

## ANTHROPOGENIC STRESSORS AND CHANGES IN THE CLEAR LAKE ECOSYSTEM AS RECORDED IN SEDIMENT CORES

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**Abstract.** Sediment cores were collected to investigate multiple stresses on Clear Lake, California, USA, through the period of European occupation to the present day. Earlier workers suggested the hypothesis that the use of mechanized earthmoving equipment, starting in the 1920s and 1930s, was responsible for erosion, mercury (Hg) contamination, and habitat loss stresses. Cores (~2.5 m in depth) were collected in 1996 and 2000 from each of the three arms of the lake. Carbon-14 dating suggests that these cores represent as much as 3000 years of the lake's history, beginning long before European settlement. Total mercury (TotHg) and methylmercury (MeHg), dry matter, water, carbon, nitrogen, phosphorus, sulfur, and the stable isotopes <sup>13</sup>C and <sup>15</sup>N were measured at 5-cm intervals. Nearly all parameters show major changes at depths of 58–135 cm, beginning at ca. 1927 (dated with <sup>210</sup>Pb). Accepting this date for concomitant major changes in seven cores yields an estimated 8.6 mm/yr average sedimentation rate after 1927. Pre-1927 sedimentation rates were ~1 mm/yr. Total mercury and MeHg, dry matter, phosphorus, and <sup>15</sup>N increase significantly, whereas nitrogen, sulfur, carbon, and water content decrease significantly above the 1927 horizon. Both TotHg and MeHg show extremely large increases (roughly 10-fold) above the 1927 horizon. A peak in inorganic deposition rate and minimum values for percentage of water is present at depths corresponding to ca. 1970. Interestingly, the first 75 years of European settlement in the Clear Lake basin (including the most productive years of the Sulphur Bank Mercury Mine) appeared to have had undetectable effects on lake cores. Changes since 1927 were dramatic. The large increase in Hg beginning about 1927 corresponds to the use of heavy equipment to exploit the ore deposit at the mine using open-pit methods. Increases in sediment deposition from increased earthmoving in the basin and sulfate loading from the mine are the most likely explanations for the dramatic changes seen in the post-1927 sections of the cores.

**Key words:** <sup>14</sup>C; Clear Lake, California, USA; dichlorodiphenyldichloroethane (DDD); human impacts; <sup>210</sup>Pb; mercury; mining; sediment cores; Sulphur Bank Mercury Mine; watersheds.

### INTRODUCTION

Data presented here from several sediment cores collected in 1996 and 2000 at Clear Lake, California, USA, represent one component of a larger ecosystem-level study that traces the origin and pathways of mercury (Hg) from the ore body at an abandoned Hg mine, through the abiotic (sediment and water) matrices, to lower trophic level species (benthic invertebrates and plankton) and ultimately to higher trophic level species

(e.g., fish, birds, and mammals). This paper provides both historic (1800s to present) and prehistoric (to ~3000 years before present) data that define the variability of Hg loading and other stressors to Clear Lake before and after European settlement in the Clear Lake Basin. Our objective is to describe the temporal pattern of anthropogenic stresses on Clear Lake in order to better evaluate proposed causal connections between stressors and effects.

Sediment cores have been used extensively over the past several decades to aid in the reconstruction and evaluation of impacts to aquatic ecosystems from a wide variety of disturbance events and processes (Engstrom et al. 1985, Von Gunten et al. 1997, Brush 2001). Some have focused on contaminants in general (Gearing et al. 1991, Macdonald et al. 2000, Gallagher et al. 2004), while others have targeted the historical accumulation of Hg, primarily as a result of atmospheric deposition (Swain et al. 1992, Engstrom et al. 1994, Benoit et al. 1998, Lockhart et al. 1998, 2000, Heyvaert et al. 2000,

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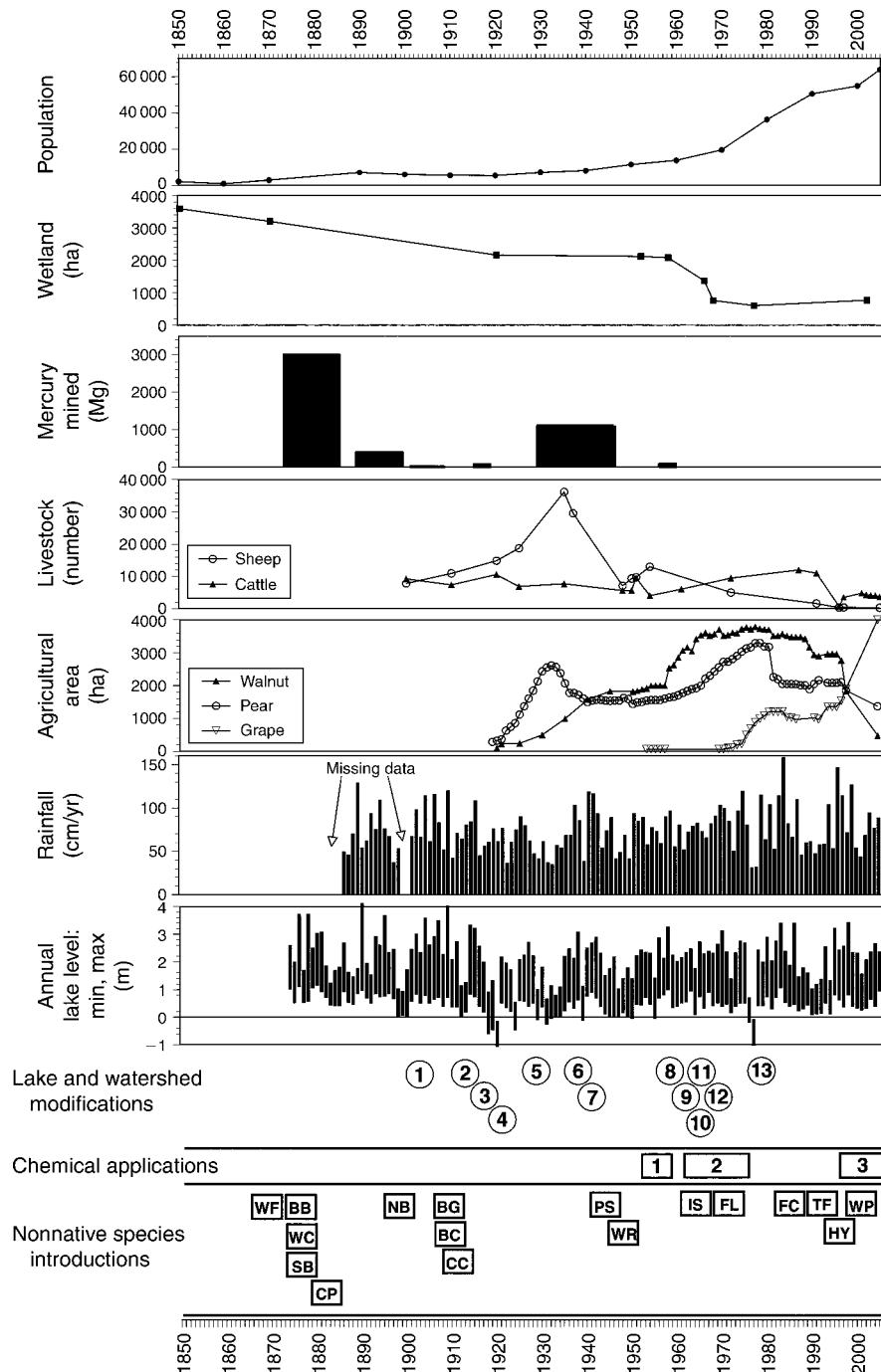


FIG. 1. Timeline for major environmental events in Lake County that have impacted Clear Lake, California, USA. Lake and watershed modifications: (1) Tule Lake wetland reclamation (destruction), early 1900s; (2) Clear Lake dam completion, 1914; (3) Cache Creek straightened above Grigsby Riffle, 1919; (4) Gopcevic Water Decree, 1920; (5) Middle Creek wetland reclamation, 1927; (6) Grigsby Riffle deepened, 1938; (7) Bemmerly Water Decree, 1939; (8) Rodman Slough wetland reclamation, 1959; (9) Adobe Creek Reservoir completed, 1962; (10) Highland Springs Reservoir completed, 1963; (11) Kelsey Creek dredged, 1955; (12) Scott's Creek gravel mining for road construction, 1969; (13) Solano Water Decree, 1978. Chemical applications to Clear Lake: (1) Dichlorodiphenyldichloroethane (DDD) applications for gnat control, 1949, 1954, 1957; (2) methyl parathion applications for gnat control, 1962–1975; (3) during the mid- to late 1990s, large quantities of the aquatic weed control agents Komeen and Sonar were used in the Hydrilla eradication program; applications post-2000 were orders of magnitude smaller and used in strategic amounts and at strategic locations. Application of aquatic weed control agents: Komeen (copper-ethylenediamine complex and copper sulfate), 1994–2006 and later; Sonar (fluridone), 1996–2006 and later; glyphosate, 2002–2006 and later; diquat dibromate, 2002–2006 and later; copper carbonate, 2002–2006 and later; potassium salts of endothall, 2004–2006 and later; triclopyr, 2005–2006 and later. Nonnative species introductions to Clear Lake: WF, whitefish (*Coregonus chupeaformis*), 1868, failed; BB, brown bullhead

Kamman and Engstrom 2002). Here we have attempted to catalog stresses that have impacted Clear Lake since the arrival of the Europeans (Fig. 1) and to use cores to evaluate the impact of as many as possible.

Clear Lake is a large (177 km<sup>2</sup>), shallow, eutrophic, polymictic lake in the central Coast Range of northern California, USA, that has been subjected to multiple stresses from natural and anthropogenic sources (Suchanek et al. 2003, 2008d). One of the most prominent stressors has been Hg contamination from an abandoned mine along its shoreline, although pesticide applications, eutrophication, and alien species introductions have also dramatically impacted the lake's ecosystem. Clear Lake is the largest lake completely contained within California and is the location of one of the oldest documented North American "early man" sites with paleo-Indian occupation ~10 000 years before present (Heizer 1963). It is also believed to be the oldest natural lake in North America, with continuous lake sediments dating to the early Pleistocene, yielding age estimates of 1.8–3.0 million years old (Casteel and Rymer 1981, Hearn et al. 1988). While the area was occupied by Native Americans since their initial settlement, the lake, its surrounding shorelines, and its watershed have undergone extensive modification since European settlement in the mid-1800s (Fig. 1). It has lost >85% of its original natural wetlands, which has dramatically altered the nutrient balance of nitrogen and phosphorus cycling, resulting in frequent noxious bluegreen algal (cyanobacterial) blooms (Richerson et al. 1994, 2000, Suchanek et al. 2003). Natural stressors on this ecosystem have included geologic and tectonic events (some changing the entire flow regime of the lake), regional and global climate change, fires, droughts, and floods. Anthropogenic stressors have included logging and deforestation, dam construction, fire, wetland destruction, livestock over-grazing, and numerous mining operations, the largest being Hg mining (see Suchanek et al. 2003, 2008d).

The Sulphur Bank Mercury Mine, along the eastern shore of Clear Lake, began as a sulfur mine in 1865, but was soon converted to a Hg mine in 1873 after cinnabar deposits were found beneath the surface sulfur deposit. Mining operations began using shaft mining and shallow cuts that had relatively minor impacts on the lake and landscape, but gave way to large-scale open-pit mining operations in 1927. Open-pit practices included bulldozing mine tailings and waste rock directly into Clear Lake. Mining continued intermittently into the

1950s, with the final closure in 1957, but Hg-contaminated mine wastes continued to erode into Clear Lake over the next 35+ years (see Suchanek et al. 2008d for more details).

Dichlorodiphenyldichloroethane (DDD) was also applied in increasing quantities to Clear Lake in the late 1940s to mid-1950s (with the largest and last application in 1954) in an attempt to control the Clear Lake gnat (*Chaoborus astictopus*), a noxious non-biting insect (Dolphin 1959, Hunt and Bischoff 1960, Cooke 1981). This resulted in an ecosystem-wide contamination that decimated Western Grebe populations. Clear Lake was one of the first ecosystems in which phenomena of chlorinated hydrocarbon bioaccumulation in food webs and of the delayed expression of contamination due to the bioconcentration of pesticides were observed. These studies at Clear Lake were popularized in Rachel Carson's *Silent Spring* (Carson 1962, Rudd 1964). A more detailed summary is provided in Suchanek et al. (2003).

During the last half of the 19th century, land clearance for farmland, road building, livestock grazing, mining, logging, and firewood cutting potentially increased erosion and eutrophication rates, as similar settlements did in the eastern United States (Brush and Davis 1984). Simoons (1952) provided a history of the settlement of the Clear Lake basin. The earliest impacts included grazing and logging. The native bunchgrasses were almost completely replaced by alien Mediterranean grasses and forbs in the 19th century. Pollen profiles from one Upper Arm core are reported in Richerson et al. (2000). Unfortunately, grass pollen grains cannot be attributed to native vs. nonnative taxa. A few distinctive exotic taxa that might have arrived in the basin before 1900 (*Eucalyptus*, *Erodium*) were not found in our core. The only distinctive European plant to be recognized in the pollen record was the relatively late appearance of walnut cultivation. Simoons (1952) remarked that the overall pattern of the vegetation of the basin has changed little, apart from cultivated areas. The pollen record confirms this impression. Simoons' reports a peak of cultivated agricultural acreage in 1880, when total cultivated land reached ~7900 ha in the whole county, ~2.4% of the total area of the county. The lake's drainage basin is 137 000 ha, so even if all the agriculture occurred in the lake's catchment (which it did not), only a little more than 5% of the basin would have been disturbed by agriculture. Agriculture today is dominated by vineyards and pears, but walnuts were important

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(*Ameiurus nebulosus*), 1875; WC, white catfish (*Ameiurus catus*), 1875; SB, smallmouth bass (*Micropterus dolomieu*), 1875; CP, common carp (*Cyprinus carpio*), 1880; NB, northern largemouth bass (*Micropterus salmoides*), 1897; BG, bluegill (*Lepomis macrochirus*), 1906; BC, black crappie (*Pomoxis nigromaculatus*), 1906; CC, channel catfish (*Ictalurus punctatus*), 1908; PS, pumpkinseed (*Lepomis gibbosus*), 1942; WR, white crappie (*Pomoxis annularis*), 1945; IS, inland silversides (*Menidia beryllina*), 1962; FL, Florida-strain largemouth bass (*Micropterus salmoides*), 1967; FC, Florida-strain black crappie (*Pomoxis nigromaculatus*), 1984; TF, threadfin shad (*Dorosoma petenense*), 1988; HY, *Hydrilla verticillata*, 1994; WP, water primrose (*Ludwigia* sp.), 2000.

