Integrated Assessment of Ecosystem Health

EDITED BY
Kate M. Scow
Graham E. Fogg
David E. Hinton
Michael L. Johnson
7. The history of human impacts in the Clear Lake Watershed (California) as deduced from lake sediment cores: P.J. Richerson et al. 2000

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Kate M. Scow, Ph.D.
Professor, University of California, Davis

Graham E. Fogg, Ph.D.
Professor, University of California, Davis

David E. Hinton, Ph.D.
Professor, University of California, Davis

Michael L. Johnson, Ph.D.
Professor, University of California, Davis

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7 The History of Human Impacts in the Clear Lake Watershed (California) as Deduced from Lake Sediment Cores*


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ABSTRACT

We have raised sediment cores to investigate multiple stresses on Clear Lake, CA over the past 250 years. Earlier work suggested the hypothesis that the use of heavy earth-moving equipment was responsible for erosion, mercury, and habitat loss stresses. Such stresses would have first become significant about 1925 to 1930. The cores are about 2.5 m long and span 200 to 300 years of the lake’s history. We present the results for our, as yet, most thoroughly analyzed core, 206Pb dating yields an estimated 1.2 cm yr⁻¹ average sedimentation rate for this core. Total (primarily inorganic) mercury and a number of other parameters were measured at 5-cm intervals down the core. Nearly all parameters show major changes at depths of 75 to 80 cm, corresponding to an estimated date of 1927. Organic matter, total carbon, water content, and total nitrogen all show significant decreases above this depth. A peak in inorganic deposition rate and minimum values for percent water is present at a depth corresponding to about 1971. Inorganic mercury concentrations show major increases in concentration (roughly tenfold) above the 1927 horizon. There is also a smaller uptick in total mercury at 145 to 150 cm deep in the core. This horizon is beyond 206Pb dating capabilities, but most likely represents the early episodes of mercury mining which started in 1873 at the Sulphur Bank Mercury Mine located on the lake’s eastern shore. Peak total mercury levels occur at an estimated date of 1961 (last mining was in 1957), and a modest decline has occurred since. Interestingly, the first 75 years of European settlement in the Clear Lake basin (including the most productive years of Sulphur Bank Mercury Mine) appeared to have had barely detectable effects on core properties despite considerable presence after the 1870s. Changes since 1925 are much more dramatic. The large increase in mercury beginning about 1927 corresponds to the use of heavy equipment to exploit the ore deposit at Sulphur Bank Mine with open pit methods. The increase in inorganic sediment load during the last 75 years is substantial in this core, but is not replicated in other cores. Increases in sulfate and/or acidity loading from the mine may be responsible for the dramatic changes seen in the upper 75 to 80 cm of the core.

Keywords: human impacts, mercury, watersheds, sediment cores, mining

INTRODUCTION

Clear Lake is a large (177 km²), shallow, eutrophic, polymeric lake in the Central Coast Range of Northern California. It sits at about 404 m elevation and has a typical Mediterranean climate with cool, rainy winters and hot, dry summers. The topography of the drainage basin is mostly steep, with typical elevations along the rim running 1000 m. About 195 km² of the total drainage basin (1219 km²) are level enough for agriculture and urban development. Mean annual high temperature is about 22°C, and rainfall averages about 700 mm yr⁻¹. The lake lies in a tectonic basin blocked by a landslide at one end and a volcanic dam at the other. Since 1914, the top 3 m of water depth has been controlled by a dam. Clear Lake is thought to be the oldest lake in North America, with continuously recorded lake sediment cores dating to approximately 500,000 ybp (years before present).¹ The lake is divided into three main basins or arms (see Figure 1), the largest of which is the Upper Arm. Nearly all of the winter inflow of water into Clear Lake is into the Upper Arm (approximately 90%, using the estimates in Reference 2). Forty-five percent of the inflow is from the Scotts Creek and Middle Creek watersheds² which enter the lake through Rodman Slough. There are some very small, seasonal inflows into the two other arms. The outflow is through Cache Creek at the southern end of the Lower Arm. Aside from the natural stresses of fire, floods, drought, etc., there are many anthropogenic stresses to the system. The most important management problems at the lake are the frequent occurrence of blooms of scum forming cyanobacteria (bluegreen algae) and the contamination of the aquatic ecosystem by mercury and, in the 1950s, by the pesticide DDD.

The objective of our study is to estimate the degree of stress imposed on the Clear Lake watershed by the successive stages of population growth and economic development, especially European growth and development. Were any of the stages of European population and economy “sustainable”? The history of human settlement in the Clear Lake basin is typical of rural California. Native American settlement reaches back to the end of the Pleistocene. One of the first “early man” (Paleo-Indian) sites in North America was discovered at Borax Lake,³ a small lake on the peninsula between the Lower and Oaks Arms of Clear Lake. Because of an abundance of acorns, fish, and other resources, the Native American populations at the
time of European contact were relatively dense; approximately 3000 people lived in some 30 villages mostly near the lake. The acorn-intensive subsistence strategy developed about 2500 years before present and continued more or less unchanged until European contact. No significant changes in anthropogenic effects during the last few hundred years of the Native American period are expected from the archaeological record, and none were observed in our cores. The history of European settlement in the basin is described by Simoons. Mexican land grants in the 1840s initiated European settlement, but only a handful of ranchers resided in the Clear Lake watershed. Agricultural settlement began in 1854, and the rate of settlement increased after 1866. Early censuses showed nearly 1000 people in 1860, nearly 3000 in 1870, and just over 7000 in 1890 in Lake County, most residing in the Clear Lake watershed. Farming, ranching, and farm services were the most important occupations, followed by mining for sulfur, borax, and cinnabar and a small lumber industry. Tourism, centered on hot spring spas, began in 1852. It was well developed in the late 19th century, with several resorts having capacities for hundreds of guests. Early farming focused on wheat, barley, beef, and wool. Sheep numbers peaked sharply in the late 1870s at around 50,000 head and declined thereafter due to deteriorating pastures. Goats and hogs peaked at the turn of the 20th century at around 10,000 head each. Cattle numbers were much more stable, with around 10,000 head from 1861 through the 1980s. Mining for sulfur began at the Sulphur Bank Mine at the east end of the Oaks Arm in 1865, and cinnabar was soon discovered at the same site. Large amounts of mercury (Hg) were mined from 1873 to 1957, with the largest episodes of mining from 1873 to 1883 (3000 metric tons [MT]) and 1927 to 1944 (1100 MT), with a total of about 4700 MT of mercury removed.7,8 Thus, 19th century European settlement in the watershed was extensive, and the economy was substantially based on the exploitation of natural resources, leading to the potential for significant anthropogenic stresses before 1900.

