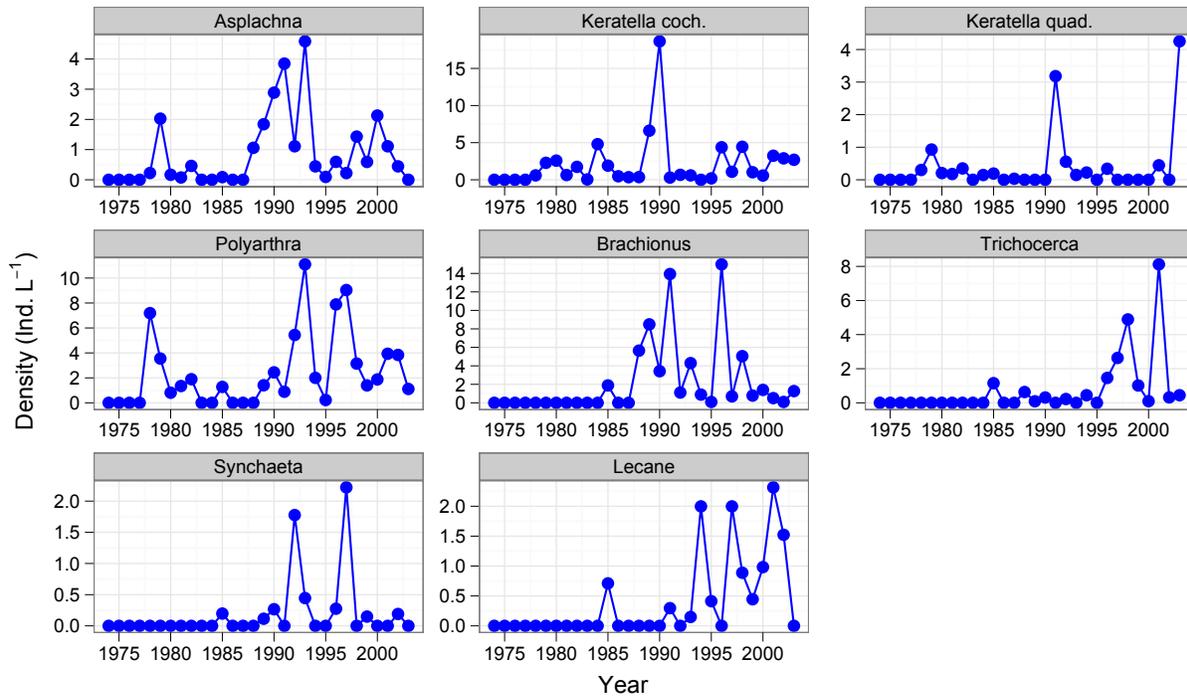


Fig. 5.12. Schindler trap data: Annual-averaged density of dominant rotifer species between 1974 and 2002.

Tow Net data: 1988 - 2008

Zooplankton taxa showed high interannual variability but major taxonomic groups did not show a significant trend between 1988 and 2008 (Table 5.1) (Fig. 5.13). Similarly, cladoceran and copepod species did not show a significant trend between 1988 and 2008 (Figs. 5.15 and 5.16). Among rotifers, *Aplanchna* spp. (-13.9 % yr⁻¹; *p* = 0.002) and *Brachionus* spp. (-11.1 % yr⁻¹; *p* = 0.002) showed a marginally significant decreasing trend (Fig. 5.17).