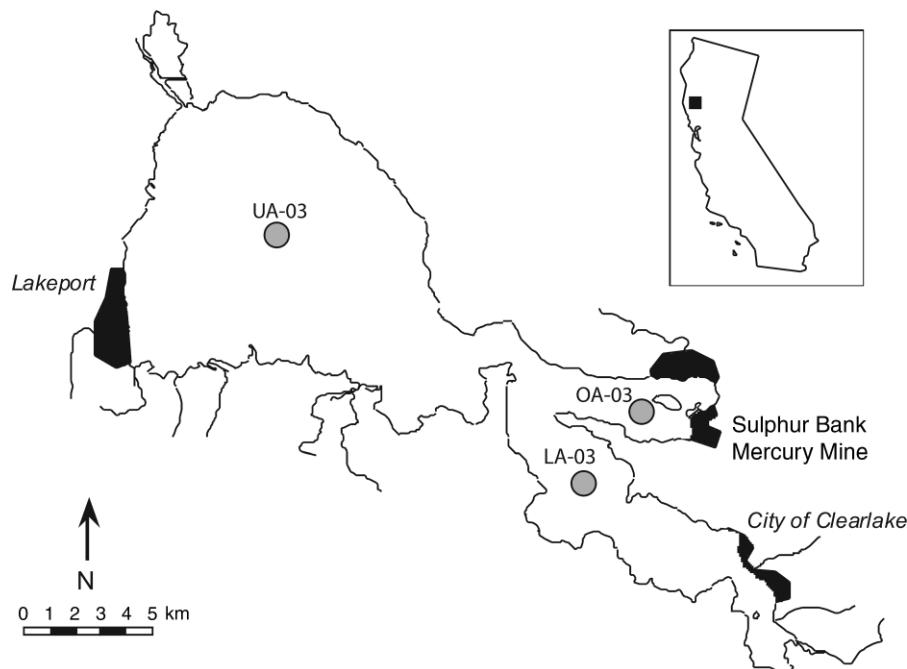


FIG. 2. Locations of coring sites in Clear Lake. See Suchanek et al. (2008*d*) for a more detailed map of the lake and watershed.

throughout most of the 20th century. These three crops together reached a peak of 7800 ha in 1980, falling to 5800 in 2000. Thus, cultivated agricultural land remains a small portion of the total. Most of the basin is steep slopes with thin soil. The oak woodland, conifer forest, and chaparral plant communities that cover these slopes are relatively little disturbed.

Previous investigations of the causes of algal blooms in Clear Lake (Richerson et al. 1994) concluded that nutrient loading, particularly of phosphorus, to the lake increased substantially between 1925 and 1938 due to heavy earthmoving equipment that came into use in the 1920s. 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 (Lindquist and Deonier 1943, Murphy 1951).

Road-building and lake-filling activities increased significantly after 1925, including the open-pit operations at the mine. In 1928, an 810-ha wetland reclamation project was constructed using heavy equipment. It eliminated most of a large wetland at the northwest end of the lake. This project created Rodman Slough (see Suchanek et al. 2008*d*), a narrowly confined wetland that conveys flood flows directly into the lake, thus removing a major sink for nutrients and sediment (Richerson et al. 1994). Until 1987, gravel mining in streambeds was also common (Zalusky 1992; S. Zalusky, *personal communication*). Evidence from these and previous studies suggests that the advent of heavy earthmoving equipment has been a significant factor in

shaping the landscape and ecosystem processes in Clear Lake.

Taking an ecosystem-level multiple stressor approach, we use inorganic and organic parameters from sediment cores to evaluate the impacts of stressors on the lake ecosystem and its watershed. The bottoms of our cores reach back well before the period of European settlement, ~3000 years before present. We have also used the known history of some of the contaminants, especially DDD and Hg, as time horizons to aid in our interpretations of events that have shaped the lake and its watershed.

#### METHODS

Sediment cores were collected in Clear Lake during 1996 and 2000 from a 6.7-m research vessel, using a push-rod operated piston corer at three locations: centrally located in the Oaks Arm (OA cores), the Upper Arm (UA cores), and the Lower Arm (LA cores) (Fig. 2). Additional cores were collected using this same method in 1998 to quantify the depth of DDD residues to assist in dating the cores. This method recovered undisturbed cores to ~250 cm depth, although in a few cases the very top portions of these cores were not intact due to the soft, unconsolidated, flocculent nature of surficial sediments. Coring procedures are described in more detail in Richerson et al. (2000).

Subsamples were collected at regular intervals (2.5 cm or 5.0 cm) for analysis of sediment dry mass, carbon, nitrogen, sulfur, total phosphorus, acid-extractable phosphorus (HCl-P), base-extractable phosphorus (NaOH-P), total Hg (TotHg), methylmercury (MeHg),

and stable isotopes ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ). Samples were dried at  $60^\circ\text{C}$  and crushed by mortar and pestle to pass through a number 60 mesh (250- $\mu\text{m}$ ) sieve. Total P concentrations were determined at the University of California Hopland Research and Extension Center by standard perchloric acid digestion (Sherman 1942). Using the methods of Hieltjes and Lijklema (1980), HCl-extractable P (seasonally dynamic iron and aluminum-bound P) and NaOH-extractable P (calcium-bound P) were analyzed. See Pettersson et al. (1988) for a critical discussion of the interpretation of these fractions. Elemental C and N concentrations were determined at the Division of Agriculture and Natural Resources Analytical Laboratory at the University of California at Davis (UC Davis), using a Carlo-Erba 1500 series nitrogen-carbon analyzer (Carlo-Erba, Milan, Italy). Total S in cores was analyzed using inductively coupled plasma emission spectroscopy following microwave digestion by nitric acid/hydrogen peroxide.

For all cores, TotHg in sediments was analyzed at the University of California Davis Environmental Mercury Laboratory on dry, powdered samples using cold-vapor atomic absorption spectroscopy (Slotton et al. 1995). Samples were solubilized through digestion in concentrated nitric and sulfuric acids, including a reflux stage with potassium permanganate, under pressure at  $90^\circ\text{C}$ . Dissolved Hg in the digests was subsequently volatilized using stannous chloride reductant for detection at 253.7-nm wavelength.

Methylmercury in 1996 core sediments was analyzed by Battelle Marine Sciences (Sequim, Washington, USA) using a "distillation" method (Bloom and Crecelius 1983, Bloom 1989, Horvat et al. 1993) that was ultimately determined to create spurious elevated MeHg concentrations as a result of the analytical procedure (Liang et al. 1996, Bloom et al. 1997). Using the distillation procedure, samples were distilled by reacting an aliquot of sediment in water with sulfuric acid and potassium chloride, then heating the distiller to  $125^\circ\text{C}$  (Horvat et al. 1993) and collecting the distillate in a Teflon receiving vial. The distillation method was later replaced by an "extraction" technique to eliminate this artifact. Using this alternate approach, samples were extracted by reacting an aliquot of sediment with acidic potassium bromide solution and copper sulfate and extracting them into methylene chloride. The sample is allowed to react for an hour, then shaken vigorously for an hour to move all the MeHg into the methylene chloride phase. The methylene chloride is then back-extracted into deionized water for analysis. Both preparation techniques put the MeHg into a clean deionized water matrix that is quantified by the same analytical technique, U.S. Environmental Protection Agency (U.S. EPA) Method 1630:draft. An ethylating agent is added to the distillate/extract to form a volatile methyl-ethylmercury derivative, and then purged onto graphitized carbon traps as a means of preconcentration

and interference removal. The samples are then isothermally chromatographed, pyrolytically broken down to elemental Hg, and quantified using a cold-vapor atomic fluorescence detector. The quantification method is based upon the emission of 254-nm radiation by excited Hg atoms in an inert gas stream at an intensity that is directly proportional to the amount of Hg in the gas stream. Typical detection limits for the method are 0.005 ng/g by distillation and 0.02 ng/g by extraction.

Methylmercury in sediments from year 2000 cores were analyzed using both the distillation and extraction methods. We used a multiple regression model to correct for artifacts in MeHg concentrations from the 1996 cores that were analyzed using only the distillation technique. The correction factor was generated using the 2000 cores for which MeHg was analyzed by both the distillation and extraction methods. We used TotHg and MeHg (distillation) as independent variables for the multiple regression algorithm in JMP version 5.1 (SAS Institute 2000). The resulting equation,  $\text{MeHg}_{\text{ext}} = 0.0913 + (0.0102 \times \text{TotHg}) + (0.29005 \times \text{MeHg}_{\text{dist}})$ , which explained 92% of the variability in the data ( $P < 0.0001$ ,  $N = 170$ ), was applied to the 1996 MeHg<sub>dist</sub> data to generate the corrected MeHg<sub>ext</sub> values reported here for 1996 cores.

Samples for  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  were dried and homogenized and then treated for the removal of carbonates by soaking in  $\sim 1$  mol/L HCl, then filtered on glass fiber filters (Whatman GF/D) with deionized water rinses. Samples were then dried again at  $60^\circ\text{C}$  for 48 h and homogenized again with mortar and pestle. Approximately 10–15 mg of dried sample was then loaded into tin capsules for C and N stable-isotope analysis. Isotope ratios were measured in a Europa Scientific Hydra 20/20 isotope ratio mass spectrometer (IRMS; Europa Scientific, Crewe, Cheshire, UK). Isotope ratios are expressed in delta ( $\delta$ ) notation, defined as the per mil (‰) deviation from the isotope standards using the following formula:  $\delta^{13}\text{C}$  or  $\delta^{15}\text{N}$  (‰) =  $[(R_{\text{sam}}/R_{\text{std}}) - 1] \times 10^3$ , where  $R = {}^{13}\text{C}/{}^{12}\text{C}$  or  ${}^{15}\text{N}/{}^{14}\text{N}$ , sam = sample, and std = standard. Standards are Pee Dee Belemnite (for C) and air (for N).

Three approaches were used to date various sections of cores: (1) DDD, (2)  ${}^{210}\text{Pb}$ , and (3)  ${}^{14}\text{C}$ . The peak of DDD application to Clear Lake in 1954 (see Suchanek et al. 2003, 2008*d*) was used to date the youngest core sediments and establish a recent stratigraphic horizon marker in the sediment column, H-1954. Fig. 3 shows that peak concentrations of DDD occur at depths of  $\sim 10$ –20 cm and approximately coincide with the decline in Hg concentration in the most recently deposited sediment in both the Upper Arm and the Oaks Arm. Using U.S. EPA Method 8081 by gas chromatography, DDD was analyzed by Battelle Marine Sciences Laboratory using fused-silica, open-tubular capillary columns with electron capture detectors (ECD).

To date intermediate aged sediments,  ${}^{210}\text{Pb}$  was used, but because its half-life is  $\sim 22$  years and because it exists

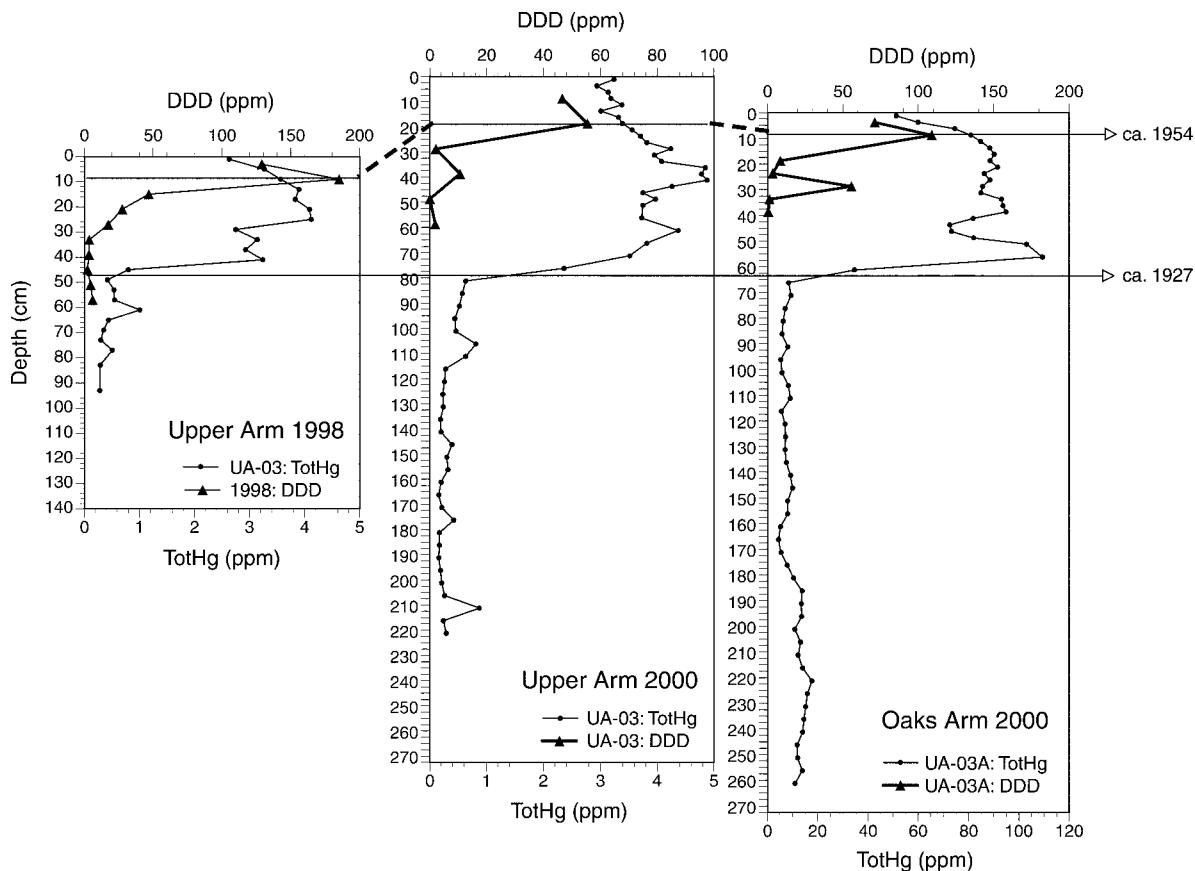


FIG. 3. Dichlorodiphenyldichloroethane (DDD) (triangles) plotted as a function of depth in representative Upper Arm cores (in 1998 and 2000) and an Oaks Arm core (in 2000). The DDD peak should correspond to the year of maximum application to the lake, ca. 1954. Total mercury (TotHg; small dots) is also plotted, along with a horizon line that represents the beginning of open-pit mining ca. 1927.

at relatively low concentrations in Clear Lake sediments, its usefulness as a dating tool is limited to sediments of the last 80–90 years. Concentrations of  $^{210}\text{Pb}$  in sediment were determined in the laboratory of D. N. Edgington (Center for Great Lakes Studies, University of Wisconsin, Milwaukee, Wisconsin, USA) by measuring the activity of  $^{210}\text{Po}$ , a decay product of  $^{210}\text{Pb}$ . Sample size was  $\sim 0.5$  g of dried sediment, prepared for counting by the methods specified in Robbins and Edgington (1975), with  $^{209}\text{Po}$  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  $< 12\%$ . Most of these replicate sets were taken from sediment sections below 100 cm and therefore contained low excess activity. The low-activity ratios preclude determination of detailed changes in sedimentation rates for the upper portions of the cores, so we only report average deposition rates even though other data suggest sedimentation rates decreased over the last few decades. Sedimentation rates for the upper sediment sections were estimated using DDD residue peaks. Deposition dates were computed from  $^{210}\text{Pb}$  concentrations using a

constant-flux, constant-sedimentation rate model described in Robbins (1978). The appropriate model for excess  $^{210}\text{Pb}$  activity at depth  $z$  ( $A_z$ ) is therefore

$$A_z = A_o \times \exp(-\lambda \times m/r) + A_s$$

where  $A_o$  is “unsupported”  $^{210}\text{Pb}$  activity due to atmospheric input,  $\lambda$  is the radioactive decay constant for  $^{210}\text{Pb}$ ,  $m$  is the cumulative dry mass at depth  $z$ ,  $r$  is the mass sedimentation rate, and  $A_s$  is the “supported”  $^{210}\text{Pb}$  background activity generated by within-sediment production of  $^{210}\text{Pb}$  from the in-situ decay of  $^{226}\text{Ra}$ . Cumulative dry-mass sedimentation was estimated using the dry mass ( $105^\circ\text{C}$ ) of each core section. The unknown parameters ( $A_s$ ,  $A_o$ , and  $r$ ) were determined by nonlinear fit of this model to the  $^{210}\text{Pb}$  data.