Presently, agriculture (especially orchard crops) and tourism are the most important industries in the basin. Orchard crops (pears, walnuts, and grapes) have replaced annual crops over almost all of the tillable acreage. Most level acreage near the lake is irrigated. There is recreational development around much of the shoreline (this development followed the construction of a state highway in the 1920s). The two incorporated cities of Clearlake (about 13,000 residents) and Lakeport (about 5000 residents) lie on the lake shore, as do several other smaller communities. The total population of the basin in 1990 was about 50,000.

European activity has generated a number of stresses in the Clear Lake watershed. During the 19th century, clearance for farmland, road building, livestock grazing, logging, and firewood cutting could have generated substantial erosion and eutrophication, as similar settlements did in the eastern U.S.9 Mercury mining could have resulted in the contamination of lake sediments. Several activities are likely to have contributed to increased stress in the 20th century. Our investigation of the causes of algal blooms in Clear Lake concluded that nutrient loading to the lake increased substantially between 1925 and 1938 due to the beginning of the use of heavy earth-moving equipment. Two early scientific reports describe the lake as having abundant rooted aquatic vegetation, as do elderly residents' recollections of conditions before 1930, recorded in the 1960s.10,11 Histories taken in the 19th century describe the lake's water quality in good terms, though one of them is quite candid about problems with noxious swarms of the Clear Lake Gnat (Chaoborus sp.).12,13 By 1938, when a series of secchi disk transparency measurements were made, the lake had become too turbid for rooted aquatic vegetation to flourish, and cyanobacterial scums had become a perennial problem.14,15 Since heavy equipment was used in the Clear Lake watershed for many kinds of earth-moving projects, we expected to find multiple impacts of its use. The cores were designed to reach well below the advent of European settlement to put the heavy equipment hypothesis into the context of earlier and later impacts of European activities. Until 1987, gravel mining in streambeds was common (S. Zalusky, personal communication). The Sulphur Bank Mercury Mine was operated using open pit methods after 1927, and approximately 100,000 MTs overburden and waste rock were moved. Some excavated material was pushed directly into the lake, and eventually 400 m of lake shore were covered with waste rock and tailings piles about 10 m high at the angle of repose. Subsequent erosion from these piles into the lake was significant.16-18 Road building and lake filling activities also increased after 1920. Rough estimates suggest that current erosion rates are roughly twice pre-European rates, with stream channel disturbance and road cuts/fills being the most important causes. In 1928, a 2000-acre reclamation of the project, also constructed using heavy equipment, eliminated most of wetland at the northwest end of the lake. The project created Rodman Slough (Figure 1) to direct flood flows directly into the lake, thus destroying a major trap for nutrients and sediment. Thus, several lines of evidence suggest that the advent of heavy earth-moving equipment was the ultimate source of the most important anthropogenic stresses on the Clear Lake watershed and lake ecosystems. Natural processes such as drought could have impacts on the lake and its watershed of the same magnitude as anthropogenic stresses.

Sediment cores provide many quantitative indicators of past conditions in lakes and their drainage basins. The extension of historical data beyond the usually short timeframe of monitoring data often taps natural "experiments" that can provide more realistic tests of hypothesis than recent data alone. Brush19,20 and others have used core data successfully to reconstruct the extent of human impacts on aquatic ecosystems. Here, we describe results from our ongoing Clear Lake coring project based on Upper Arm Core 2a and a replicate core taken at the same site, Upper Arm Core 2b (Figure 1). We measured parameters designed to estimate inorganic sedimentation rate and the degree of contamination from the Sulphur Bank Mercury Mine. Inorganic mercury was measured to estimate the load of this heavy metal to the aquatic ecosystem. Changes in organic matter content, nitrogen, phosphorus, and diatoms were measured to detect a change in trophic status. Pollen grains were counted to determine if anthropogenic disturbances due to logging, land clearance, grazing, or changes in fire frequency were likely to have been significant. This reasonably broad suite of indicators of physical, chemical, and biological conditions in the lake should detect changes in many of the most important anthropogenic and natural stresses that we believe could plausibly have occurred in the last few centuries.

The cores document a suite of major changes in the Clear Lake system dating from about 1927, much as suggested by the heavy equipment hypothesis. However,
the evidence for an increase in inorganic sedimentation rate in recent decades is ambiguous. An increase occurred in the Upper Arm 2 cores, but preliminary data from four other cores from other locations in the lake suggest that sedimentation rates may have fallen in the last 75 years. A plausible alternative hypothesis is that the sulfate and/or acid load, generated by the operation of the Sulphur Bank Mine using open pit methods, substantially altered the microbiology and chemistry of the lake’s sediments, leading to eutrophication as well as to a greatly increased level of mercury contamination.