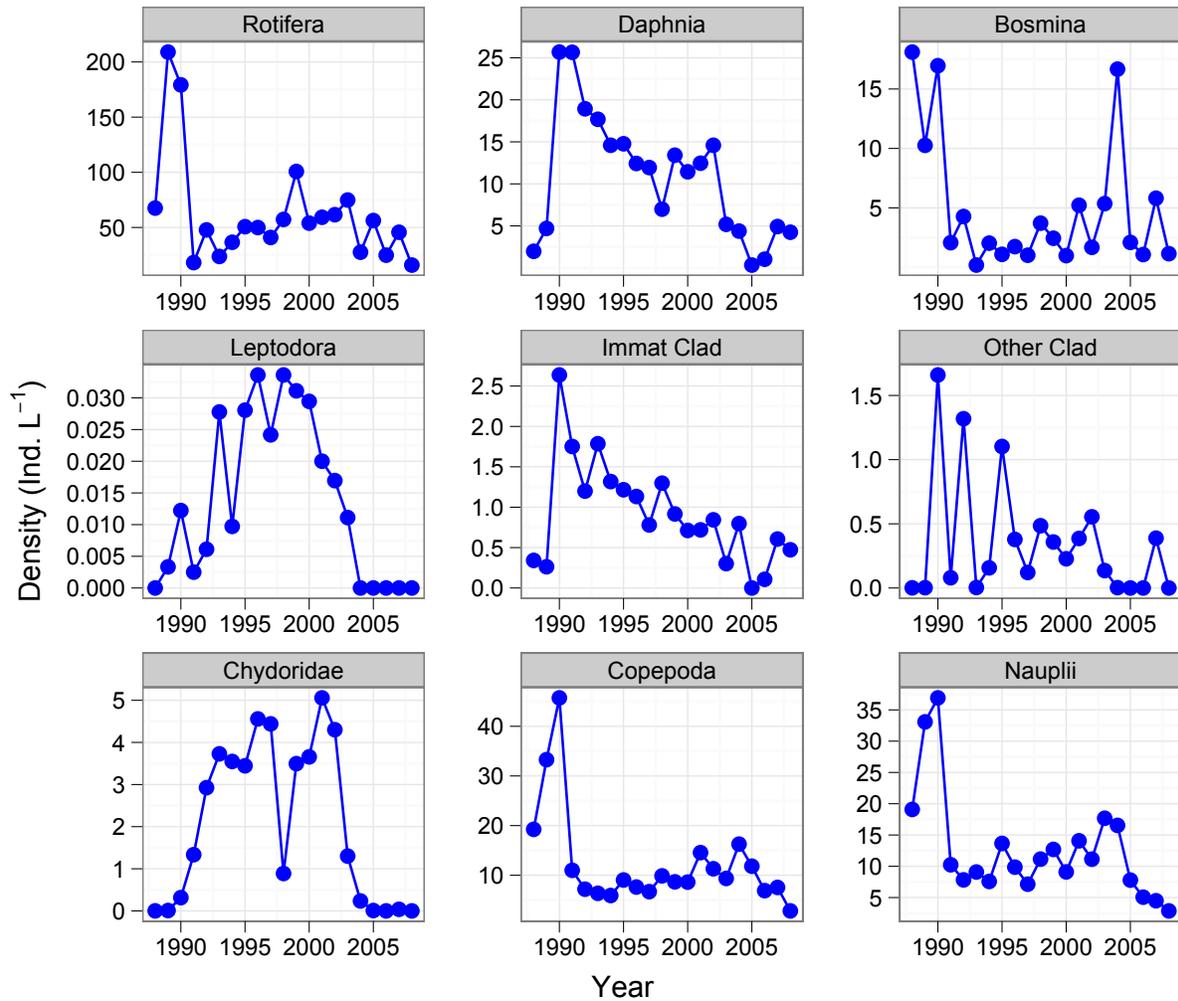


Fig. 5.13. Tow net data: Annual-averaged density of major zooplankton taxonomic groups between 1988 and 2008.

It is however noticeable that *Daphnia* spp., *Leptodora* spp., and immature cladocerans increased substantially in 1990, as did other cladocerans (dominated by *Ceriodaphnia* spp. and *Diaphanosoma* spp.) in the early 1990s and maintained higher densities afterwards compared to the late 1980s. In contrast, copepods densities declined after 1990s, which is supported by both data sets and likely a response to exploitative competition for shared food resources and interference with cladocerans.

Zooplankton taxa showed high seasonal variability and *Daphnia* spp., *Bosmina* spp., and *Leptodora* spp. dominate during the summer months (Fig. 5.14). In contrast, rotifers are most abundant during winter and spring, and copepods during fall and spring.