The top portions of some cores (i.e., UA-03 and OA-03 in 1996 and LA-03 in 2000) were not fully retrieved; thus, the tops of those profiles do not represent the sediment–water interface. In addition, the top portion of core OA-03C in 2000 exhibited  $\sim 33$  cm of sediment that appeared to represent uniform-aged sediments, possibly the result of slumping or multiple penetration of the coring device.

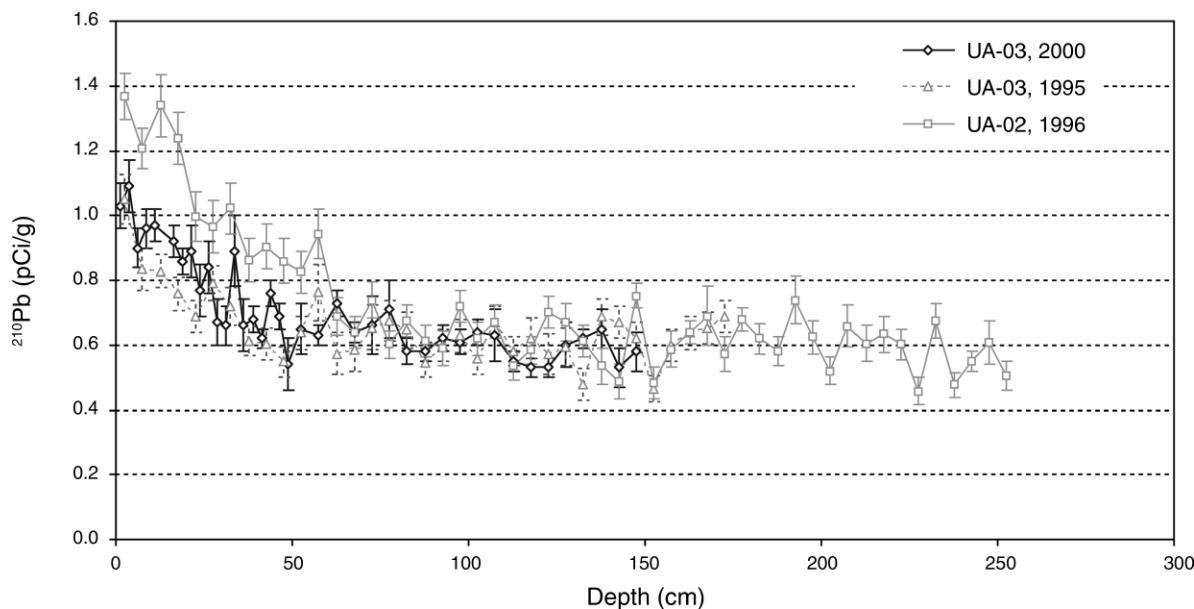


FIG. 4.  $^{210}\text{Pb}$  (mean  $\pm$  SE) vs. depth for Upper Arm cores.  $^{210}\text{Pb}$  in all three cores drops to background ("supported") levels by 50–80 cm depth in these cores, establishing the limits of  $^{210}\text{Pb}$  dating in the relatively slowly deposited Upper Arm sediments of Clear Lake.

Carbon-14 was used to place age constraints on deeper sections of the cores using accelerator mass spectrometry analysis of coarse woody organic matter separated from the cores (Osleger et al. 2008). Comparison to  $^{210}\text{Pb}$  dates shows that  $^{14}\text{C}$  dates are  $\sim 300$  years too old due to incorporation of  $^{14}\text{C}$ -depleted geothermal  $\text{CO}_2$  that outgases from the Clear Lake volcanic field underlying the southeastern end of the lake. Details of the analyses, correction procedures, and calibration for the  $^{14}\text{C}$  data are presented in Osleger et al. (2008).

## RESULTS

### Core dating

The coherence of downcore geochemical changes recorded in cores collected in the various sub-basins in Clear Lake provides a stratigraphic basis for correlation between cores. Two important stratigraphic horizon markers are defined and used as the basis for both correlation and as time horizons on which we define sediment accumulation rates determined by the three different dating techniques. The lower-most horizon marker (labeled as "H-1927") is our estimate of the date for many coincident changes in sediment physical properties and composition. It is clearly identified in all cores and represents a sudden and dramatic shift in the depositional environment of the lake around 1927. As we detail below, the changes above this horizon are the direct and indirect effects of the deployment of heavy earthmoving equipment in mining, road building, and reclamation projects in the basin. The upper horizon marker ("H-1954") is defined by a peak in DDD concentrations in the sediments around 1954. Samples

for DDD analysis were collected over 6-cm intervals in order to have sufficient material for the analysis. Therefore the resolution on the depth of the H-1954 horizon is  $\pm 3$  cm. The DDD concentration vs. depth profiles (Fig. 3) are plotted at the midpoint of the sampled interval. Since mining ceased in 1957, H-1954 also marks the date of abandonment of the mine within the resolution of our sampling.

The age of sediments below H-1927 can be constrained by  $^{14}\text{C}$  dating (Osleger et al. 2008), but this technique cannot resolve the exact age of H-1927. We use  $^{210}\text{Pb}$  dating to constrain the timing of the dramatic changes in the lake recorded in the sediment cores and obtained an average date of ca. 1927 for this stratigraphic horizon. Dating of sediments above H-1927 is more problematic, as changes in the geochemical profiles and grain size analysis suggest that an assumption of constant sedimentation rate is probably invalid (Osleger et al. 2008). However, the use of DDD peaks to define H-1954 provides evidence that is consistent between and within cores in comparison with the calculated  $^{210}\text{Pb}$  dates.

The down-core variations in  $^{210}\text{Pb}$  for the Upper Arm cores and Oaks Arm cores are shown in Figs. 4 and 5, respectively. The low atmospheric flux of  $^{210}\text{Pb}$  at Clear Lake ( $0.23 \text{ pCi}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$ ; Richerson et al. 2000) combined with the high sediment accumulation rates result in low activity of  $^{210}\text{Pb}$  in Clear Lake sediments. The low activity makes it difficult to discern details that could be used to estimate changing sedimentation rates; therefore only a bulk sedimentation rate was calculated. The upper 33 cm of core OA-03C (from the Oaks Arm in 2000) shows no decrease in  $^{210}\text{Pb}$  with depth and

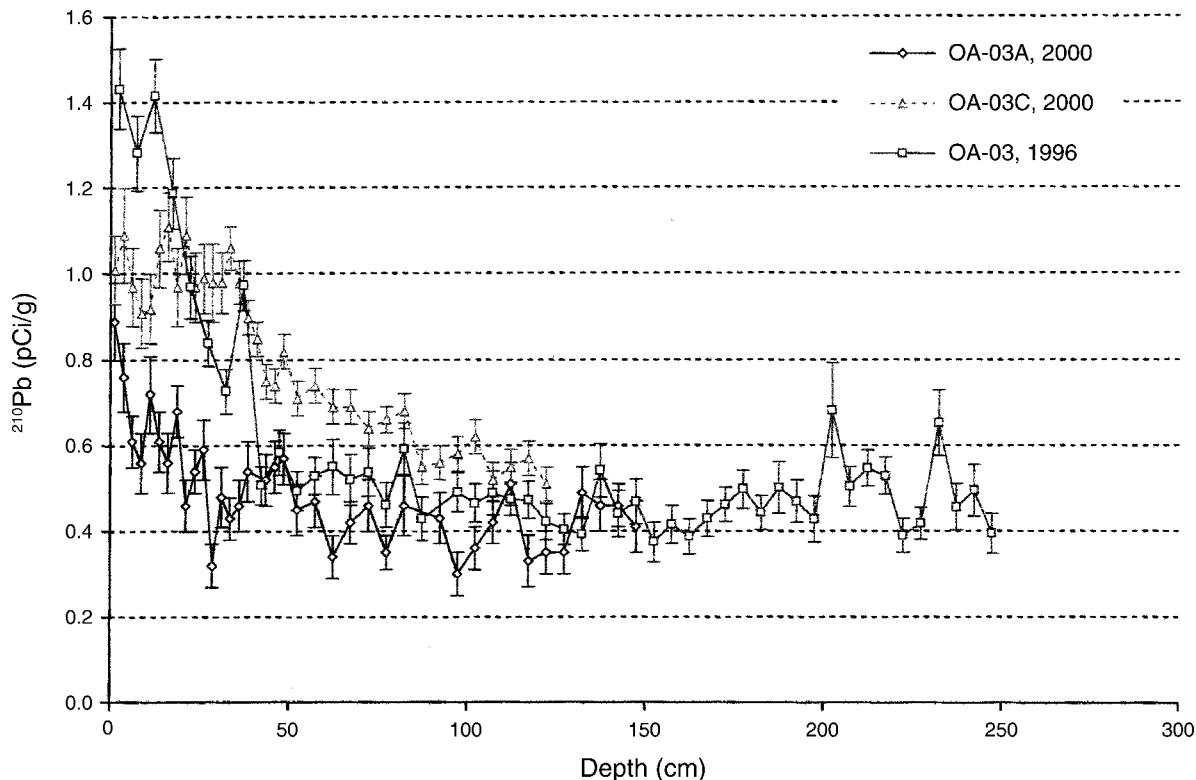


FIG. 5.  $^{210}\text{Pb}$  (mean  $\pm$  SE) vs. depth for Oaks Arm cores.  $^{210}\text{Pb}$  in each of these cores drops to background ("supported") levels by 60–100 cm depth in the cores, establishing the limits of  $^{210}\text{Pb}$  dating in the relatively rapidly deposited Oaks Arm sediments.

therefore plots at zero age on the depth vs. sediment deposition age plot (Fig. 6), an indication that this section of sediment may have undergone a recent disturbance (slumping or massive bioturbation/mixing) and suggests a uniform-aged layer. Sedimentation rates for this core were calculated for the interval below 33 cm, assuming zero age for the uppermost 33 cm of

sediment. Although the data shown in Fig. 6 are extended back beyond the H-1927 horizon, the decay curves plotted in Figs. 4 and 5 show that there are no significant constraints on the ages of the deeper portions of the cores as  $^{210}\text{Pb}$  has decayed to steady state at these depths. We therefore only use the  $^{210}\text{Pb}$  data to constrain the age of sediment above the H-1927 datum.

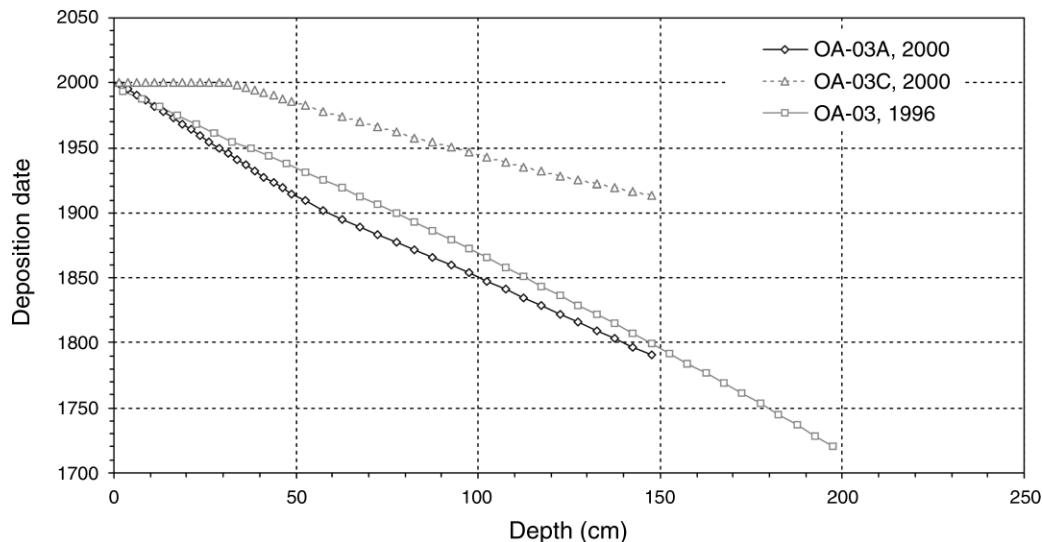


FIG. 6. Deposition rate as a function of depth in Oaks Arm cores, derived from  $^{210}\text{Pb}$  data.



PLATE 8. Sulphur Bank Mercury Mine showing steeply sloped waste rock piles that comprise the waste rock dam with overflow channel into Clear Lake (on right side of dam) before the 1992 slope remediation by U.S. EPA. Note 30 m deep Herman Pit (pH~3) in background. Clear Lake is in the foreground. (Courtesy of Charles Chamberlin, Humboldt State University; photo taken in 1987, before waste rock pile remediation in 1992).

Based on the combined results of the DDD,  $^{210}\text{Pb}$  data here, and  $^{14}\text{C}$  data (reported in Osleger et al. 2008), we are confident that H-1927 represents a highly significant period in the history of Clear Lake for many reasons. First, it represents a period when heavy, mechanized earthmoving equipment (bulldozers, steam shovels, dump trucks) began to be used extensively for road construction and the development of residential home sites as Lake County began steady growth during this period (Suchanek et al. 2003). This process created scars on the landscape and increased erosion into the lake. Second, this was also a period during which the Sulphur Bank Mercury Mine began open-pit mining (possible because of the availability of the mechanized earthmoving equipment), including the bulldozing of Hg-contaminated waste rock directly into the lake, which resulted in the first major anthropogenic introduction and subsequent transport of large concentrations of Hg into the Clear Lake aquatic ecosystem (Suchanek et al. 2008*d*). This is reflected in the large step-like increase of TotHg at this horizon. Third, wetlands surrounding Clear Lake were being “reclaimed” and converted into agricultural production, again because of the availability of more efficient earthmoving equipment. This dramatically reduced the

retention capacity of the previous wetlands and significantly altered nutrient cycling in the lake (Richerson et al. 1994, 2000). As we document below, virtually all parameters measured have dramatic changes at H-1927 (see also Osleger et al. 2008).