METHODS

The cores were taken from a 22-ft research vessel using a push-rod operated piston corer. The core sleeve was constructed from 2 in. i.d. \times 10 ft Schedule 80 PVC conduit. The piston was a modified 2 in. pipe test plug with a nylon rope attached to the boat to keep the piston at the sediment–water interface during the insertion of the core. The push-rod was 1.5 in. galvanized steel pipe in 11-ft sections. The corer was lowered to just above the sediment–water interface, and the piston rope was tied off. The core was driven in one steady push, as smoothly as possible, and retrieved using a winch on the boat. Just before the core was removed from the water, the bottom was capped to prevent any loss of material. Once on board, the core was split into three sections, approximately 1 m long, by sawing around the core sleeve and then cutting through the core with a knife. The sections were then capped and stored in a refrigerator. Any storage was done at approximately 4°C in the dark. The core was extruded in 5-cm sections within 12 h of retrieval. Approximately 30 cm at the top of extrusion had to be done vertically, as the sediments were very soft and easily disturbed. Below this level, cores were extruded horizontally onto an aluminum foil sheet, marked in 5-cm intervals, and sectioned. All sections were placed in preweighed 4-oz specimen containers, weighed, homogenized, and then stored at 4°C under no-light conditions.

The remaining sample was stored in darkness at 4°C. Percent loss on ignition (equivalent to organic matter) and percent water were determined at the UC Davis Clear Lake Environmental Research Center. Loss-on-ignition subsamples were dried at 105°C and then combusted at 500 to 550°C for 2 h. The remaining sample after combustion is an estimate of the inorganic matter in the sample. The percent water presented is the average between the percent water values for the C/N and loss-on-ignition subsamples. The inorganic accumulation rate was calculated assuming that inorganic matter has a specific gravity of 2, that the midpoint of 80- to 85-cm core slice represents 1927, and the 145- to 150-cm slice core represents 1873 (see the following discussion of date estimates). Total phosphorus (P) concentrations were determined at the University of California Hopland Research and Extension Center using the methods of Sherman. C/N concentrations were determined at the DANR Analytical Lab at UC Davis using a Carlo-Erba 1500 series Nitrogen Carbon Analyzer.

Total mercury was determined at the UC Davis Environmental Mercury Laboratory on dry, powdered subsamples using a modified cold vapor atomic absorption method.

An accurate reconstruction of the depositional record is dependent upon establishing a reliable sediment chronology. One method for establishing this geochronology in sediments of recent origin is with 210Pb. The usefulness of this natural radionuclide is limited to sediments of the last 100 to 130 years because its half-life is about 22 years. An alternative sediment dating method matches pollutant profiles, such as mercury, to periods of known production and input. Application of multiple methods generally improves the accuracy and confidence in age estimates. Concentrations of sediment 210Pb were determined in the laboratory of D.N. Edgington (Center for Great Lakes Studies, University of Wisconsin, Milwaukee) by measuring the activity of 210Po, a decay product of 210Pb. Sample size was approximately 0.5 g of dried sediment prepared for counting by the methods specified by Robbins and Edgington, with 210Po added as an internal yield tracer. Alpha activity was measured on an argon purged, low-background counter. Eight sets of replicate extractions yielded an average coefficient of variation less than 12%. Most of these replicate sets were taken from sediment sections below 100 cm and, therefore, contained low excess activity. The deposition dates were computed from 210Pb concentrations using a constant flux, constant sedimentation rate model described in Robbins. We carefully inspected the data (Figure 2) and determined that a more complex model, assuming heterogeneous sedimentation rates, was not warranted. The appropriate model for excess 210Pb activity at depth z (A, f) is therefore

$$A_z = A_0 \cdot \exp(-\lambda \cdot m/r) + A_g$$

where

- $A_0$ = "unsupported" 210Pb activity due to atmospheric input
- $\lambda$ = the radioactive decay constant for 210Pb
- m = the cumulative dry mass at depth z
- r = the mass sedimentation rate
- $A_g$ = the "supported" 210Pb background activity generated by within-sediment production of 210Pb from the in situ decay of 226Ra

Cumulative dry mass sedimentation was estimated using the dry weight (105°C) of each core section. The unknown parameters ($A_0$, $A_g$, and r) were determined by nonlinear fit of this model to the 210Pb data.

Pollen counts were done by modifying the method of Faegri and Iversen. Each 1-g, fresh weight sediment subsample was boiled 10 min in 10% KOH to remove organic materials and washed with distilled and deionized water. Ten percent HCl and 95% ethanol were added to remove calcium carbonate and boiled in water bath. HF was added, and samples were boiled in water bath for 5 min to remove siliceous matter. The ethanol/HCl treatment was repeated. To remove cellulose on pollen
surface, a 3-min acetolysis with glacial acetic acid was performed in a water bath. After three washings with distilled, deionized water, glycerol was added. One drop of this solution was mounted on slide glass, and a minimum of 300 pollen grains was counted. The remaining solution was stored in a small glass vial. All data analyses were based on pollen percentage.

Samples of 100 to 150 mg of dried sediment were prepared for diatom enumeration by oxidizing with 30% hydrogen peroxide and washing with deionized water. Homogenized sediments in 2-ml aliquots were placed on a Battarbee plate (evaporation plate fitted with four cover slip depressions). Cover slips were mounted onto slides with Cargile mounting media. For each slide, 300 diatom valves were counted using a Zeiss phase contrast microscope at 1000X. Diatom taxonomy was based on standard references.