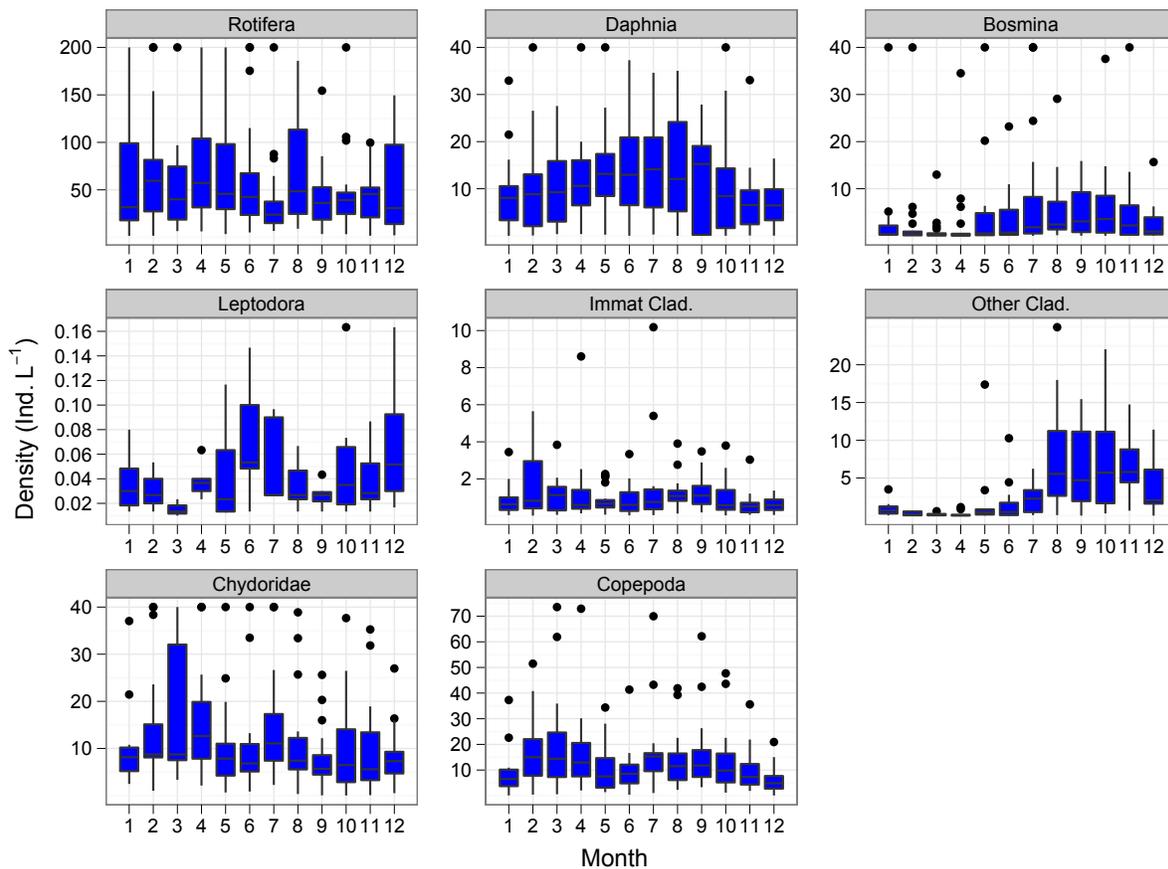


Fig. 5.14. Tow net data: Boxplots of monthly-averaged density by month of major zooplankton taxonomic groups between 1988 and 2008. An upper limit is set for Rotifera, *Daphnia*, *Bosmina*, Chydoridae, and Copepoda for better illustration of the data.

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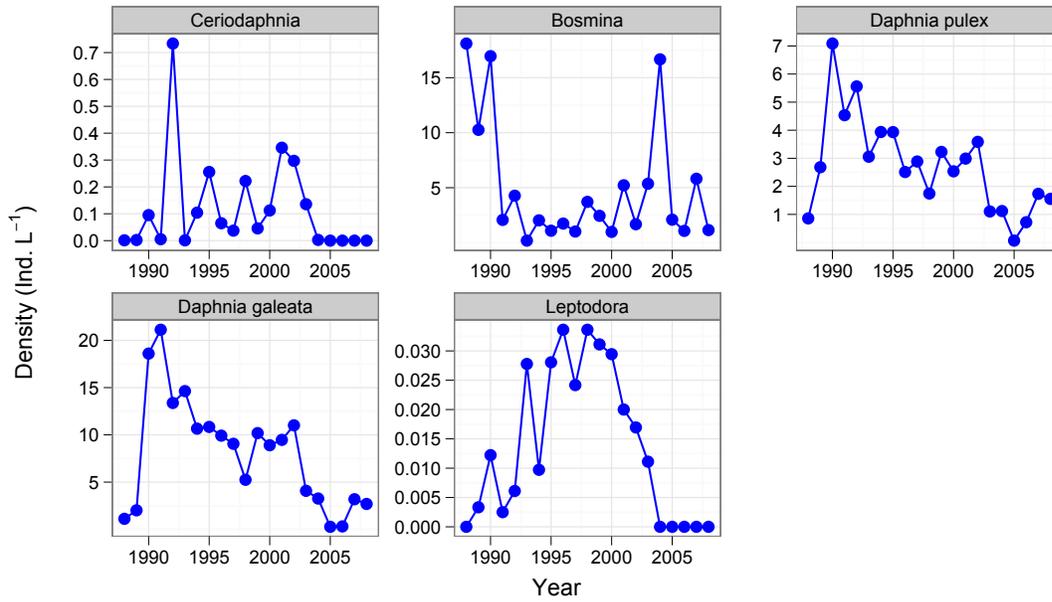


Fig. 5.15. Tow net data: Annual-averaged density of dominant cladoceran species between 1988 and 2008.

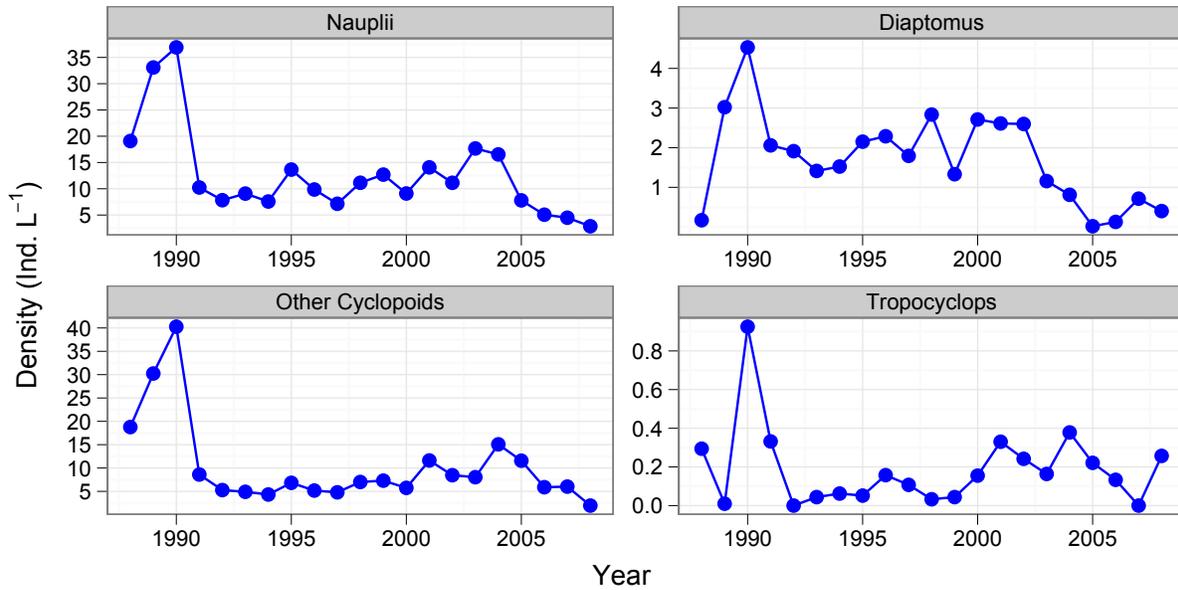


Fig. 5.16. Tow net data: Annual-averaged density of dominant copepod species between 1988 and 2008.