Therefore, we use H-1927 as a stratigraphic datum upon which we register the depth scales of all the cores (see Fig. 7). The absolute depth from the surface to the 1927 horizon is variable due in part to differences in sedimentation in the different regions of the lake, but also in part due to variable degrees of core over-penetration and loss of the uppermost loosely consolidated sediment in some cores. Observations by divers and sonar confirm there is an ill-defined sediment–water interface in Clear Lake due to the flocculent nature of the organic-rich sediments, a zone identified as the “nepheloid layer” by Chamberlin et al. (1990). This layer is particularly evident near the mine where the bottom sediments are highly heterogeneous due to disposal of mine wastes ranging from boulder-sized material to finely powdered tailings (see bathymetry contours near the mine in Shipp and Zierenberg [2008]). These effects make detailed correlation of the stratigraphy of the long cores above 1927 difficult, but the similarity of the major geochemical trends is apparent. Mapping the near-

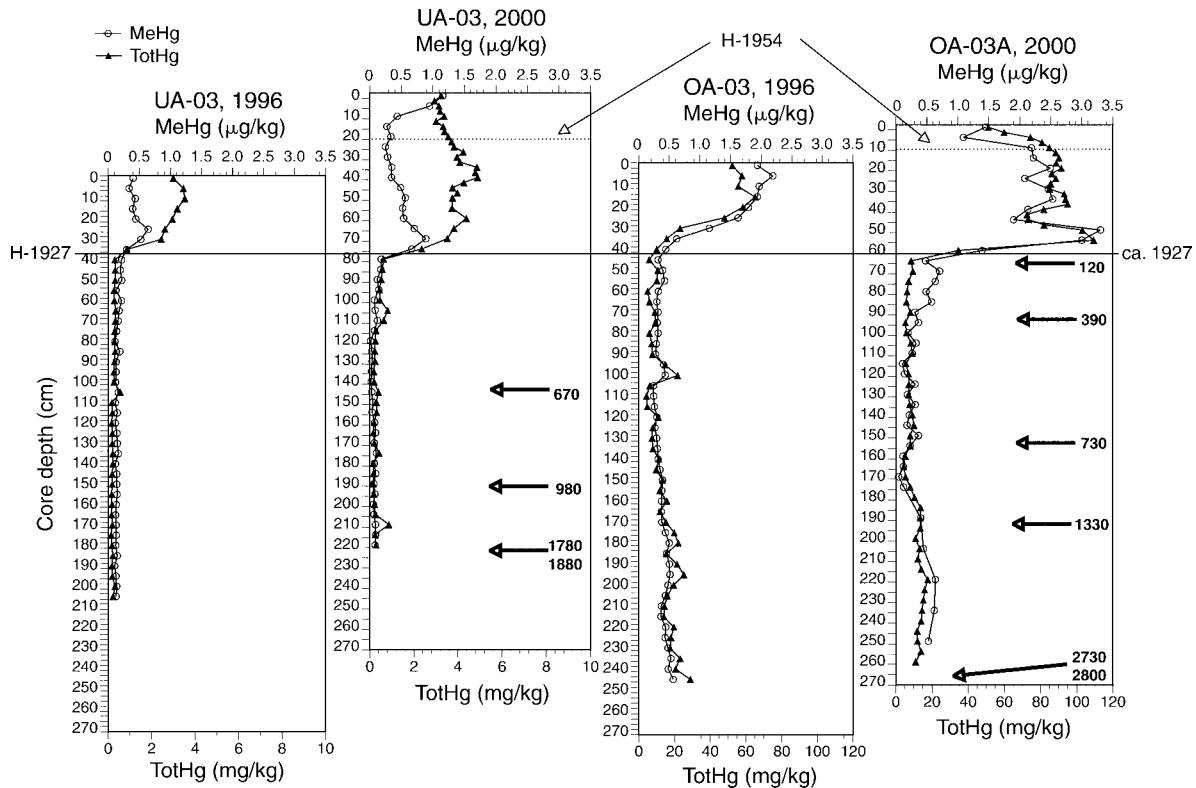


FIG. 7. Total mercury (TotHg; triangles), methylmercury (MeHg; circles), and  $^{14}\text{C}$  data (at arrows, in years before present) from cores collected in 1996 and 2000. H-1927 and H-1954 represent horizons estimated by  $^{210}\text{Pb}$  and dichlorodiphenyldichloroethane (DDD), respectively. The dashed line at 33 cm in the OA-03C, 2000 core indicates the bottom of the region of uniform-age sediments. Note the different scale for TotHg (but not MeHg) in Oaks Arm (OA) cores.

surface distribution of Hg in the sediments relied on samples collected by Ekman dredge, which more reliably recovers the uppermost sediments (see Suchanek et al. 2008b). Thus, we have aligned the vertical positions of the cores to register along the H-1927 horizon as the best way to compare comparable changes in all parameters that changed at approximately the same time periods. Because of variable sedimentation rates in each arm these vertical alignments are not perfect, but they appear quite consistent between each of the cores from the different arms and do provide confidence that concomitant changes in virtually all parameters are varying in a consistent manner over time. Furthermore, the  $^{14}\text{C}$  dates provided in the cores from 2000 also provide consistent age/depth profiles across all three arms of the lake.

#### *Sedimentation rates and mass accumulation rates*

We used the lengths of sediment cores between estimated dates to calculate average sedimentation rates (in millimeters per year) for that section of the sediment column. Sedimentation rates in each of the arms of the lake are similar in the interval from H-1927 to

approximately 1500 years before present (500 AD,  $\sim 125$  cm below H-1927; horizon defined by interpolation between corrected  $^{14}\text{C}$  dates) at  $\sim 1$  mm/yr (Table 1), but the sedimentation rate in the Lower Arm ( $\sim 2.0$  mm/yr) diverges from the Upper and Oaks Arms ( $\sim 0.63$  mm/yr) below this level (Osleger et al. 2008). The sedimentation rates for pre-H-1927 sediments calculated from these cores are similar to the average Holocene sedimentation rates at Clear Lake reported by Hearn et al. (1988) based on  $^{14}\text{C}$  dating of long cores that reached the Pleistocene–Holocene transition at  $\sim 7$  m depth.

The distinct changes that mark the H-1927 horizon allow us to constrain the thickness of sediment accumulated above this horizon. For dating purposes, the main source of error lies in the degree to which each core faithfully retrieved the sediment–water interface. Mean sedimentation rates for the time period from 1927 to 2000 are approximately an order of magnitude higher than pre-1927 rates and are well constrained to values between 5.5 and 12.2 mm/yr (Table 1). Although the average rate is well constrained, geochemical profiles and changes in sediment properties above the H-1927

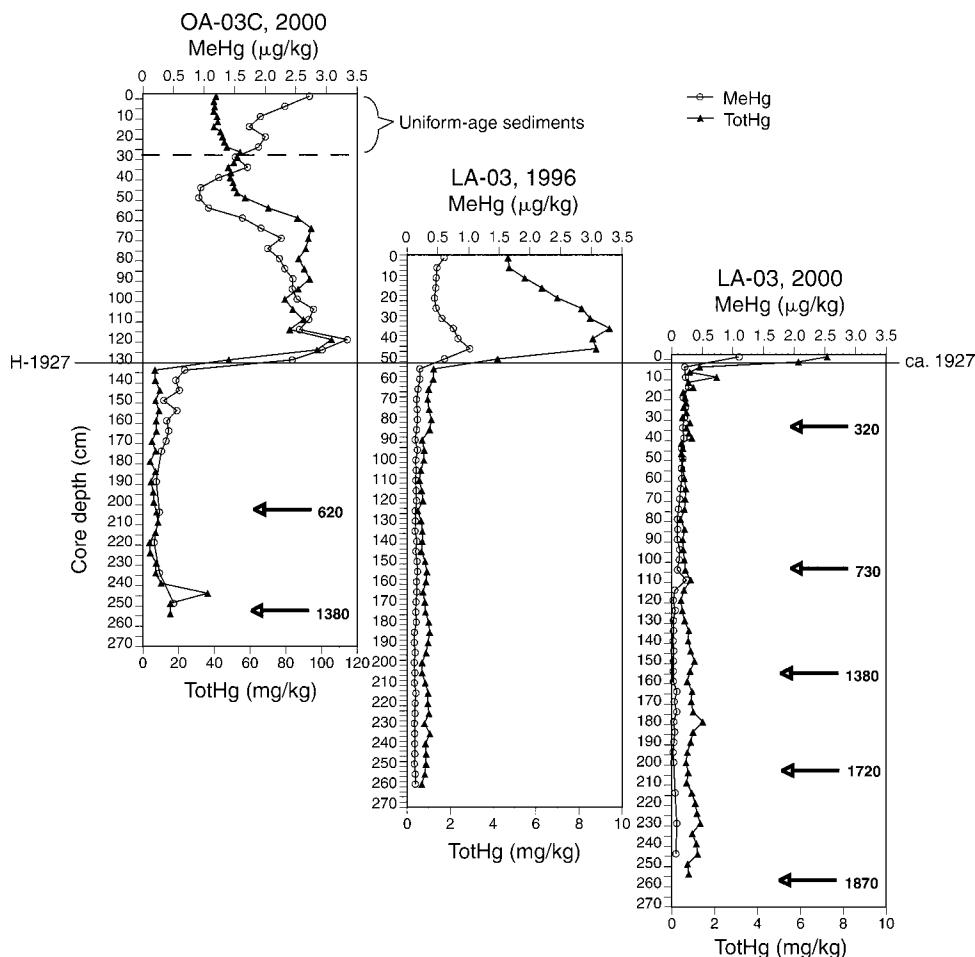


FIG. 7. Continued.

horizon indicate that sedimentation rates were variable throughout this time period. The low activity levels of  $^{210}\text{Pb}$  preclude us from using these data to refine the changing sedimentation rates.

We used the H-1954 horizon both to confirm that sedimentation rates must have varied during this interval and to provide an estimate of the changes in rates. The location of the H-1954 horizon was determined in only three cores, and the depth to H-1954 is less accurate than

that of the H-1927 depth. We identify the H-1954 datum by the peak in DDD, but the location of the peak cannot be determined more accurately than the sampling interval, which was 6 cm for DDD (compared with 2.5 cm sampling intervals for determination of H-1927). The uncertainty of the exact locations of the peaks within the sampled intervals results in a 15–24% uncertainty in the sediment thickness between these horizons and therefore in the calculated sedimentation rates. The situation is

TABLE 1. Mean bulk post-1927 sedimentation rates in Clear Lake, California, USA.

Core, year	Depth to H-1927 (cm)	Estimated age of $^{210}\text{Pb}$ -based H-1927	Sedimentation rate (mm/yr) 1927–2000	Depth to H-1954 (cm)	Sedimentation rate (mm/yr)	
					1927–1954	1954–2000
UA-03, 1996	33	1931	5.5	ND		
UA-02, 1996	78	1935	12.2	ND		
UA-03, 1998	43	ND	6.3	9	13.3	2.2
UA-03, 2000	78	1922	9.6	18	20.4	4.3
OA-03, 1996	43	1945	7.9	ND		
OA-03A, 2000	63	1910	6.7	8	18.5	2.2
OA-03C, 2000	133	1920	12.2	ND		

Notes: For core OA-03C in 2000, sedimentation rate and date of the 1927 horizon (H-1927) were calculated from the bottom of the upper 33-cm unit of uniform-aged sediment. “ND” indicates not determined.

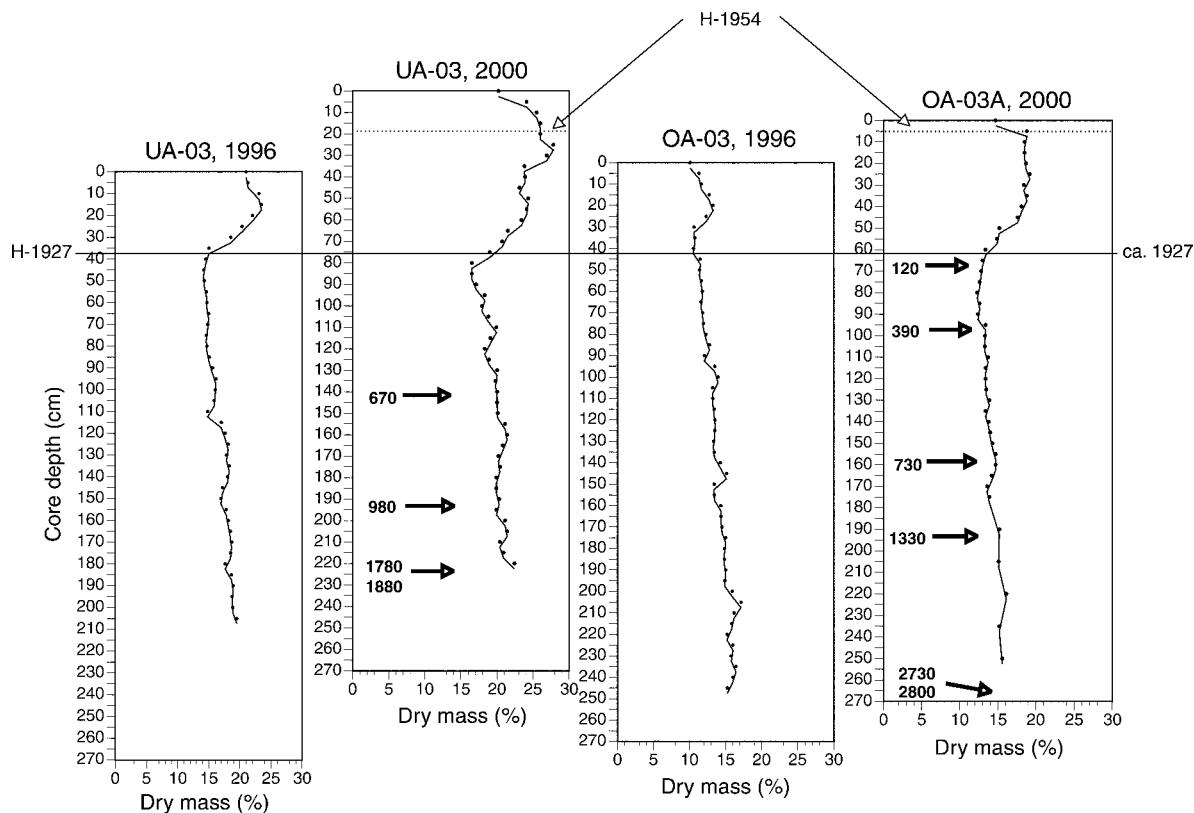


FIG. 8. Percentage of dry mass of sediments and  $^{14}\text{C}$  data (at arrows, in years before present) in cores collected in 1996 and 2000. See the legend to Fig. 7 for further details.

exaggerated further for the interval from H-1954 to the surface since the sediment cores may not have recovered the uppermost unconsolidated surface sediment and may therefore be biased on the low side. Nonetheless, the calculated sedimentation rates for the period 1927–1954 (13.3–20.4 mm/yr) are much higher than the average sedimentation rates (Table 1), and the calculated rates drop substantially between 1954 and 2000 (4.3 to 2.2 mm/yr), consistent with the changes observed in the geochemical profiles and changes in sediment grain size (Osleger et al. 2008).

Sedimentation rates for near-surface sediments are biased by the fact that surface sediments are uncompacted and have not dewatered. To evaluate changes in the behavior of Clear Lake with time, including anthropogenic effects, we need to calculate dry inorganic mass accumulation rates (in grams per square centimeter per year) by correcting for differences in water content and density of the sediments that result from compaction, dewatering, and organic diagenesis. For the deeper compacted and dewatered section of the cores below H-1927, water content decreases very slowly with depth (Fig. 8) and sediment burial rate is directly related to dry inorganic mass accumulation rate (mass deposition per unit area over time). Changes in water content and

density in the young sediments above H-1927 preclude simple extrapolation of sedimentation rates to determine depositional age vs. depth because sediments compact and dewater, and these processes are not constant in a regime of changing sedimentation and/or diagenesis. Mass accumulation rates measure fluxes and are therefore more readily interpreted in terms of processes, such as changes in inorganic sediment loading to the lake or changes in biological productivity and diagenetic oxidation of organic matter.