**FIGURE 2** $^{210}$Pb profile for core Upper Arm 2a. Smooth line indicates the best nonlinear fit to the data.

The $^{210}$Pb data for the Upper Arm 2a core is presented in Figure 2. The best nonlinear fit to this data was derived with simplex and quasi-Newton minimization algorithms. The data are described by an exponential decay equation, as given earlier, with the following parameters and their asymptotic standard errors: $r = 0.272 \pm 0.032 \text{ g cm}^{-2} \text{ y}^{-1}$, $A_n = 0.829 \pm 0.048 \text{ pCi g}^{-1}$, and $A_s = 0.580 \pm 0.018 \text{ pCi g}^{-1}$. The residuals are random, homogenous, and monotonic. Table 1 shows the calibration dates corresponding to midpoints for each sediment section. Any error in the estimated sedimentation rate would introduce an error in assignment of the deposition date which increases cumulatively with depth. This is evident in the upper and lower 95% confidence limits for each date, as calculated from the error associated with our estimate of sedimentation rate ($r$). Although dates are extended to the bottom of this core, the deeper dates are extrapolations beyond information actually contained in the signal of excess $^{210}$Pb, which typically decays below the limits of detection within approximately five half-lives (112 years). This extrapolation assumes a constant sedimentation rate below the excess $^{210}$Pb profile which is equal to the sedimentation rate calculated from the upper core profile. Similarly, confidence intervals were extrapolated to core bottom from the asymptotic standard error on our estimate of sedimentation rate. We should note that these confidence intervals were calculated from the standard error for an estimated parameter of a nonlinear function, and, thus, are not exact because they are based upon linearizing assumptions that tend to underestimate the true uncertainty.

The atmospheric flux of $^{210}$Pb can be estimated from these data if we assume that $^{210}$Pb has a short residence time in the water column and that its loss to outflow is negligible. These are reasonable assumptions given that Clear Lake is a shallow, eutrophic system with a hydraulic retention time of 4.6 years. Further assuming that $^{210}$Pb is uniformly distributed across the lake surface and then evenly deposited to the underlying sediments, the atmospheric flux is calculated to be 0.23 pCi cm$^{-2}$ y$^{-1}$. This is equivalent to the lower range of values (approximately 0.2 to 1.1 pCi cm$^{-2}$ y$^{-1}$) calculated by Turekian for the atmospheric flux to hemispheric latitudes between 15 and 55°N. At Clear Lake the deposition of $^{210}$Pb is low because it is close to the Pacific Ocean, where the prevailing maritime winds are depleted in $^{210}$Pb relative to continental sources.

Since the atmospheric flux of $^{210}$Pb at Clear Lake is relatively low and the mass sedimentation rate is relatively high, the specific activity of excess $^{210}$Pb in surface sediments is proportionately reduced. For this reason, the signal of excess $^{210}$Pb in the Clear Lake core has decayed nearly to the level of "supported" background activity by about 80 to 85 cm, which is equivalent to about 1929 from our estimated sedimentation rate for this core. With excess activity near the limits of detection at this depth, we cannot use $^{210}$Pb methods to directly test the hypothesis that sedimentation rates increased beginning at about 1929. Given the scatter in the $^{210}$Pb data and the low excess activity in these sediments, the most reliable approach in this case is an estimate of the average sedimentation rate from a
### TABLE 1 (CONTINUED)
Estimated Deposition Date of the Midpoint of Each Sediment Slice Derived from $^{210}$Pb Estimates

<table>
<thead>
<tr>
<th>Midsection Depth (cm)</th>
<th>Total $^{210}$Pb Activity (pCi g$^{-1}$)</th>
<th>Cumulative Section Mass (g cm$^{-2}$)</th>
<th>Midsection Deposition (date)</th>
<th>Confidence Intervals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-95%</td>
</tr>
<tr>
<td>207.5</td>
<td>0.66</td>
<td>41.8</td>
<td>1846</td>
<td>1796</td>
</tr>
<tr>
<td>212.5</td>
<td>0.61</td>
<td>42.9</td>
<td>1842</td>
<td>1791</td>
</tr>
<tr>
<td>217.5</td>
<td>0.63</td>
<td>43.9</td>
<td>1838</td>
<td>1786</td>
</tr>
<tr>
<td>222.5</td>
<td>0.60</td>
<td>45.0</td>
<td>1834</td>
<td>1781</td>
</tr>
<tr>
<td>227.5</td>
<td>0.46</td>
<td>46.1</td>
<td>1830</td>
<td>1776</td>
</tr>
<tr>
<td>232.5</td>
<td>0.67</td>
<td>47.2</td>
<td>1826</td>
<td>1770</td>
</tr>
<tr>
<td>237.5</td>
<td>0.48</td>
<td>48.3</td>
<td>1822</td>
<td>1765</td>
</tr>
<tr>
<td>242.5</td>
<td>0.55</td>
<td>49.4</td>
<td>1818</td>
<td>1760</td>
</tr>
<tr>
<td>247.5</td>
<td>0.61</td>
<td>50.5</td>
<td>1814</td>
<td>1754</td>
</tr>
<tr>
<td>252.5</td>
<td>0.51</td>
<td>51.6</td>
<td>1810</td>
<td>1749</td>
</tr>
</tbody>
</table>

Note: Dates and the confidence interval for sediments deeper than 82.5 cm are extrapolations from the upper part of the sediments to which the decay model was fit.

nonlinear fit to the profile, as explained previously. Averaged over the length of this core above 82.5 cm, where the $^{210}$Pb dating is reasonably reliable, the calculated linear sedimentation rate is 1.2 cm y$^{-1}$. Any flattening of the $^{210}$Pb profile commonly associated with active bioturbation appears to be limited to the top 10 to 15 cm in this core. This would place a lower limit on the temporal resolution of specific events at approximately 10 years. Other features of the core, especially mercury concentrations, permit further inferences about the sediment chronology, as discussed in the next section.