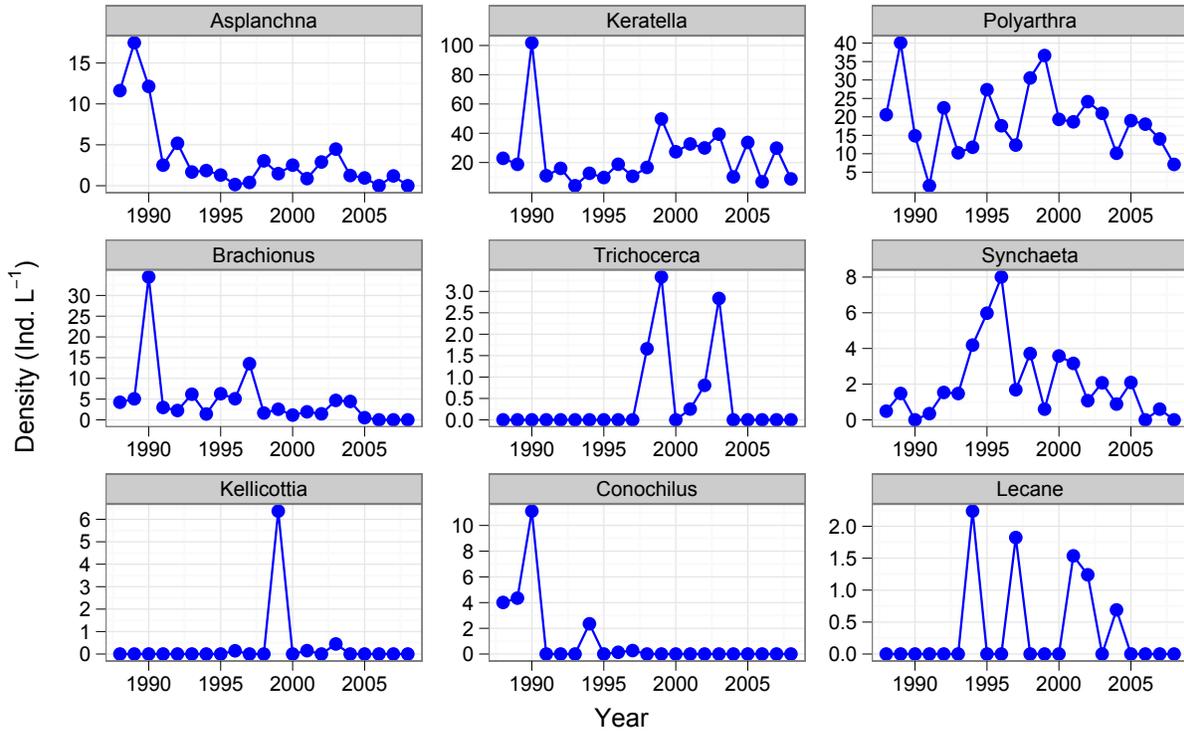


Fig. 5.17. Tow net data: Annual-averaged density of dominant rotifer species between 1988 and 2008.

Table 5.1. Trend statistic of major zooplankton taxonomic groups for the Schindler trap and Tow net dataset.

	Trend Ind. L ⁻¹ y ⁻¹	Trend % y ⁻¹	P		Trend Ind. L ⁻¹ y ⁻¹	Trend % y ⁻¹	P
Schindler data				Trow net data			
Rotifera	0.47	4.76	0.001	Rotifera	-1.15	-1.85	0.381
Daphnia	0.71	1.38	0.354	Daphnia	-0.93	-8.61	0.002
Bosmina	0.05	0.18	0.887	Bosmina	-0.07	-1.34	0.415
Leptodora	0.00	0.00	0.376	Leptodora	0.00	-1.41	0.343
Immatclad	0.05	3.40	0.002	Immatclad	-0.07	-8.19	0.004
Chydoridae	0.12	4.02	0.002	Chydoridae	-0.01	-0.46	0.587
Copepoda	-1.34	-3.22	0.003	Copepoda	-0.23	-1.85	0.319
Nauplii	-1.18	-2.15	0.020	Nauplii	-0.48	-3.79	0.043

5.3 Macroinvertebrates

Chaoborid larval densities showed a sharp decline in the early 1960 and remained at low densities after that time (Fig. 5.18). Densities were slightly higher between 1975 and 1985 and decreased thereafter again (Fig. 5.19). There was no significant trend for chaoborids after 1969 ($p > 0.8$). In contrast, chironomids densities increased after the 1980s compared to values in the late 1950s (1.6 % yr⁻¹, $p = 0.0019$) (Fig. 5.20).