Density profiles for the cores were calculated for each sample interval from the measured mass percentage of dry sediment and the carbon content for each interval by assuming a density of 1.0 g/cm<sup>3</sup> for water and organic matter and a grain density of 2.5 g/cm<sup>3</sup> for inorganic sediment. The upper few meters of Clear Lake sediment are still poorly compacted with water contents varying from 72% to 92% by mass (average ~84%). Most of the dry mass of the sediment is composed of organic matter. The mass of inorganic sediment was calculated from the measured dry mass of the sample and the carbon content by assuming that the organic matter was typical of humic material with 50% C (Walther 2005). The result of the mass accumulation rates calculated for core intervals

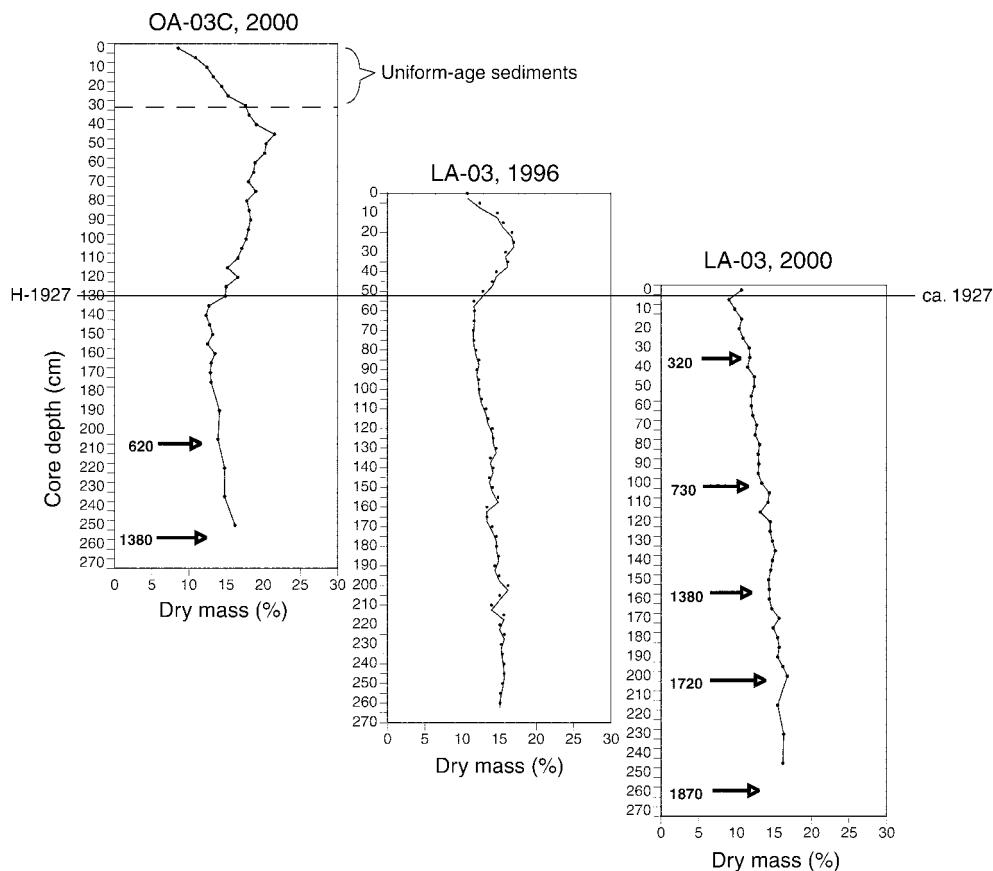


FIG. 8. Continued.

TABLE 2. Calculated mass accumulation rates (MAR) of inorganic dry sediment in cores collected in 2000.

Core	Depth interval	Sedimentation rate	Inorganic MAR	Hg MAR
Pre-1400 ybp				
UA-03	227–200	0.63	13–16	0.004–0.015
OA-03A	280–185	0.63	9–10	0.15–0.22
LA-03	265–130	2.00	26–33	0.025–0.055
1400 ybp to 1927				
UA-03	200–78	1.0	17–24	0.004–0.020
OA-03A	185–63	1.0	10–14	0.076–0.170
OA-03C†	230–133	1.0	11–15	0.069–0.310
LA-03	130–4	1.0	8–14	0.006–0.024
1927–2000				
UA-03	78–0	9.6	200–350	0.55–1.50
OA-03A	63–0	6.7	80–140	3.70–15.0
OA-03C†	133–0	12.2	170–310	11.0–28.0
LA-03	4–0	ND	ND	ND
1927–1954				
UA-03	78–18	20.4	420–740	1.20–3.30
OA-03A	63–8	18.5	225–390	10.0–42.0
1954–2000				
UA-03	18–0	4.3	105–145	0.37–0.55
OA-03A	8–0	2.2	35–50	2.00–4.40

Note: “ND” indicates not determined due to non-deposition or erosion at this site; “ybp” indicates years before present.

† For core OA-03C, mass accumulation rate and date of the 1927 horizon were calculated from the bottom of the upper 33-cm unit of uniform-aged sediment.

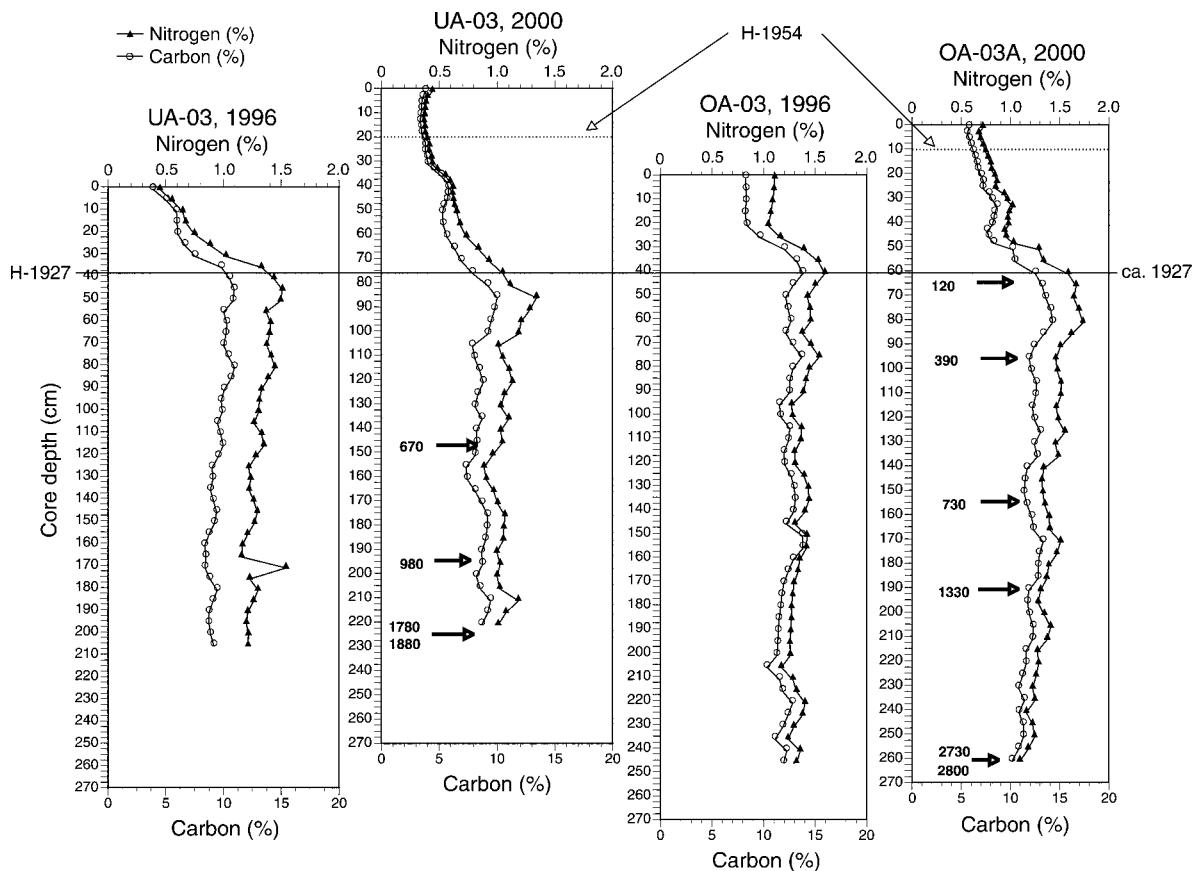


FIG. 9. Percentage of total nitrogen (triangles), percentage of total carbon (circles), and  $^{14}\text{C}$  data (at arrows, in years before present) in cores collected in 1996 and 2000. See Fig. 7 for further details.

with different sedimentation rates are presented in Table 2.

Inorganic mass (IM) accumulation rates for the pre-500 AD sections of the cores from the Oaks Arm and Upper Arm are similar, ranging from 9 to 16  $\text{mg IM}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$ , while those from the Lower Arm range from 26 to 33  $\text{mg IM}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$ , consistent with the higher sedimentation rate (Osleger et al. 2008). For the period from 500 AD to 1927, IM accumulation rates for the Lower and Oaks Arms are similar (8–15  $\text{mg IM}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$ ), with slightly higher depositional rates (17–24  $\text{mg IM}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$ ) in the Upper Arm, consistent with the present fluvial drainage into Clear Lake being predominantly into the Upper Arm. Inorganic matter deposition rates increase dramatically for the post-1927 sediments, with values ranging from 80 to 350  $\text{mg IM}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$ , with rates generally increasing upcore from the H-1927 horizon to just below the anticipated

level of H-1954 horizon based on the geochemical profiles and then generally decreasing towards the surface. The post-1954 IM deposition rates estimated for the two cores for which we determined H-1954 by DDD concentrations are 35–50  $\text{mg IM}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$  in the Oaks Arm and 105–145  $\text{mg IM}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$  in the Upper Arm. These rates are subject to the same uncertainties as the sedimentation rate estimates, but they clearly exceed the mass accumulation rates that characterize the pre-European sediments in Clear Lake.

#### *Environmental parameters*

Analysis of sediment cores collected in 1996 and 2000 demonstrate that a basin-wide increase in Hg concentration in Clear Lake sediments around 1927 marks the onset of large, coincident changes in many physical and chemical properties of the sediments, signaling a change in the depositional/diagenetic regime (Richerson et al.

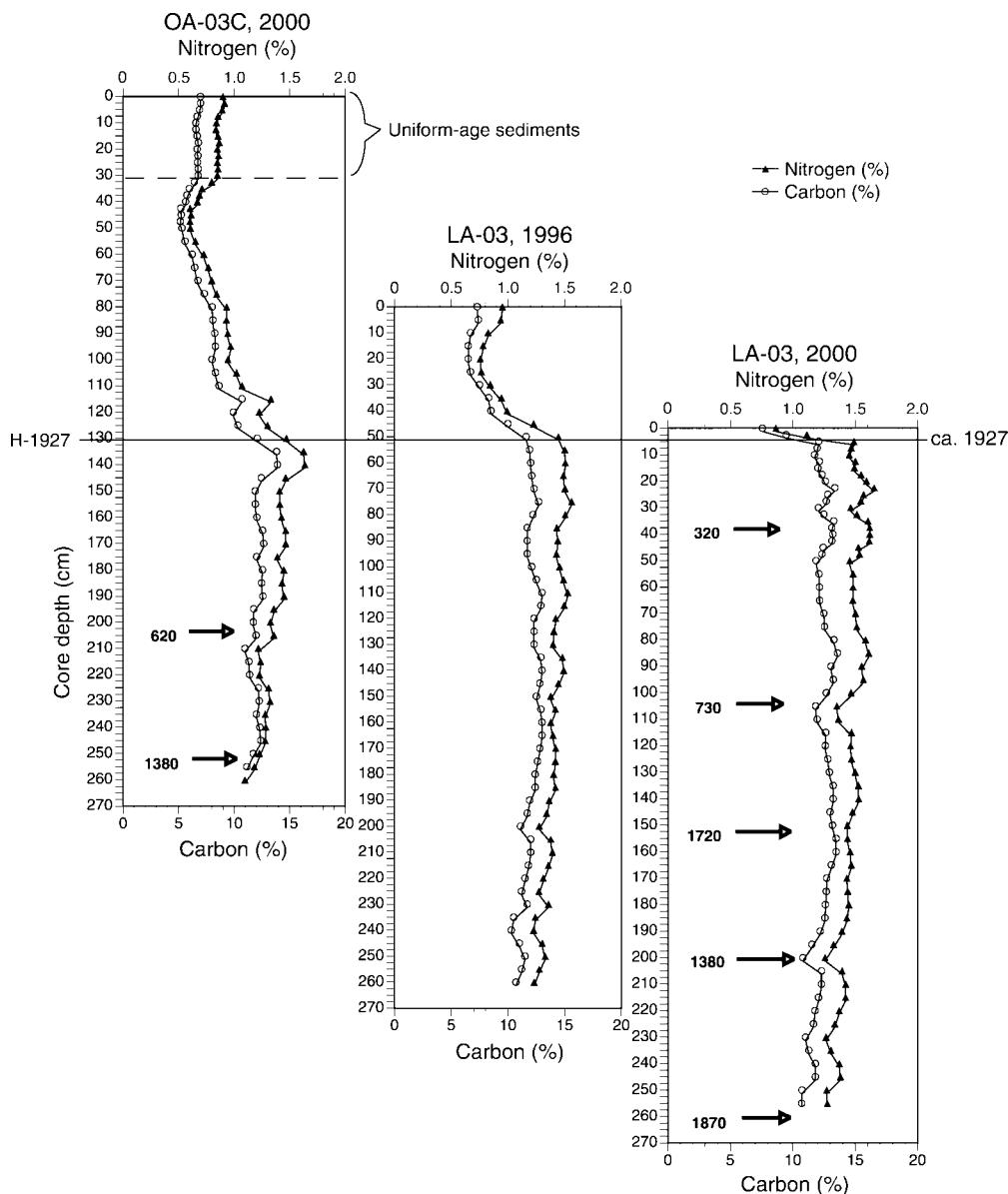


FIG. 9. Continued.

2000, Osleger et al. 2008). Fig. 7 shows large, abrupt increases in the concentrations of TotHg in each sub-basin of the lake at the H-1927 horizon. Mercury concentrations are highest in the Oaks Arm closest to the mine and lowest in the Upper Arm, with intermediate values in Lower Arm sediments. Variations in Hg concentrations from cores in different basins are consistent with the more detailed spatial distribution of Hg in surficial sediments, which shows a rapid decrease with distance from the mine (Suchanek et al. 2008b), exhibiting a classic point source distribution of Hg contamination from the mine. Methylmercury, the more bioaccumulative and toxic form of Hg, exhibits trends that are similar to TotHg (Fig. 7). Interestingly,

significant peaks and zones of elevated MeHg remain at depth, especially in Oaks Arm sediments near the mine. Note that these peaks and elevated zones occur not only in recent (post-1927 era) sediments, but at depth in sediments that are up to ~3000 years before present. Some investigators have hypothesized that Hg should diffuse upward through the sediment column and exhibit a declining profile downward from the surface. These cores, however, demonstrate vertical stability of both TotHg and MeHg peaks at depth; this process is examined more closely in Suchanek et al. (2008c).

