Proposal submission for the CALFED 2007 Supplemental PSP

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Title of Supplemental Proposal: Salinity Fluctuations During the Last 7000 Years in the Sacramento-San Joaquin Delta

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Original Proposal Title: Rates and Evolution of Peat Accretion Through Time (RE-PEAT) in the Sacramento San-Joaquin Delta, California

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SALINITY FLUCTUATIONS DURING THE LAST ~7000 YEARS IN THE SACRAMENTO-SAN JOAQUIN DELTA

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Project Purpose

The purpose of this supplemental budget request is to use previously collected peat cores from the CBDA-funded REPEAT project (Rates and Evolution of Peat Accretion through Time in the Delta) to determine the paleo-salinity of the Delta. Research from the REPEAT project has shown that the original 1400 km^2 marsh located at the confluence of the Sacramento and San Joaquin rivers (hereafter the Delta) started forming approximately 7000 years ago (Drexler et al., 2007). Knowledge of salinity conditions throughout the 7000-year history of the Delta is crucial for effective and scientifically sound management of this region. There are currently several different scenarios for how the Delta may be managed in the future (e.g., Lund et al., 2007). Some of these would result in a saltier Delta whereas others would maintain it as a freshwater ecosystem. None of these choices can be made intelligently without an understanding of the natural variability of salinity in the Delta throughout its history.

This proposed supplemental work represents value-added science because we already have a wealth of background information on the physical and chemical properties of the peat as well as all the peat cores that need to be analyzed in order to answer the key questions. In addition, we have already used sodium (Na) and strontium (Sr) concentrations to construct a qualitative paleo-salinity record for Brown's Island and Sherman Island in the western Delta. In this proposed supplemental work, we will extend this approach by (1) including an additional method (strontium isotopes) that provides quantification of paleo-salinity, and (2) analyzing additional cores to extend the geographical extent of our paleo-salinity analysis from the western Delta into the central Delta. We have already developed the radiocarbon age models that are required to tie measures of paleo-salinity to the different periods of the Delta's history. Overall, this proposed work will determine whether areas in the western and central Delta have remained exclusively freshwater habitats or whether they were brackish or even saline for significant time periods during the past 7000 years.

Background and Conceptual Models

Today the Sacramento-San Joaquin Delta is classified as a tidal *freshwater* delta, yet whether this has been the case throughout its 7000-year history remains largely unknown. Currently, the water flow in the Delta is highly regulated so the saltwater wedge originating in the San Francisco Bay has little chance to travel much further east than Brown's Island at the Delta's western boundary. The salinity is regulated for the purpose of maintaining water quality as well as managing a parameter called X_2, which is the distance from the Golden Gate up the axis of the estuary to where the tidally-averaged bottom salinity is 2 psu (where psu refers to the unitless Practical Salinity Scale on which seawater is approximately 35). Research has shown that in the spring when X_2 occurs more than 85 km from the Golden Gate (this distance is approximately at the western edge of the Delta), the abundance and/or survival of several pelagic species plummet (Jassby et al., 1995, Kimmerer, 2002, 2004). Such measurements of X_2 are only available beginning in the late 1960s, when dams had already been built on the major rivers flowing into the Delta.

Prior to dam-building, salinity incursions into the Delta were much greater than they are today (e.g., Figure 1). In addition, the *variability* of salinity was likely much greater than it is now. Such heightened variability is the key to developing a conceptual model of paleo-salinity for the Delta. In any given year, salinity likely ranged from fresh or very fresh during the rainy season to slightly brackish or very brackish during the dry season depending on the amount of annual precipitation. On top of this, there was always a transect of decreasing salinity from west to east and twice daily fluctuations of salinity throughout the Delta due to the tides. During periods of extreme drought, brackish conditions could have dominated the entire Delta for years at a time. Therefore, the overall picture of paleo-salinity is one of considerable daily and seasonal variability with periodic major incursions of salinity due to drought.

Currently, there is debate over what the future of the Delta should be and how it should ultimately be managed to provide for water transfer as well as sustainable habitat for flora and fauna. Clearly, a better understanding of paleo-salinity would inform this debate by demonstrating what the natural range of salinity was in the Delta prior to anthropogenic alternations in the Delta and its watershed.