### PHYSICAL AND CHEMICAL CHANGES DWCORE

The most striking patterns in the record are the coincident changes of many parameters in the upper 80 cm of the core (see Figure 3 for mercury data, Figure 4 for physical data, and Figure 5 for chemical data). Above this horizon, sediments become markedly drier, have lower organic and nitrogen content, and contain about ten times more total (essentially inorganic) than the pre-European background. The $^{210}$Pb estimate for age of the last section before the sharp increase in mercury begins is 1929. Open pit operations began at Sulphur Bank Mine in 1927, and we have taken 1927 as the midpoint date for the 80- to 85-cm core slice. There is a doubling of mercury concentrations beginning at 145 to 150 cm in the Upper Arm 2a core, with an extrapolated $^{210}$Pb date of 1888. This increase probably represents the opening of the mine. Hg production began in 1873, but sulfur mining operations encountered mercury-contaminated material a few years before (sulfur mining began in 1865).

The lower 95% confidence interval for the 1888 extrapolated $^{210}$Pb date is 1853
Whether mercury first reached the lake in 1873 or a little before or after is impossible to tell, given the need to extrapolate dates below the level of excess $^{206}$Pb and an inexact history of mine operations. We have taken 1873 as the midpoint date for the 145- to 150-cm core slice.

If our hypothesis that sedimentation rates increased significantly above 80 to 85 cm is correct, then the $^{206}$Pb extrapolated age of the 145- to 150-cm section where the first mercury increase appears would be an underestimate. In support of the interpretation that the sedimentation rate changed after about 1927, water content in both cores taken at this site shows a dramatic decrease above 80 to 85 cm as if the deposition rate of inorganic sediment increased sharply (Figure 4). Normally, water content would increase monotonically toward the sediment surface, as it does below 80 to 85 cm. Observations of sediment consistency, recorded during the core sectioning process, noted a dramatic change at this horizon as well. As with water content, nearly all of the analyzed constituents show a major change at the 80- to 85-cm (≈1927) horizon. Total C and N and loss-on-ignition (organic matter) percentages show a large and rapid decrease above this depth (Figure 5). Total P declines slightly, but rises again at the surface. The total P content of creek sediments is about 1000 ppm, similar to values in the cores. The N-to-P ratio, an important index of the lake's nutrient status because of the role of N-fixing cyanobacteria, declines sharply after 1927.

If the date of the first mercury increase in the sediments is taken to be 1873, and the second larger increase is 1927, the rate of dry inorganic deposition changes substantially, from 0.14 gm cm$^{-2}$ yr$^{-1}$ 1873–1927 to 0.22 gm cm$^{-2}$ yr$^{-1}$ post-1927. The total sediment accumulation rate for 1873 to 1927 is almost exactly the same as the post-1927 rate (1.20 and 1.18 cm yr$^{-1}$, respectively), and the considerably higher content of inorganic material in the upper part of the core accounts for the higher inorganic deposition rate. A replicate core at Upper Arm 2 agrees, using the almost identical mercury profile for dating, almost exactly with these estimates, as indicated by the very similar water profiles shown in Figure 4. Cores from one other location in the Upper Arm, two locations in the Lower Arm, and one location in the Oaks Arm all have rather thinner sections of drier, mercury-rich sediments than the Upper Arm 2 core. $^{206}$Pb dates for the last section before the beginning of the large increase in mercury from a third Upper Arm core at a site distant from Station 2 is 1916,
and the estimate from the Oaks arm core is 1937. The mean of the three dates is 1927.3 years, and 1927 is well within the 95% confidence interval for all three estimates. The changes in other chemical, physical, and biological parameters is also similar to Upper Arm 2 in the other cores, as far as these have been analyzed to date. Thus, so far we have detected only ambiguous evidence that inorganic sedimentation rates have increased basin wide since 1927, despite the large changes in sediment physical and chemical composition suggesting just such an increase. Indeed, the Upper Arm 2 cores are the only ones that do not imply a decrease in inorganic sedimentation rate since 1927.

For several parameters, the upper few centimeters of sediment show a partial return to pre-1927 values. This return is considerable for percent water, which rises to near the values one would expect by extrapolating the slowly rising pre-1927 values to the surface. Loss-on-ignition (organic matter) N content show the smallest returns to earlier concentrations. The decline in inorganic mercury is considerable.

**Pollen Profile**

Pollen diagrams (Figures 6A and 6B) show a very different pattern from the physical and chemical constituents discussed previously. Major taxa in the pollen record show little or no evidence of changes over the whole period represented in the core. The dominant pine and oak pollens show no detectable pattern of change at all. TCT (Taxodiaceae, Cupressaceae, Taxaceae) group pollen shows a small decrease over the past 100 years as does Compositae. *Salix*, *Acer*, *Artemisia*, and *Chrysopilus* increase somewhat in recent times. Only *Juglans* (walnut) records the agricultural activities of the European settlers. There is a hint that *Potamogeton* was absent after around 1925 and reappeared recently.