The depositional/diagenetic changes that occur across the H-1927 horizon are also apparent in the other parameters measured. The close consistency of results

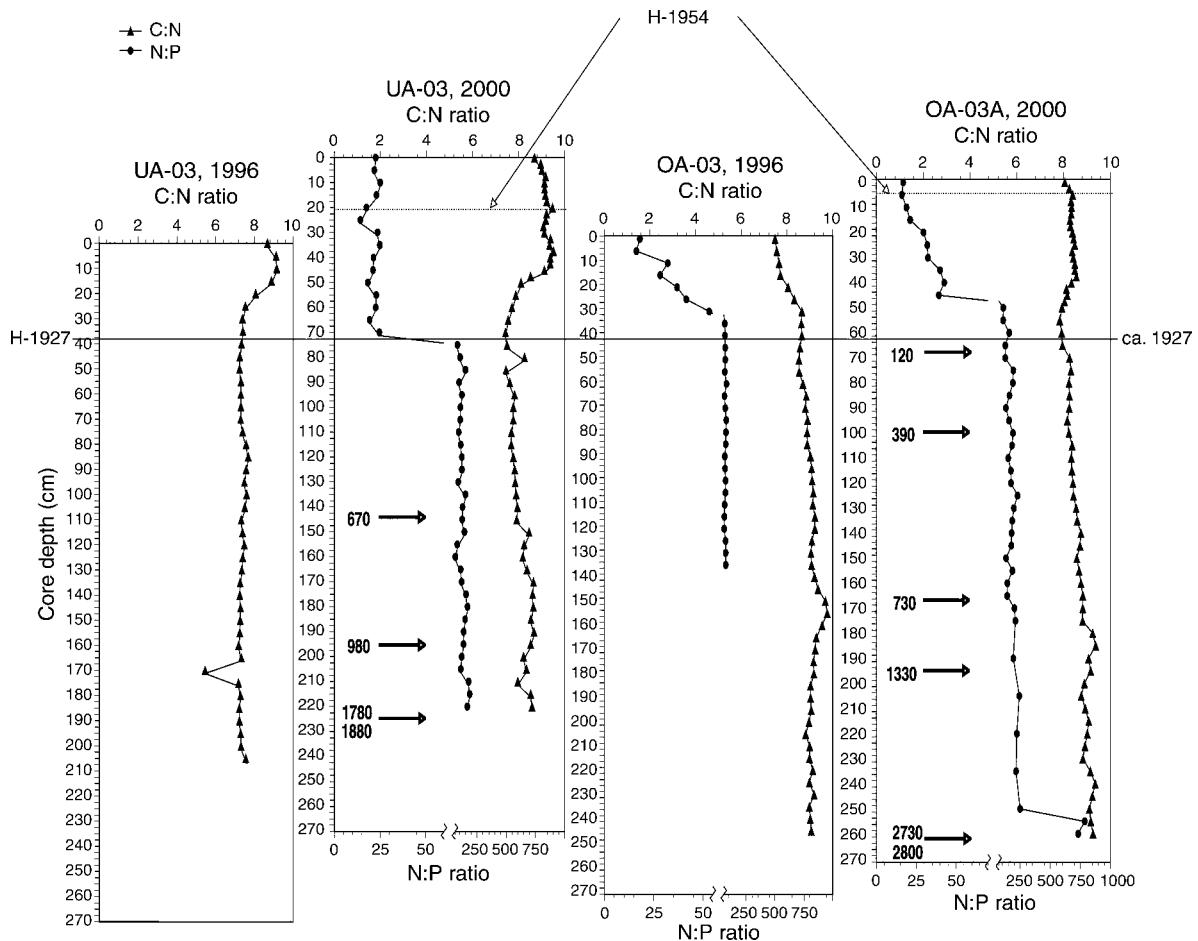


FIG. 10. Organic C:N ratios (triangles), N:NaOH-extractable P ratios (circles), and  $^{14}\text{C}$  data (at arrows, in years before present) from cores collected in 1996 and 2000. See Fig. 7 for further details.

between 1996 and 2000 cores provides confidence that these processes and trends are occurring lake-wide and are consistent over time. Moreover, the same qualitative picture is present in cores taken from all three arms of the lake, although TotHg and MeHg concentrations are higher in the Oaks Arm, on which the Sulphur Bank Mercury Mine site is located. Percentage of dry mass (Fig. 8) shows a consistent and abrupt increase above H-1927 in nearly all cores, while below H-1927 the sediments become slowly denser with depth, as expected due to compaction and organic diagenesis. This reversal at H-1927 is consistent with increased terrigenous sediment input into the lake due to land use changes (Osleger et al. 2008). Percentage of C and N (Fig. 9) show corresponding decreases across H-1927. Based on sediment concentrations, the loading of organic matter to the sediments apparently decreases above H-1927, but in fact the opposite is true. The decreases in percentage

of C and N above H-1927 reflect a dilution of the organic component of the sediment due to an increase in the terrigenous sediment input accompanied by increased organic diagenesis in the more oxidized post-1927 sediments. The per-unit-time accumulation rate of C and N increases substantially above H-1927. The section of cores from the Lower Arm that is older than ca. 1400 BP has carbon accumulation rates of  $5 \text{ mg C}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$ . The carbon accumulation rates from the period 500–1927 range between 1 and  $2 \text{ mg C}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$  in each of the lake basins. Post-1927 carbon accumulation rates jump to  $7\text{--}26 \text{ mg C}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$ , reflecting the higher sedimentation rate. Organic C:total N ratios (Fig. 10) decrease from  $\sim 10$  to  $\sim 8$  gradually up-core until H-1927, after which time they usually increase to a peak before beginning declining again well before H-1954. Total P (Fig. 11) is generally higher above H-1927 in the Oaks Arm and Lower Arm, but decreases up-core in the

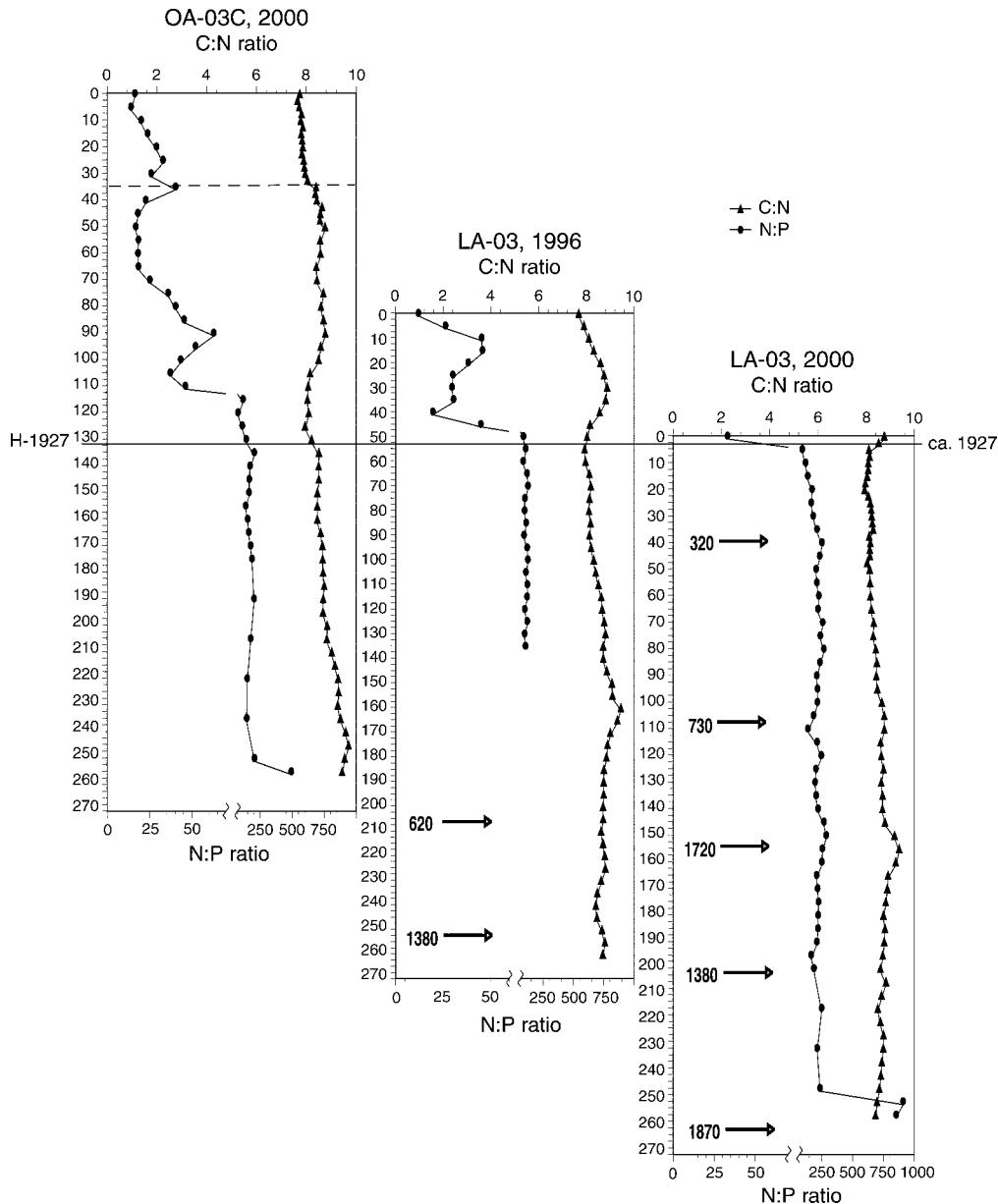


FIG. 10. Continued.

Upper Arm after a sharp peak just above H-1927. The profiles in base (NaOH)-extractable P (Fe and Al bound) tend to match those for total P, generally increasing above H-1927 (Fig. 12). Acid (HCl)-extractable P (Ca-bound) (Fig. 12) initially increases above H-1927 and then declines toward the surface. Total S content exhibits similar trends in each core (Fig. 11), but the Upper Arm has about half the sulfur concentration of the Oaks and Lower Arms. In each case, the S content increases with depth, with a discontinuity at the 1927 horizon, across which sulfur content approximately doubles. The lower sulfur concentrations of the post-1927 sediments again mask the fact the sulfur accumu-

lation rate increases dramatically above this horizon (0.1–0.5, mean  $0.17 \text{ mg S} \cdot \text{cm}^{-2} \cdot \text{yr}^{-1}$  pre 1927 vs. 0.2–2, mean  $0.92 \text{ mg S} \cdot \text{cm}^{-2} \cdot \text{yr}^{-1}$  post-1927), likely reflecting an increase in sulfur loading resulting from the open-pit operations at the mine. The  $\delta^{13}\text{C}$  of sedimentary organic matter (Fig. 13) shows similar patterns in each basin with approximately constant values in the lowermost part of each core, followed by a broad peak in which values increase by  $\sim 1\text{‰}$  and then drop back to near their previous values in the interval of sediment deposited between ca. 1000 and 1927. The H-1927 horizon is followed by a small increase and then a general decline upwards, except for the upper 10 cm of

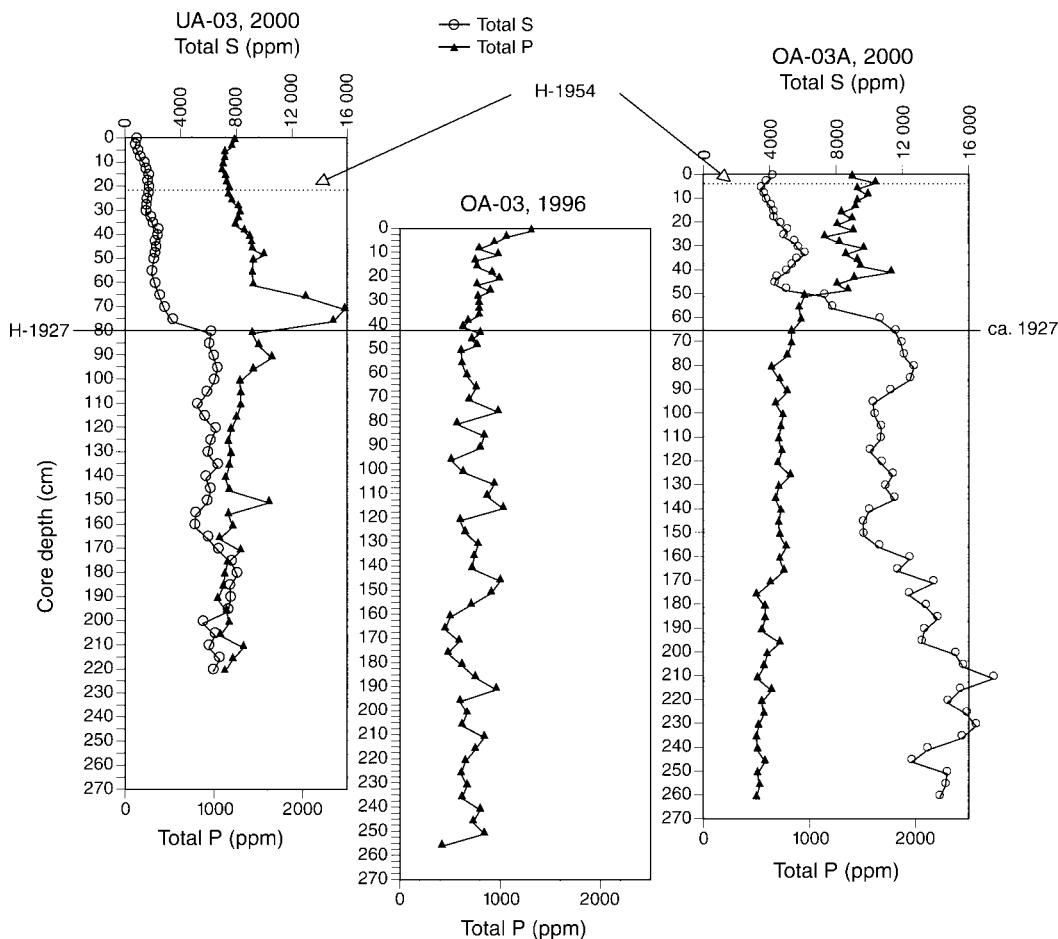


FIG. 11. Total phosphorus (triangles) and total sulfur (circles) from cores collected in 1996 and 2000. See Fig. 7 for further details, including  $^{14}\text{C}$  dates.

the cores, where  $^{13}\text{C}$  appears to increase again. The stable isotope  $\delta^{15}\text{N}$  is relatively constant with values near 0‰ in the deeper portions of the cores and increases steadily to  $\sim 3\text{--}4\text{‰}$  above H-1927 (Fig. 13).

Scatterplots of biologically important chemical species and isotopes against one another are provided in Fig. 14. The Upper Arm core shows little sign of any systematic variation in pre H-1927 sediments, but the Oaks and Lower Arms tend to show a more marked distinction between H-1927–1400 BP and older sediments. The UA-03 and OA-03A cores show distinctive differences broken by the H-1954 horizon. The post H-1954 sediments are clearly missing in LA-03 and may be missing in OA-03C. Note that even though sedimentation rates appear to have dropped after H-1954, sediment chemistry in no core shows any signs of returning to pre H-1927 composition. The continuing load of sulfate to the lake due to acid mine drainage

from the Sulphur Bank Mercury Mine is a plausible reason for this continuing difference from pre H-1927 sediments (Shipp and Zierenberg 2008). Note also that the Lower and Oaks Arms are small sub-basins compared to the Upper Arm, and shoreline length relative to volume is much smaller for the Upper Arm than for the two smaller sub-basins. Relatively small pre-Columbian human impacts might be more easily detectable in the smaller sub-basins.

## DISCUSSION

### *Mercury*

Mercury mining at Clear Lake is reflected dramatically in the sediment record. The period of largely underground shaft mining (1873–1920s) left no reliably detectable impact on the lake. With the onset of open-pit mining (1927), the disturbance of large volumes of overburden and rock contaminated with metal sulfides

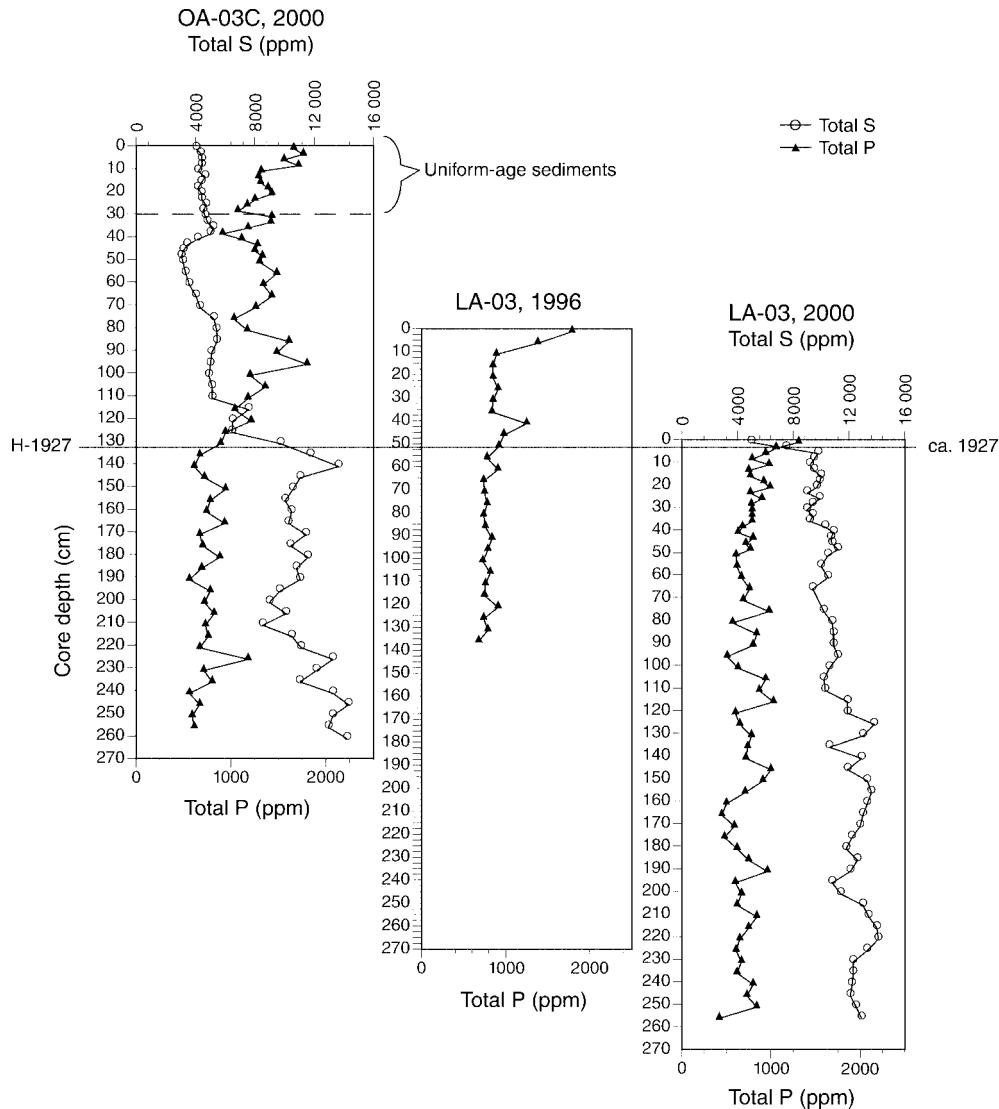


FIG. 11. Continued.