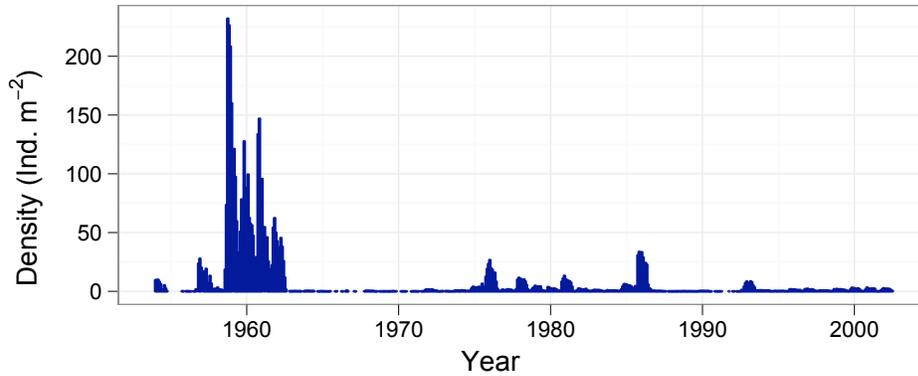


Fig 5.18. Monthly-averaged Chaoborid larvae densities across all sampling stations between 1954 and 2002.

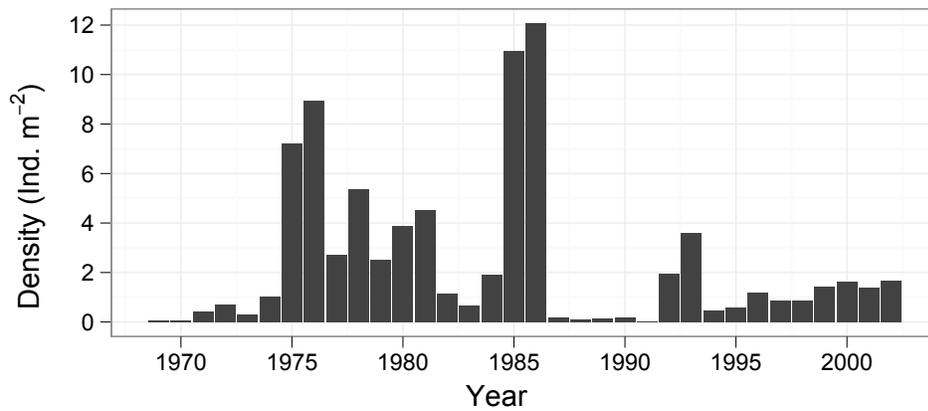


Fig 5.19. Annual-averaged Chaoborid larvae densities averaged over all stations (entire lake) 1969-2002.

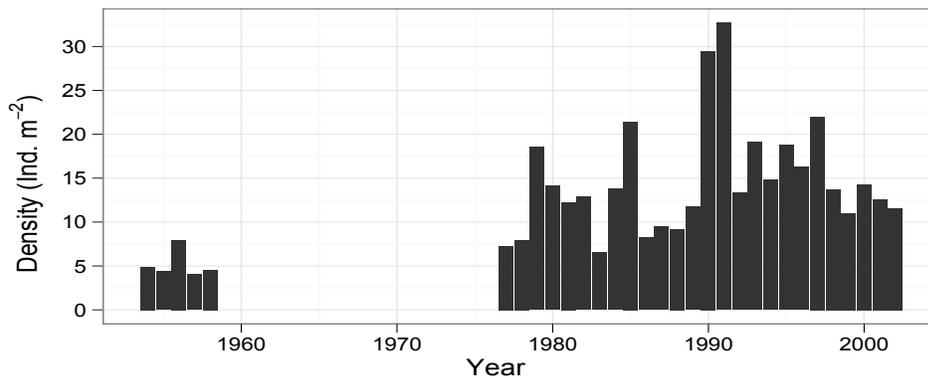


Fig 5.20. Annual-average densities of chironomids across all stations (entire lake) from 1969-2002.

5.4 Fish

Clear Lake has a diverse fish community, dominant species include inland silverside (*Menidia beryllina*), largemouth bass (*Micropterus salmoides*), bluegill (*Lepomis macrochirus*), prickly sculpin (*Cottus asper*), and threadfin shad (*Dorosoma petenense*) (Fig. 5.21). There was no significant long-term trends over the sampling period for these fish species. However, there were abrupt changes in some fish species.

Threadfin shad dropped significantly in 1989 and were not caught after 1990 (except a few species in 1997), and Prickly sculpin increased in the mid 1990s. In addition, Largemouth bass appears to have higher densities after 1990s compared to the late 1980s (Fig. 5.21).