**Diatom Profile**

Figure 7 shows the diatom profile in the core. The dominant diatom taxa encountered in Clear Lake are various species of *Aulocoseira* (formerly *Melosira*) and *Stephanodiscus*. The most dramatic change in the profile is the appearance and rise to subdominant status of *Aulocoseira distans* (Ehrenberg) Simonsen, while *A. antiqua* (Ehrenberg) Simonsen declined. This change correlates exactly with the many changes in physical and chemical variables dating to about 1927 described earlier. As with some other variables, there is a reversal of this change at the very top of the core. Less abundant species also suggest changes post-1927, including the appearance of *Cyclotella pseudostigmatos* costiformis (Kobayashi & Kobayashi) Stoerm. Håkansson & Theriot and S. *vestibulis* Håkansson, Theriot & Stoerm. Diatom diversity and equitability also increased after 1927, and diatom productivity declined, but irregularly, after 1927 (L. Meiller, unpublished data). As we remarked earlier, there is historical evidence that cyanobacteria became more abundant after 1927. In support of the sparse direct evidence, the N-to-P ratio in the sediments drops sharply after 1927 (Figure 5), suggesting that N became more limiting relative to P, a condition which favors N-fixing cyanobacteria. The decline in diatom abundance and species shifts evident in the core may reflect either the direct effects of altered
DISCUSSION

The early, relatively small increase in total mercury at 145 to 150 cm in Upper Arm Core 2 is almost certainly a result of the early mining at the Sulphur Bank Mercury Mine (Figure 3). The much larger amounts of Hg in the sediments after 1927 are almost certainly due to the use of open pit mining methods. The disturbance of large volumes of overburden and rock contaminated with metal sulfides, and the production of large volumes of tailings likely increased the loading of mercury to the lake ecosystem. The waste piles contain amounts of mercury ranging from nondetectable to 2400 mg kg⁻¹, with typical values of around 100 mg kg⁻¹. About 25% of the surface of the regraded piles contains sulfide minerals in sufficient concentrations to prevent the growth of annual vegetation (authors' observations). Mercury and related contaminants have entered the lake by three routes. First, mine waste rock containing cinnabar and elemental mercury was pushed directly into the lake as long as the mine was active. Much fine material was perhaps carried away from the immediate vicinity of the mine. Second, sheetwash erosion and mass wastage from wave undercutting of the waste piles transported mercury directly into the lake until the U.S. Environmental Protection Agency reduced the slope and rip-rapped the toe of the piles in 1992. Third, the mine currently discharges acid mine drainage into the lake, which we believe to be the only remaining significant source of mercury.

Since the toe of the waste rock pile rests in the lake, flow from the mine site into the lake is almost entirely subsurface and not easily measured. A rough estimate is possible. In the spring of 1995, a coherent layer of acid mine drainage precipitate covered about 1 km² of lake bottom adjacent to the mine about 10 cm deep, containing about 120 kg of mercury. Since the precipitate is very finely divided when it first forms, most of it was probably carried away from the vicinity of the mine before it could be incorporated into the distinctive layer near the mine. A plausible calculation suggests that the acid drainage source could account for all of the approximately 400 kg yr⁻¹ of mercury necessary to contaminate sediments to the levels recorded in our cores (Chapter 7 in Reference 19). We have also measured depressed pH and elevated sulfate in lake water near the mine (authors' unpublished data). Thus, acid mine drainage may have been the main, if not the only, source of mercury contamination of the lake, with the immediate area of the mine excepted. The modest declines in total mercury from post-1927 peaks (estimated turning point 1961) appear to have begun too long ago to be explained by the recent drough or the erosion remediation work at the mine site in 1992. We have done microstratigraphic analyses on the upper few centimeters of some short cores which indicate a considerable recent drop in inorganic mercury loading, probably due to the remediation (Chapter 5b in Reference 19).

The other coincident changes in physical and chemical characteristics of the core above the 75 to 80 cm level are consistent with the heavy equipment hypothesis, except for our failure to replicate an increase in deposition of inorganic matter per unit time in other cores. Drier sediments with less organic matter and N are consistent
with a greater ratio of inorganic to organic deposition. This hypothesis was previously proposed, based on historical records and limited erosion surveying. In addition to the internal data from the cores, historical evidence suggests a significant increase in watershed disturbance around 1927. At this time, the application of powered earth-moving technology to streambed gravel mining, road construction, wetland reclamation projects, and mercury mining began. This type of machinery was developed just before and after World War I, and its use became widespread in the late 1920s. By the early 1930s, Caterpillar had a line of earth-moving machinery much like contemporary types. The end of active mercury mining in 1957 and the end of gravel mining in most streams by 1987 should have resulted in a reduction in sediment loading. Consistent with this expectation, there is a trend toward moister, more organic sediments above 30 to 35 cm after the peak of inorganic deposition (~1971). Beginning in the winter of 1971 to 1972 and persisting until the present, water quality monitoring data show less winter turbidity, which is normally due to inorganic material derived from streams. Unfortunately, water quality data are only available back to 1968. Since the pattern of post-1927 increase in inorganic deposition is not present in other cores, it is quite possible that the Upper Arm 2 cores reflect disturbances to the nearest stream, Kelsey Creek (Figure 1). Kelsey Creek began a major episode of downcutting in its lower reaches when its delta was channelized to construct a boat harbor in the mid-1960s. The peak of inorganic deposition in the core dates to about 1971.

Sediment deposition directly from mining operations cannot account for changes in bulk sediment characteristics as distant from the mine as the Upper Arm 2 station. Inorganic mercury in surficial sediments declines exponentially with distance from the mine. Oaks Arm surficial sediments near the mine have total mercury concentrations of about 100 to 300 mg kg⁻¹ (dry weight basis). In contrast, concentrations are only 3 mg kg⁻¹ at Upper Arm 2, indicating that erosion products from the mine are disproportionately deposited near the mine. The fine precipitate produced when acid mine drainage is neutralized by lake water is likely to be disproportionately represented in the mercury deposited at the Upper Arm 2 site.