(some bulldozed directly into the lake) and the production of large volumes of tailings greatly increased the loading of Hg to Clear Lake. The increase in loading is even more dramatic than meets the eye in Fig. 7 because diluting inflows of inorganic sediment also increased substantially around the same time. The terrestrial waste rock piles contain amounts of Hg ranging from nondetectable to 2400 mg/kg, with typical values in the range 100–1000 mg/kg (U.S. EPA 1994). The maximum Hg concentrations in our lake cores from the period of most active mining are ~3–20 times higher than present-day surface concentrations and 5–50 times higher than the pre-H-1927 concentrations (see Suchanek et al. 2008*b* for surface concentrations). Approximately 25% of the surface of the regraded waste piles contains sulfide minerals in sufficient concentrations to prevent the growth of annual vegetation (Suchanek et al.

2008*b, d, in press*; P. J. Richerson and T. H. Suchanek, *personal observations*). Mercury and mine-related contaminants have entered the lake by four main routes: atmospheric deposition, erosion of waste rock piles, deliberate dumping/bulldozing of tailings and waste rock into the lake (Suchanek et al. 2008*d*) and subsurface acid rock drainage flow (Shipp and Zierenberg 2008). Even after mining ceased, sheetwash erosion and mass wastage from wave action undercut the shoreline waste rock piles until a U.S. EPA remediation project in 1992. The mine currently discharges acid rock drainage into the lake, which we believe is the most ecologically significant source of ongoing Hg loading (see further discussion in Shipp and Zierenberg 2008 and Suchanek et al. 2008*b, d*).

Mercury concentrations in the deeper post-H-1927 sections of the cores are proportional to those patterns

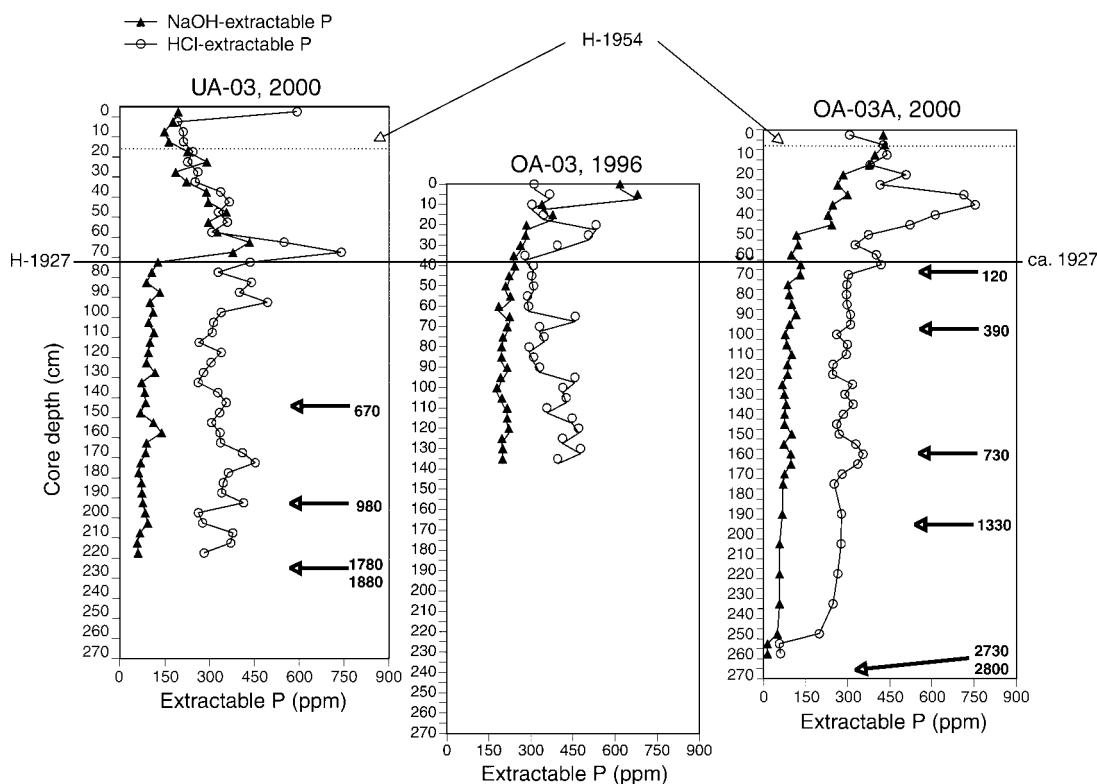


FIG. 12. Base (NaOH)-extractable (Fe- and Al-bound) phosphorus (triangles), acid (HCl)-extractable (Ca-bound) phosphorus (circles), and  $^{14}\text{C}$  data (at arrows, in years before present) from cores collected in 1996 and 2000. See Fig. 7 for further details.

in surface sediments throughout the lake (Suchanek et al. 2008b) and decrease with distance from the mine site. The ratio of MeHg:TotHg is  $\sim 10$ -fold lower in the heavily contaminated Oaks Arm compared to the less contaminated Upper and Lower Arms that are distant from the mine (Suchanek et al. 2008a). As a consequence, MeHg levels in the less contaminated arms are  $\sim 30\%$  of those in the Oaks Arm, much greater than would be the case if the relationship between the concentrations of the two Hg species was linear.

#### *Sedimentation rates*

Changes in physical and chemical characteristics of the cores coincident with the 1927 horizon are consistent with the hypothesis that introduction of heavy earthmoving equipment into the watershed resulted in anthropogenic changes in lake sedimentation (Richerson et al. 1994). Drier sediments with less organic matter and nitrogen would result from a greater ratio of inorganic to organic deposition. Long cores (to 28 m depth) recovered from Clear Lake by the U.S. Geological Survey in 1973 (Sims and White 1981, Sims 1988) record average Holocene sedimentation rates similar to the  $\sim 1$  mm/yr indicated by  $^{14}\text{C}$  dates in the deeper parts of our cores. The increase in sediment loading above H-1927

also resulted in a change in diagenesis. Sediments above this horizon are more oxic and contain lower concentrations of C and N, perhaps due in part to decreased preservation of organic matter. However, recall that C and N mass accumulation rates do increase coincident with the increase in inorganic sedimentation rate. In the absence of organic matter loading rates we cannot resolve the roles of organic matter loading vs. diagenetic loss in the deposition of C and N in the sediments.

Although the sharp increase in Hg loading to the lake around 1927 points to open-pit mining as the major source, the coincident change in sedimentation rate at this horizon likely also represents a basin-wide increase in erosion rates due to the introduction of heavy earthmoving equipment (Richerson et al. 2000). Additional sources of sediment loading to the lake include home building, road construction, streambed gravel mining, and wetland reclamation projects (Suchanek et al. 2003). More enlightened land use practices during the last several decades have resulted in a return to lower sediment accumulation rates, as indicated by the depth to the ca. 1954 DDD peaks detected in the cores. However, post-H-1954 sediments do not tend to return to a composition similar to those deposited before 1927, probably because of high sulfate loading and vigorous

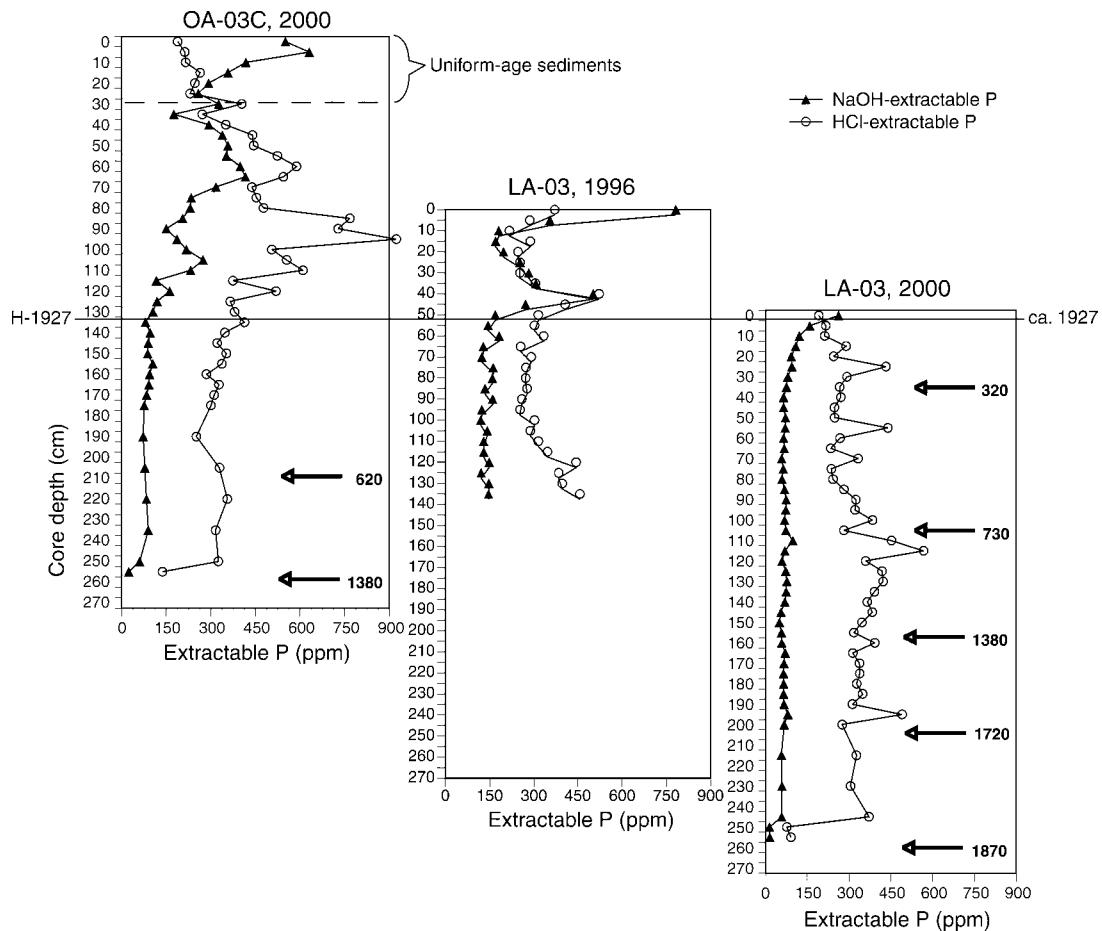


FIG. 12. Continued.

sulfate reduction near the sediment surface, maintaining conditions more oxic and with lower organic matter than before 1927.

#### *Water clarity/nutrient cycling*

Note from Fig. 10 that N:P ratios declined sharply after H-1927. Fig. 11 shows that base-extractable P increases above H-1927 as well. This is the P fraction in the sediments that is released into the water column during the period of summer sediment anoxia (Richerson et al. 2004). Increased loading of sediment rich in P is no doubt partly responsible for this shift, but note that post-H-1954 sediments show no sign yet of a return to higher N:P ratios. Li's (1998) experiments confirmed that photosynthesis and nitrogen fixation remained iron limited as Wurtsbaugh and Horne (1983) discovered in the 1970s. Iron limitation of N fixation presumably prevents the lake from reaching a situation in which the N:P ratio reaches levels approximating algal demand for growth (molar ratio of ~16:1). Hence, N-fixing cyanobacteria are still moderately abundant in the summer when N:P ratios are lowest (Richerson et al. 1994).

The nitrogen isotope values (Fig. 13) near 0‰ throughout the older portions of the sediment cores suggest that the lake has always been eutrophic and that the lake's primary productivity has been dominated historically by nitrogen-fixing cyanobacteria (Fogel and Cifuentes 1993, Brenner et al. 1999). The dramatic increase at H-1927 in Lower and Oaks Arms cores but not Upper Arm cores is likely reflective of increased nitrate input into the lake from agricultural activities along the lakeshore, cattle grazing, and sewage as human development increased (Teranes and Bernasconi 2000). However, the carbon isotope signatures of our sediment cores (Fig. 13) are relatively stable over time and do not provide much information regarding changes in lake productivity or sedimentary organic matter sources.