We, along with colleagues at UC Davis and Hydrofocus, Inc. of Davis, CA, are currently conducting a project funded by the CALFED Science Program entitled "Rates and Evolution of Peat Accretion through Time" (REPEAT) in the Delta. In this 3-yr project, which began in June 2005 and will be completed in December 2008, we are studying the rates and processes of peat formation during the entire 7000-yr history of the Delta. We collected 165 m of peat (organic soil) cores along a transect in the Delta ranging from brackish to fresh water and from high energy conditions (high flows) to low energy conditions (quiescent areas) (Figure 2). As stated in the original proposal, we are using a wide variety of approaches (age determination with radiocarbon, ^{137}Cs, and ^{210}Pb; analysis of physical characteristics of peat; pollen analysis; magnetic properties of peat; trace element analysis; and predictive modeling) to determine: (1) rates of vertical peat accretion through the history of the Delta and potential rates of accretion in the future, (2) how climate and geomorphological processes have controlled peat formation, and (3) how the physical and chemical properties of peat soils changed subsequent to reclamation of the Delta for agriculture. As part of this project we have determined the concentrations of major and trace elements in the peat using inductively coupled plasma (ICP) and atomic fluorescence methods. Analysis of contaminants such as antimony (Sb), copper (Cu), lead (Pb), and mercury (Hg) has provided information on the timing of human impacts on the Delta. Analysis of relatively insoluble elements such as aluminum (Al), scandium (Sc), titanium (Ti), and zirconium (Zr) has provided measurements of the inorganic sediment contributions to the peat. In addition, the analysis of elements such as sodium (Na) and strontium (Sr) in the peat has provided qualitative evidence for major variability in paleo-salinity throughout the history of the Delta.

Researchers in the San Francisco Bay have used isotopes of strontium in fossil bivalves to construct quantitative records of paleo-salinity (Ingram and Sloan, 1992; Ingram and DePaolo,1993; Ingram et al., 1996). This approach relies on differences between the $^{87}Sr/^{86}Sr$ content of seawater vs. river water. The $^{87}Sr/^{86}Sr$ value of seawater is 0.7092 compared with an average value of 0.7065 for freshwater entering the Sacramento-San Joaquin delta estuary (Ingram and DePaolo, 1993). Although the difference between these two end members (pure seawater and river water) appears small, it is highly significant due to the high precision possible in $^{87}Sr/^{86}Sr$ measurements. Because the $^{87}Sr/^{86}Sr$ and salinity of each end member is well known, a simple mixing model can be used to determine salinity for an area between the end members where $^{87}Sr/^{86}Sr$ has been measured. Although no fossil shells are available in our Delta peat cores, similar Sr-isotope methods can also be applied to organic materials such as peat (e.g., Shand et al., 2007; von Carnap-Bornheim et al., 2007).

Summary of progress to date

Our research on major and trace elements in peat has revealed two major patterns in the peat profile: one for contaminants and one for elements associated with salinity. Depth profiles of contaminant metals such as lead (Pb) and mercury (Hg) in Delta peat show significantly higher concentrations in the top meter or so of peat than lower down in the peat profile. This depth range corresponds to peat ages of less than 500 years before present (ybp). For example, the profile of Pb at Brown's Island (Figure 3a) shows elevated concentrations at the top, reflecting anthropogenic inputs, but has lower concentrations in the material of age 3500 to 500 ypb relative to the material at depth (> 3500 ybp). However, the apparent decline in Pb concentration between 3500 and 500 ybp turns out to be an artifact caused by variations in the amount of inorganic sediment in the peat.

Titanium (Ti) is an element that resides predominantly in the inorganic fraction of the peat, and, therefore, it can be used as a proxy for total inorganic material. The depth profile of Ti (Figure 3b) mimics that of Pb (Figure 3a) in all but the top part of the profile. A plot of Ti vs. Pb (Figure 3c) indicates that the two elements are tightly correlated in material older than 500 ybp but the most recent material has significantly more Pb for a given amount of Ti. This means that anthropogenic inputs have increased the concentration of Pb on inorganic particles. Normalizing Pb concentrations by Ti leads to a depth profile that shows near-constant values of Pb/Ti between about 7000 and 2000 ybp and an increase in Pb/Ti values beginning about 2000 ybp (Figure 3d). These results are consistent with studies elsewhere that report an increase in global Pb contamination at around 2000 ybp, which is associated with an increase in base-metal mining and smelting by the Romans (e.g., Hong et al., 1994).