The 1987 to 1992 drought, during which time there was very little sediment (and sulfate) input to the lake, may have had some influence on the upper few centimeters of the core. Bioturbation undoubtedly integrated the sediments deposited during these years with the four more normal years since the end of the drought. Nevertheless, recent changes appear to have started well before the drought. One exception is the surface peak of total P. We know that increasingly large amounts of base extractable (iron and aluminum bound) P cycled from the water column (late summer) to sediments (winter) during the drought years. The large mass of P that appeared during the drought has resisted burial in the subsequent years, presumably due to its mobility and consequent upward diffusion during summer sediment anoxia.

The long 1986 to 1991 drought reduced the delivery of erosion products to the lake. Thus, it is a natural experimental test of the heavy equipment hypothesis. In several respects, the drought did induce conditions that were characteristic of the pre-1927 period. Historical records also suggest that rooted aquatic vegetation was abundant before 1925. Turbid water after 1927 inhibited the growth of Potamogeton and other submerged macrophytes for many decades. In the last few years, severe iron limitation, the causes of which we are continuing to investigate, have produced clear water conditions again, and Potamogeton and other rooted aquatic species thrived, consistent with the record of Potamogeton pollen. The changes in the diatom flora are not dramatic, but certainly indicate changes in nutrient or light status. The decline in the N-to-P ratio to one third of predisturbance values is consistent with N becoming more limiting relative to P (Figure 5), which would have favored N-fixing cyanobacteria, consistent with the limited historical data indicating that cyanobacterial scums were not a serious problem before the late 1920s or early 1930s. Work by Horne also suggested that winter light limitation due to inorganic turbidity favored winter buoyant Antithamnion populations and limited diatom growth. Clear water in winter favors diatoms that do not use buoyancy to stay near the surface. The significance of the shifts in the diatom community is obscure. It is interesting that the rise in A. ambiguus and decline in A. distans right at the top of the core coincides with the clear-water conditions accompanying the recent drought event (Figure 7). However, diatom productivity has not increased in recent years. Thus, lake water quality in the period from 1991 to the present in some senses resembles the conditions reported by 19th and early 20th century observers, and this resemblance is reflected in some core measurements.

The increases of Salix and Acer pollen may represent the colonization of disturbed stream channels by willow and box elder, whereas intact riparian vegetation tends to be dominated by oaks (Quercus lobata). The essentially constant proportions of Pinus and Quercus pollen, the dominant genera in upland communities, rule out wholesale disturbance of terrestrial ecosystems as a cause of changes seen in the core. If heavy equipment activity is the cause of the post-1927 changes, it must be due to increased erosion from relatively small areas such as road cuts and fills and disturbance to riparian areas. Whatever changes occurred in the upland areas of the basin with the advent of European settlement left very modest traces in the paleontological record. As Simons noted in his history of the impacts of European settlement, there is very little evidence of gross anthropogenic impacts on upland watersheds.

Notwithstanding the considerable circumstantial evidence in favor of the heavy equipment hypothesis, support from cores collected to date is ambiguous. It is possible that with only two cores from the Upper Arm, and only five independent stations in the whole lake, we have failed to detect an increase in sedimentation rate. What are the alternative hypotheses to explain the coincident changes that began about 1927? It is conceivable that other anthropogenic changes have counterbalanced the use of heavy equipment in the basin. Most conspicuously, sheep and goat grazing and pig herding was significant in the late 19th century and highly detrimental to upland pastures, but all these stresses declined to insignificance well before 1927. If high animal stocking was responsible for increased erosion, it left no signature in the pre-1927 sediments we have been able to detect. Unlike the watershed of the Chesapeake, only a relatively small proportion of the Clear Lake watershed has been converted from grassland, chaparral, and oak and pine forests.
to intensive uses. Most intensive farming and human settlement is on level alluvial soils with little erosion potential. Distinguishing natural from anthropogenic causes of erosion is difficult, and the steep uplands in the headwaters of the basin will have high natural erosion rates. The only direct study of erosion in the basin was very cursory and could well have erred in its estimation of anthropogenic influences on erosion rates.

Alternatively, uncertainties in the \(^{210}\text{Pb}\) dates are appreciable, especially in the levels older than about 1927 where excess \(^{210}\text{Pb}\) activity is minimal. The 1873 date based on the first appearance of mercury is reasonably well corroborated by our \(^{210}\text{Pb}\) date of 1888. It is possible that we have mistided the core sufficiently to lead to significant errors in interpretation of sedimentation rates and other processes. It is also possible that sedimentation rates in the basin have increased, but that human activities have resulted in the storage of the sediment in the watershed rather than in the lake (J.F. Mount, personal communication). Perhaps the Upper Arm 2 core reflects the fact that significant erosion occurred on the lower reaches of Kelsey Creek and that sediment mobilized higher up in other drainages has yet to reach the lake in quantity.

We are currently focusing our main effort on testing the hypothesis that increases in sulfate and/or acidity loading are wholly or partly responsible for the changes observed in the core. The Sulphur Bank Mercury Mine potentially became a major source of sulfate and acidity loading after it began to be operated by open pit methods in 1927. Approximately \(10^6\) m\(^3\) of sulfide-rich overburden and waste rock were excavated in the course of open pit operations, leaving a flooded impoundment of 860 \(10^4\) m\(^3\) (data here and for the following calculations from the U.S. Environmental Protection Agency\(^{19}\)). Sulfate concentrations in the impoundment waters, groundwater downgradient toward the lake from the impoundment, and surface runoff from waste piles are about 30 m\(\text{M}\), with pHs around 2.5. The standing mass of sulfate dissolved in impoundment water alone is about 2500 MT. The standing mass in the lake is around 17,000 MT in nondrought years. The hydraulic residence time of the lake is about 4.6 years, so a sulfate load on the order of 2500 MT yr\(^{-1}\) could be an important term in the sulfate budget of the whole lake.