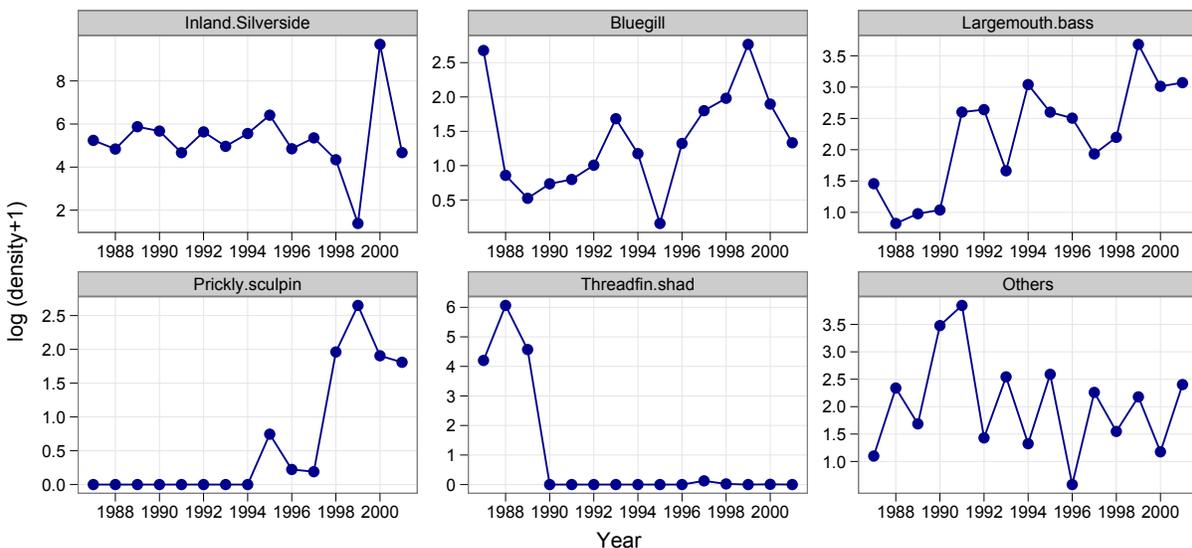


Fig. 5.21. Annual-averaged density for five common nearshore fish species and remaining taxa from Clear Lake between 1987 and 2001; density $1/4(n+1)/\text{ha}$ where n 1/4 number of individuals.

Threadfin shad appeared in the lake in 1985 as a result of an accidental or unapproved introduction (Richerson et al. 1994), and were abundant until late 1989 but were not caught after 1990 (except a few species in 1997). The reasons for the abrupt eradication of this species in the winter of 1989/90 are unclear. Threadfin shad is in general sensitive to cold temperature and a cold temperature spill could have caused the decline of this species in the winter of 1989. However, temperature data for 1989 and 1990 are not different compared to the winter before (Fig. 5.21).

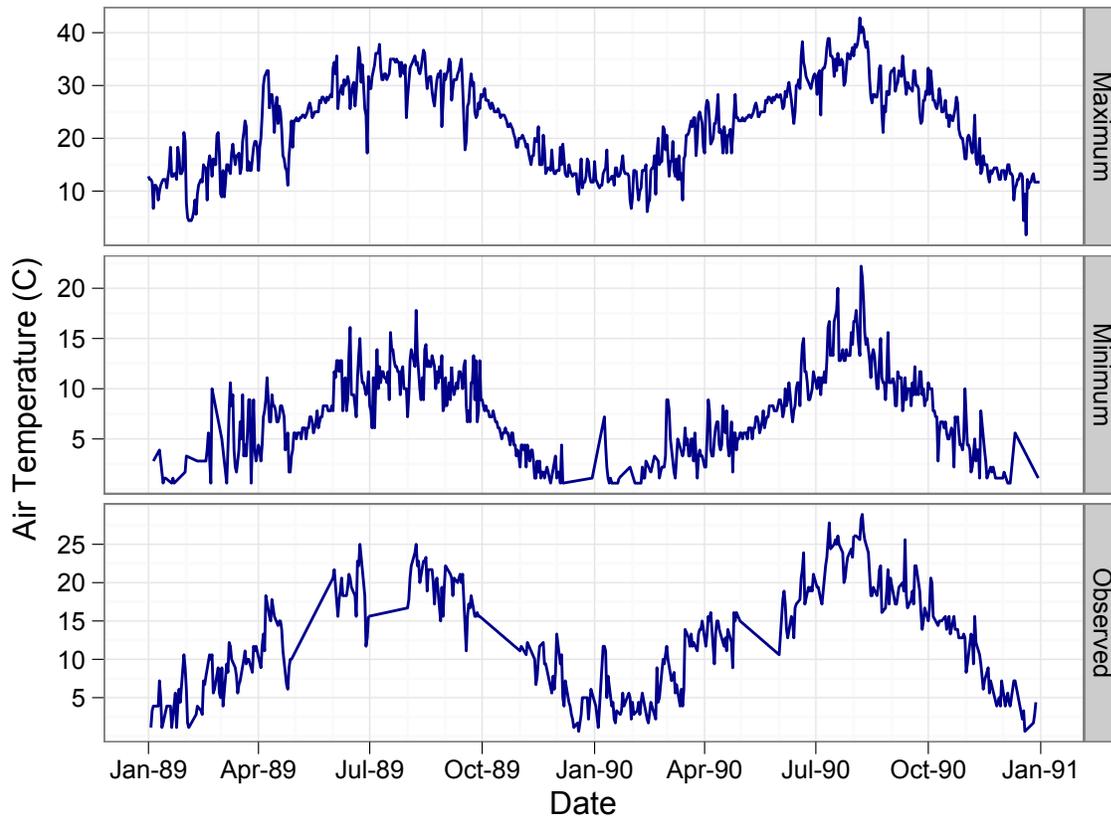


Fig. 5.21. Daily maximum, minimum and observed air temperature at Lakeport between 1989 and 1990.