The effect of increased sulfur loading to the lake (Fig. 11) as the result of acid rock drainage coincident with open-pit mining will be enhanced mineralization of organic matter in the sediments by sulfate reduction (Mack 1998) and more oxidizing conditions, as reflected in the color change observed above the H-1927 horizon (Osleger et al. 2008). Sulfur concentrations decreased by

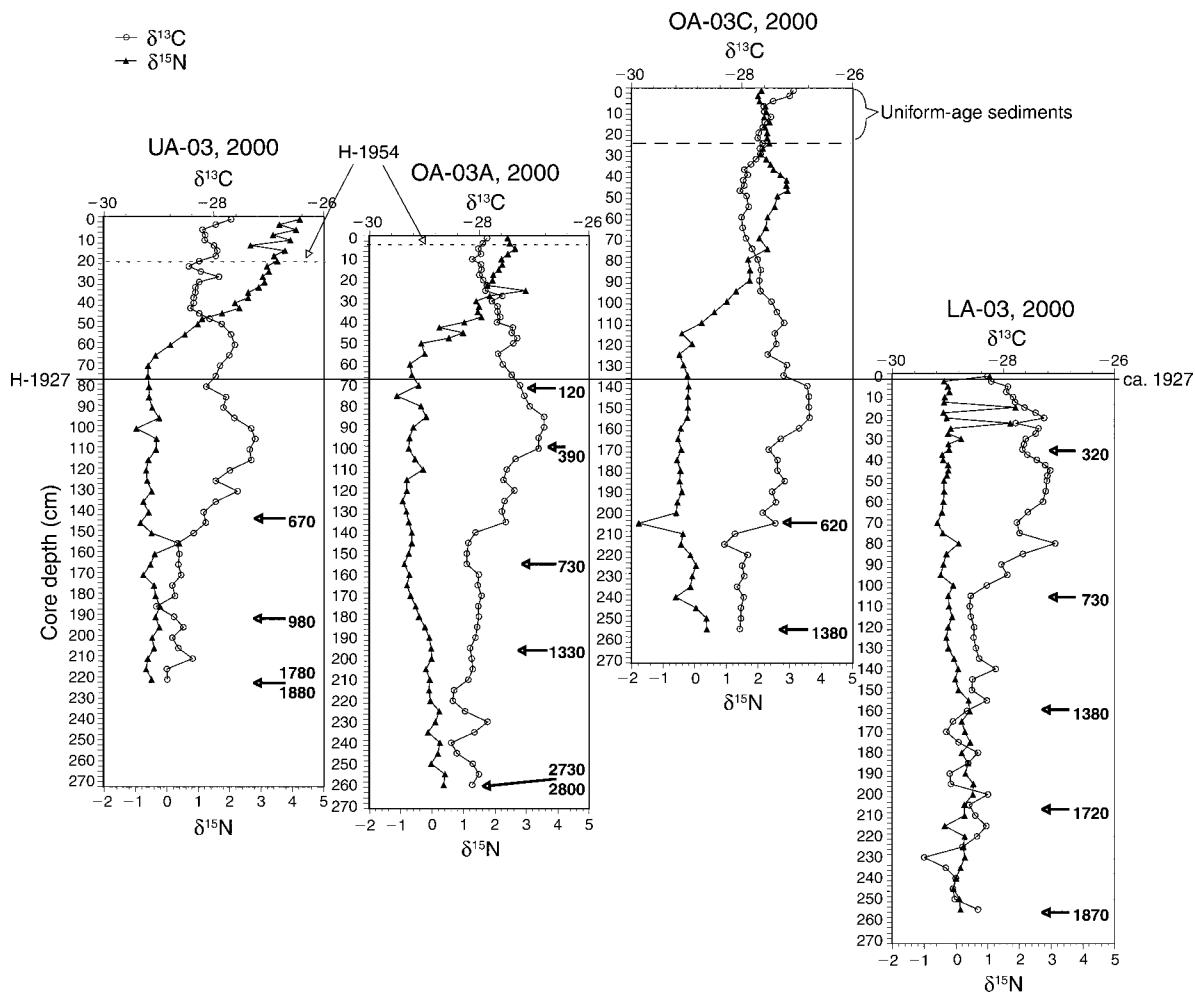


FIG. 13. Stable isotopes:  $\delta^{13}\text{C}$  (circles),  $\delta^{15}\text{N}$  (triangles), and  $^{14}\text{C}$  data (at arrows, in years before present) from cores collected in 2000. See Fig. 7 for further details.

approximately twofold above the 1927 horizon, but sedimentation rates increased by  $\sim 10$ -fold. Thus, the total S storage per unit time must have risen by a factor of approximately five. Unfortunately, no pre-1927 sulfate analyses are known from Clear Lake. Higher rates of sulfate reduction coupled with oxidation of organic matter plus higher rates of deposition of inorganic sediments in some combination explain the lower mass accumulation rate of organic matter per unit sediment depth and drier and more nitrogen-poor sediments, as we observe above H-1927.

The mine became a major source of sulfate and acid loading presumably after it began to be operated by open-pit methods in 1927. Our data suggest that increased sulfate loading due to acid rock drainage from the mine is responsible for continued deposition of Hg in the lake. Approximately  $1 \times 10^6 \text{ m}^3$  of sulfide-rich overburden and waste rock were excavated during the course of open-pit operations, leaving a flooded impoundment (Herman Pit) of  $0.860 \times 10^6 \text{ m}^3$  (data here and for the following calculations from U.S. EPA

[1994]). Sulfate concentrations in the impoundment waters, groundwater down-gradient toward the lake from the impoundment, and surface runoff from waste rock piles are  $\sim 30 \text{ mmol/L}$ , with  $\text{pH} \sim 2.5$ . The standing mass of sulfate dissolved in impoundment water alone is  $\sim 2500 \text{ Mg}$ . The standing mass in the whole lake ( $1.43 \times 10^9 \text{ m}^3$ ) is  $\sim 17000 \text{ Mg}$  in non-drought years. The hydraulic residence time of the lake is  $\sim 4.6 \text{ yr}$ , so a sulfate load on the order of  $2500 \text{ Mg/yr}$  could be an important term in the sulfate budget of the whole lake.

We suspect that sulfate from acid mine drainage is a contributor to the eutrophication of the lake due to enhanced iron cycling that stimulates cyanobacterial blooms. Considerable iron is released from the lake's sediments during summer months when high temperatures and high organic matter cause anoxia at the sediment interface (Richerson et al. 1994, Li 1998). Under present conditions, sulfate levels near the sediment-water interface enhance the degradation of organic matter and keep sulfide concentrations near the sediment surface low. Before H-1927, sulfide concentra-



PLATE 9. Waste rock piles from the Sulphur Bank Mercury Mine along the Clear Lake shoreline. (Left) Before the 1992 U.S. EPA shoreline remediation. Note the steeply sloped waste rock pile that eroded mercury-laden soils into Clear Lake during heavy rains. (Right) After the 1992 remediation. Note the vegetated slope, reduced angle of the piles and rip rap along the shoreline to reduce erosion.

tions near the sediment surface would have bound iron as FeS, leading to more stringent iron limitation of nitrogen fixation and photosynthesis.

Note in Fig. 14 that the chemical conditions in sediments deposited since H-1927 are rather similar in composition. Although sedimentation rates appear to have dropped substantially since H-1954, we detect no trend toward a sediment chemistry resembling that below H-1927. Continuing addition of sulfate to the lake appears to enable oxidation of organic matter deeper below the sediment surface compared to pre-1927, leading to increased degradation of organic matter by oxidative rather than fermentative bacteria. Increasing the depth of the sulfate reduction zone also increases that depth at which iron in the sediments is immobilized due to pyrite formation and burial. Since sulfide binds iron much more strongly than other anions, the result is more internal loading of iron and elements bound to iron oxide such as phosphorous, from the near-surface sediments during the summer period of near-surface sediment anoxia (Li 1998). Vigorous sulfate reduction is in turn most likely supported by sulfate loading from the mine.

#### CONCLUSIONS

The Clear Lake ecosystem has experienced a major, partly continuing series of important, temporally coincident stresses beginning ca. 1927. Several of the changes recorded in our sediment cores (such as lower water, nitrogen, and organic matter content after 1927) are consistent with increased inorganic sedimentation. Direct estimates of sedimentation rates support this conclusion. The contamination of lake sediments with Hg from the Sulphur Bank Mercury Mine became serious only after the mine began to be operated using open-pit methods in 1927. These data, together with other historical data (Richerson et al. 2000) and estimates of anthropogenic contributions to erosion rates, support the long-standing idea that the advent of mechanized earthmoving equipment in the late 1920s and early 1930s was responsible for both the increased

Hg in the sediments due to the advent of open-pit mining and the increase in sedimentation rate due to other applications of earthmoving equipment in the surrounding watershed. As a corollary to the heavy equipment hypothesis, sulfate loading from the mine probably contributed to these changes by increasing the depth at which oxidative digenesis of organic matter can proceed.

Interestingly, we do not detect any impact of European settlement (that began in the early to mid-1800s) prior to the dramatic events beginning at H-1927. The absence of major impacts from the early period of European settlement is strikingly different from the easily detectable agricultural activities in cores from other water bodies due to marked effects on sedimentation rates (e.g., Brush and Davis 1984, Cohen et al. 2005). The transformation of grasslands to grain fields and the replacement of native pasture grasses by Mediterranean weeds in the Clear Lake watershed was a major impact that, unfortunately, is difficult to detect in the pollen record (West 1989). Richerson et al. (2000) report the results of a pollen profile indicated modest effects of European settlement on pollen taxa found in Clear Lake sediments. Nevertheless, the overall stability of the vegetation and the lack of a conspicuous increase in sediment yield are remarkable. As Simoons (1952) noted, the woody vegetation of the upland areas of the Clear Lake basin were not appreciably altered by early settlers, whose land clearance was focused on level ground with low erosion risk. Our cores tentatively suggest that 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, semiarid environments apparently supported a fairly large, active human population in a reasonably sustainable fashion. A narrow range of activities, open-pit mining and large-

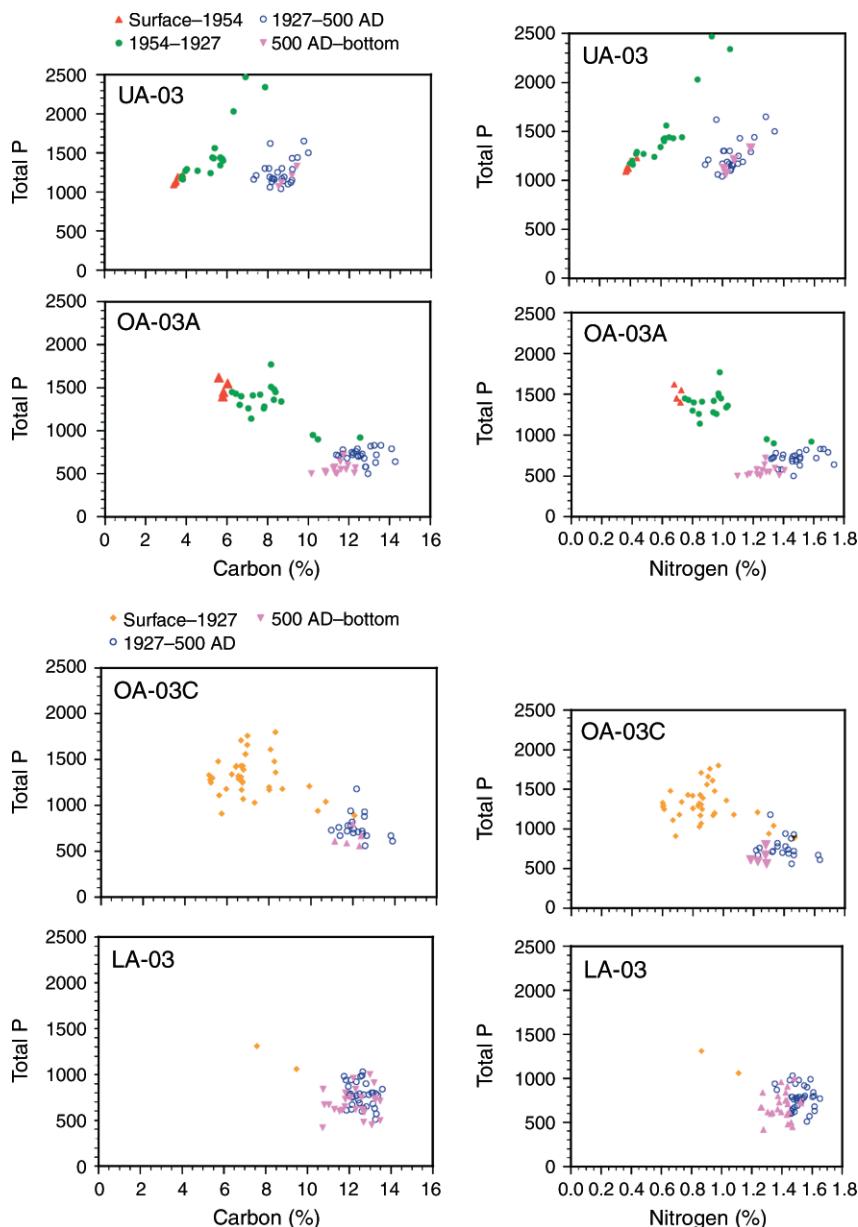


FIG. 14. Scatterplots of biologically important elements and isotopes in Clear Lake cores, color-coded to reflect different date horizons. For UA-03 and OA-03A: red, surface of core to 1954; green, 1954–1927; blue, 1927–500 AD; pink, 500 AD to bottom of core. For OA-03C and LA-03: dark yellow, surface of core to 1927; blue, 1927–500 AD; purple, 500 AD to bottom of core.

scale earthmoving, would appear to have been responsible for the stresses most obvious in our cores.

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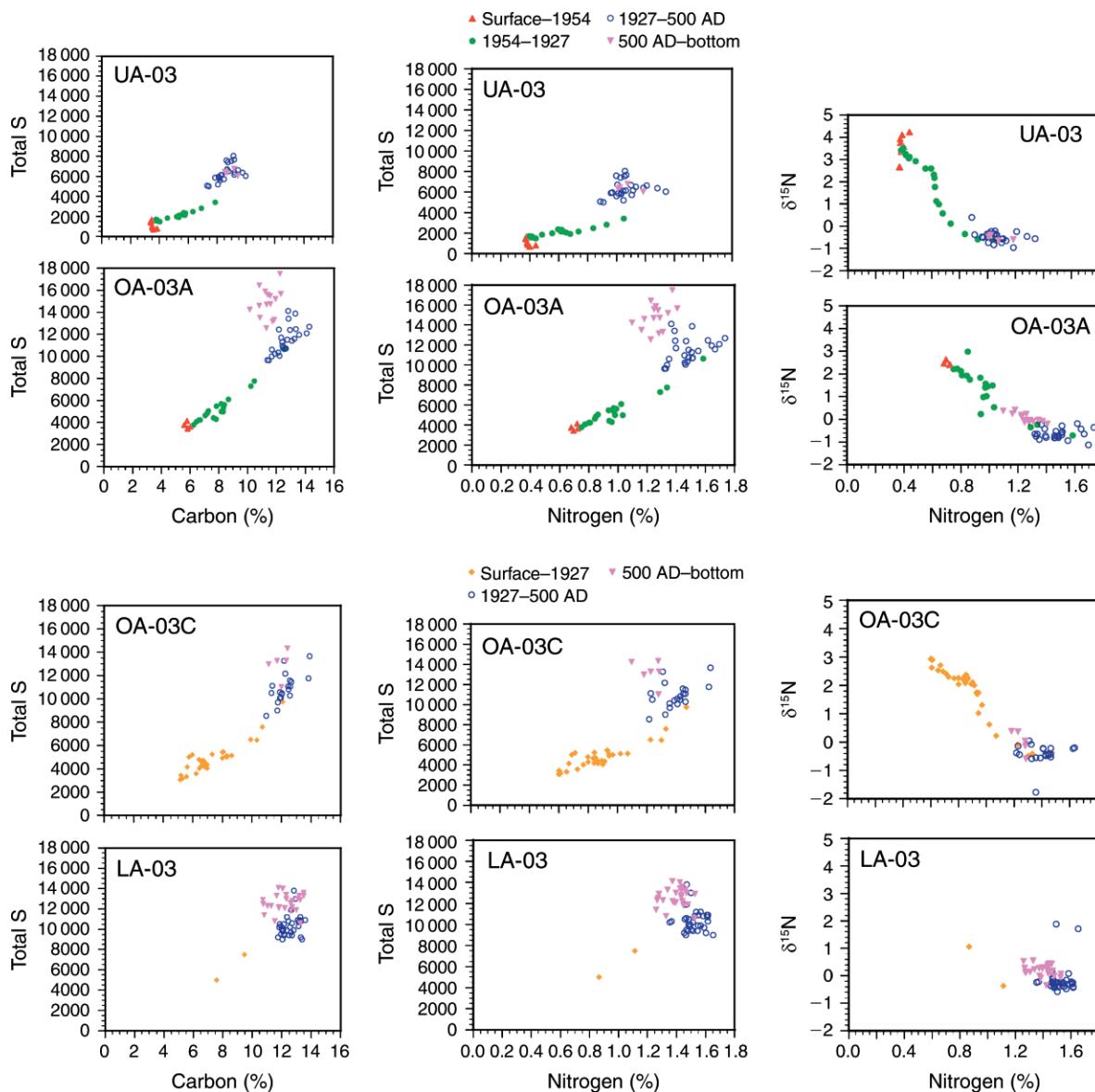


FIG. 14. Continued.

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