How might sulfate and/or acidity loading cause dramatic changes in sediment physical and chemical properties? Independent lines of evidence do strongly suggest that major changes occurred about 1927, roughly contemporaneous with the beginning of open pit mining. There is little doubt that water quality deteriorated after Coleman's visits in 1925, as discussed earlier. The severe drought of the late 1980s and early 1990s again provides an interesting natural experiment. Sulfate loading from the mine and the basin was presumably sharply curtailed. The proximal reason for the return of clear water in 1991 was the result of severe iron limitation of plankton primary productivity and of N fixation by cyanobacteria.\(^{31}\) At the same time, the amount of P cycling out of the sediments rose from a predrought average of 150 MT to a peak of 650 MT in 1990, falling back to 200 MT in 1995 and 1996. The P cycles almost entirely from the iron-bound pool in the sediments, so it is puzzling that iron fell during the drought (authors' unpublished data). A peak of total iron in deep water occurred during the late summer peak of P release from the sediments.\(^{32}\) This peak, however, was accompanied by a minimum in dissolved iron.

Geochemical modeling\(^{33}\) suggests that iron was being bound as ferrous sulfide as rapidly as it was mobilized from ferric phosphate. Sulfate reduction is an important process in Clear Lake sediments.\(^{34}\) During the drought, sulfate concentrations in the lake fell from about 125 to 60 \(\mu\text{M}\) (California Department of Water Resources, unpublished data), reflecting the failure of sulfate loading to balance active net sulfate reduction. Gross sulfate reduction is much higher than net sulfide storage in the sediments.\(^{35}\) Presumably, much sulfide is reoxidized at the sediment surface or in the overlying water. Sulfur thus acts as a conveyor of relatively high-energy-potential oxidizing power into the sediments. When sulfate is abundant, sulfide isomers are, all else being equal, likely to lie deeper in the sediments. Since the sediment surface is less likely to be anoxic, ferric phosphate reduction is less intense, reducing the amount of P recycled from the sediments. However, by confining sulfide to greater depths in the sediment, ferrous iron is scavenged less efficiently, leading to more available iron in the water column. If this line of reasoning is correct, increased sulfate loading will tend to relieve the iron limitation of N fixation by cyanobacteria, leading to eutrophication of the lake. The effect of the sulfur conveyor will also be a more thorough mineralization of organic matter in the sediments, hypothetically leading to low organic matter and drier and more nitrogen-poor sediments, as we observed.

Kilham\(^{34}\) discusses the case of a soft water lake in a basin with significant carbonate rock becoming alkalized by acid rain. After the acidity of the rain is neutralized by \(\text{CaCO}_3\) in the watershed, sulfate reduction and denitrification by microbes in the lake's sediments generate alkalinity, ending with the apparent paradox of acid loading generating net alkalinity. In general, phytoplankton production rises with alkalinity. Clear Lake is presently a fairly alkaline system (pH 8, alkalinity 125 ppm). Presumably, the acidity from the acid mine discharge has been neutralized by sediment \(\text{CaCO}_3\), and net alkalinity is generated by sulfate reduction, by analogy with Kilham's system.

CONCLUSIONS

The Clear Lake ecosystem has experienced a major, continuing stress, or series of temporally coincident stresses, beginning about 1927 and continuing to the present. Several of the changes recorded in our sediment cores are consistent with increased inorganic sedimentation, such as lower water, nitrogen, and organic matter content after 1927. These data, together with some historical data and a limited erosion survey, suggest that the advent of heavy earth-moving equipment in the late 1920s and early 1930s was responsible both for the increased mercury in the sediments and the apparent increase in sedimentation rate. However, evidence of increased sedimentation rates is mixed. Four out of five cores so far raised suggest a lower sedimentation rate after 1927. Either these cores are misleading in some way or some other process caused the simultaneous change of several properties of the sediments beginning about 1927. The tight correlation of these changes with the increase in mercury in the sediments suggests that some direct link with mine operations is possible. An alternative to the heavy equipment...
hypothesis is that acidity and/or sulfate loading from the mine caused these changes. Our current research is devoted to distinguishing between the heavy equipment and acid/sulfate hypotheses.

The absence of major impacts from the early period of European settlement is striking. The transformation of the grasslands to grain fields and the replacement of native pasture grasses by Mediterranean weeds was a major impact which is unfortunately difficult to detect in the pollen record. Nevertheless, the overall stability of the vegetation and the lack of a conspicuous increase in sediment yield are remarkable. Judging from impacts so far uncovered in our cores, grazing, wood cutting and lumbering, agricultural clearing, and the development of small towns and recreation facilities, as conducted from 1854 to 1927, were relatively low-impact activities from a watershed mass-balance perspective. It is encouraging to think that one of California's rugged, semi-arid environments apparently supported a fairly large, active human population in a reasonably sustainable fashion. A narrow range of activities would appear to have been responsible for the stresses visible in our cores.

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For questions or further information regarding the work described in this chapter, please contact:

Peter Richerson
Dept. of Environmental Science and Policy
One Shields Avenue
University of California
Davis, CA 95618

e-mail: pjricherson@ucdavis.edu

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