Another reason for the abrupt decline in threadfin shad could be related to the drought period. Inflow in spring was very low during that time period and approached zero over the entire season (see Fig. 4.5) and salinity increased. Threadfin shad can tolerate low salinities but typically requires freshwater for successful reproduction. Threadfin shad usually spawn from April to August in California (Feyrer et al. 2009). Spawning is typically associated with floating or partially submerged objects, especially submerged aquatic vegetation. Eggs and fry may have not tolerated low water levels during the drought years 1989-1993 or eggs may have been exposed to open air due to low water level. However, the causes for the rapid decline and eradication of this fish species during the winter of 1989/90 need to be investigated.

Threadfin shad are typically planktonic feeders at all life stages (Feyrer et al. 2009), focusing on crustacean zooplankton, although it has the ability to switch feeding modes in response to prey availability (Ingram & Ziebell 1983). Their diet consists largely of rotifers and zooplankton crustaceans (cladocerans, copepods). The decline in threadfin

shad can thus explain the subsequent increase of *Daphnia*, *Leptodora* and other cladoceran species in Clear Lake in 1990.

Threadfin shad competitively displaced other planktivorous fish, such as inland silversides, young-of-year (YOY) largemouth bass and YOY bluegill, by reducing zooplankton abundance. These species shifted from a diet dominated by zooplankton to almost entirely zoobenthos, as has been demonstrated by stable carbon isotopes (Eagles-Smith et al. 2008). The diet shift resulted in an increase of mercury concentration in these fish species of about 50 %.

6. Conclusions and Conceptual Model

Overall, the data analysis of various physical, chemical, mineral, and biological variables from Clear Lake since the late 1960s revealed high interannual variability. Few variables showed a significant change, which is in part related to poor data quality (e.g., phytoplankton data) and length of time period (e.g., fish densities, zooplankton).

However, an abrupt shift occurred in 1990, when water transparency increased abruptly in all three arms of the lake and doubled from 1 to 2 m depth (Fig. 4.2). This change coincided with one of the longest drought periods in California in the last decades of the 20th century. Changing nutrient concentrations that could have affected phytoplankton growth can not explain the abrupt increase. In fact, nutrient concentrations were elevated during this time period as a result of low precipitation and high evaporation (Figs. 4.21 and 4.23). There was no significant change in phytoplankton biovolume (Figs. 5.1 and 5.2) in the early 1990s, although there was a tendency of lower chlorophyte, and cyanobacteria biovolume after 1990s. The long-term phytoplankton patterns however need to be treated with caution because of poor data quality (discussed above).

In 1990, there was an abrupt increase in *Daphnia* densities (Figs. 5.9 and 5.10), mainly of *Daphnia galeata*. The increase of this species could be related to the decline in Threadfin shad as this species feeds readily on plankton crustaceans and rotifers. The eradication of the shad population likely allowed daphnids, *Leptodora* and rotifers to increase. Daphnids are proliferate grazers and can reduce phytoplankton biomass, which results in an increase in lake clarity. For example, after *Daphnia* spp. appeared in Lake Washington as a result of food-web changes in the mid 1970s, transparency increased further after the reduction of nutrient input (Edmondson 1994).

Thus it can be expected, that the abrupt increase in water transparency in Clear Lake is the result of a trophic cascade (Fig. 6.1). Eradication of Threadfin shad allowed daphnids and rotifers to increase, which kept phytoplankton at low level and subsequently transparency increased. It is however still unclear what kept daphnids at lower densities before Threadfin shad introduction. Unfortunately, long-term fish data are not available. Low daphnid densities before shad appearance could be related to high predation pressure of other fish species, such as YOY large-moth bass, bluegill, and inland silversides, which shifted to benthic diet after shad introduction (Eagles-Smith et al. 2008). In addition, blooms of *Aphanizomenon* in the 1970s and 1980s (Richerson et al. 1994) likely interfered with grazing of the filter feeder daphnids, and phytoplankton species composition might have been better for growth and reproduction after 1990s.

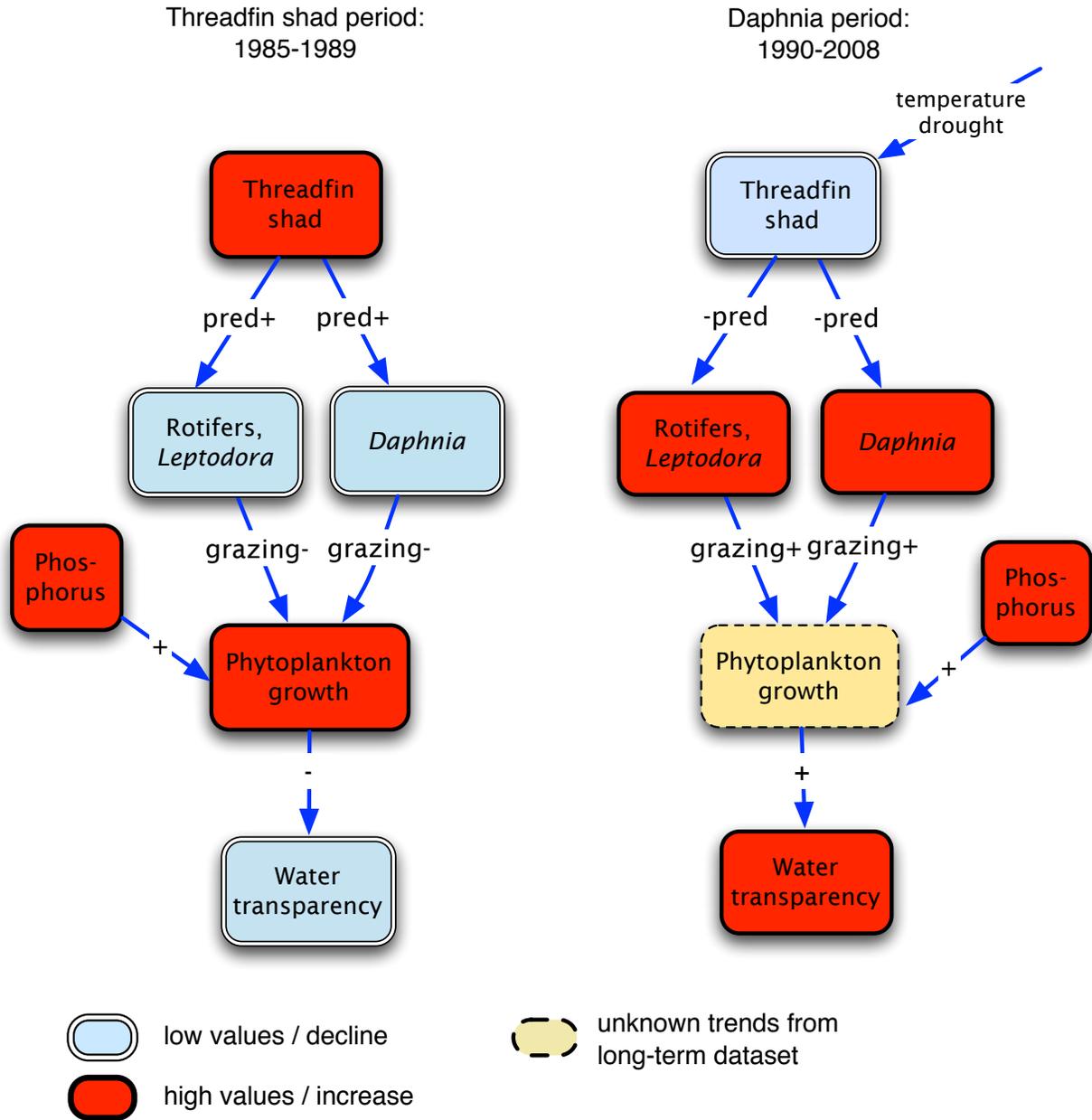


Fig. 6.1. Conceptual model of abrupt changes in Clear Lake in 1990s. The increase of rotifer densities is supported by the long-term Schindler trap data.

Declined fish predation pressure on zooplankton in 1990 is further supported by the increase of *Leptodora* spp. densities. This large-size zooplankton species does typically not coexist in high densities with high fish predation pressure, as this is a preferred food item for visual predators, such as planktivorous fish. Their low number in the 1980s is likely a result of high shad predation.

Alternatively, cladoceran densities can be further regulated by Chaoborid larvae, which display high densities in Clear Lake at times. However, Chaoborid densities remained low after the mid 1980s (Fig. 5.19), suggesting that predation pressure from chaoborids on cladocerans was negligible, which allowed these taxa to increase after the decline of the shad population and reduced fish predation.

In summary, the historical analysis of chemical, physical, and biological data from Clear Lake indicate that the increase in lake clarity since the early 1990s was not a result of a reduction in nutrient concentration. The data suggest that the doubling of lake clarity was due to a trophic cascade that resulted in reduced zooplankton predation and a subsequent increase in cladoceran and rotifer densities. Cladocerans are efficient filter feeders and likely reduced phytoplankton abundance. Reduced phytoplankton growth after cladoceran increase is however poorly supported as a result of low phytoplankton data quality and lack of chlorophyll concentration measurements. Moreover, this analysis suggest that both chemical and biological parameters are important monitoring variables to understand processes affecting the water quality of Clear Lake.

7. Recommendations for the Water Quality Monitoring Program

The present analysis demonstrates that a comprehensive monitoring including chemical, physical and biological variables is important to fully understand controlling mechanisms of the water quality. Based on these observations, it is recommended that in addition to the physical and chemical parameters, it is of importance to monitor phytoplankton, zooplankton, and the fish community.

Overall we recommend continuing monitoring of the following lake variables:

Physical variables:

Temperature, Secchi depth, transparency

Chemical variables:

Conductivity, phosphorus, nitrogen, pH

Biological variables:

Phytoplankton, zooplankton, fish

It is recommended that these variables are sampled at a monthly interval, if funding available. In case of funding shortcuts, sampling during the winter month can be reduced to twice per winter season.

It should also be noted that the phytoplankton data need a more careful attention and documentation of the analysis, particularly if methods and personnel shifts occur. In addition, data need to be calibrated whenever a change in method occur to ensure proper analysis of the long-term data set.

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