Depth profiles of Na and Sr (Figures 4a and 4b), which are both associated predominantly with seawater, are quite different than those for Pb and Ti (Figures 3a and 3b). The Na and Sr profiles from Brown's Island indicate a gradual increase from the oldest peat (~ 7000 ybp) to a maximum value in peat of age 500 to 2000 ybp. The top meter mostly has lower Na and Sr concentrations, similar to those at the bottom of the profile. There are also some differences between the Na and Sr profiles, such as the concentrations near the top of the peat column (Figures 4a and 4b). Despite such small differences, however, overall these data suggest that salinity at Brown's Island was significantly higher than the present during much of the past 7000 years.

Plots of Ti vs. Na (Figure 4c) and Ti vs. Sr (Figure 4d) do not show positive correlations of the kind observed for Ti vs. Pb in the older material (Figure 3c). This indicates that significant amounts of Na and Sr are associated with the organic fraction of the peat. This finding is further substantiated by our data regarding % organic matter and % organic carbon (not shown).

Sherman Island was drained and reclaimed for agriculture. This resulted in major land-surface subsidence, resulting in the loss of the top several meters of peat from the island. The remaining peat has radiocarbon ages of approximately 3650 to 6450 ybp. Na and Sr values for peat core samples from Sherman Island are comparable to those of the same age from Brown's Island (not shown), indicating salinity conditions similar to the present during that period. Because farmed islands throughout the Delta have an incomplete sedimentary record, future work on paleo-salinity and other paleo-environmental analyses will focus on relatively undisturbed marsh islands and not highly subsided farmed islands.

Approach and Scope of New Work

To ascertain whether the patterns mentioned above are reproducible as well as representative for both the western and central Delta, we need to analyze peat from other marsh islands in addition to Brown's Island and Sherman Island. However, we have currently exhausted our budget for further analysis of major and trace elements. Therefore, we are seeking funds to perform value-added science by using peat cores already collected for the REPEAT project to determine the variability in paleo-salinity in the Delta during the last 7000 years. We will measure concentrations of Na and Sr as well as $^{87}Sr/^{86}Sr$ in peat cores from Frank's Wetland and Bacon Channel Island (Figure 2) and we will analyze $^{87}Sr/^{86}Sr$ in Brown's Island core samples to obtain a quantitative measure of paleo-salinity. The additional sites will allow us to expand our paleo-salinity record from the western Delta into the central Delta.

In order to apply the $^{87}Sr/^{86}Sr$ method to peat in the Delta, we will first need to make an assumption. With regard to paleo-salinity, it is the properties of the dissolved components in the water that respond to conservative mixing (Ingram and Sloan, 1992). Therefore, we will assume that the plant material preserved in the organic fraction of the peat has incorporated Sr that reflects the ambient water at the time the plant was growing. We will use two approaches to determine the $^{87}Sr/^{86}Sr$ values of the organic material: an indirect method and a direct method.

The indirect method will consist of analyzing the $^{87}Sr/^{86}Sr$ of total peat, and then subtracting the Sr corresponding to the inorganic fraction based on the Ti concentration. The $^{87}Sr/^{86}Sr$ values of suspended sediment from the Sacramento and San Joaquin rivers are well known (Ingram and Lin, 2002). A weighed average value for the two rivers will be used based on the proportion of sediment from the two rivers. This will be estimated by using other geochemical tracers such as concentrations of samarium, neodymium, potassium, and rubidium (Ingram and Lin, 2002).

The direct method for determining the $^{87}Sr/^{86}Sr$ of the organic fraction of the peat will consist of performing a partial digestion of the peat to extract the organic fraction. Because of the higher cost of this approach, it will be used on a subset of the samples to confirm results from the indirect method.

Additional confirmation of the applicability of these approaches will be achieved by sampling plant material and associated Delta waters from selected field sites along a salinity gradient in the San Francisco Bay Estuary and analyzing the plant material for $^{87}Sr/^{86}Sr$. We will then compare the strontium values of the plants to the expected values of $^{87}Sr/^{86}Sr$ based on the known salinity gradient caused by the mixing of seawater and river water (i.e., the mixing model we described earlier). This will verify that the plants do indeed integrate the signal of Sr isotopes from the ambient water.

The scope of work will include sectioning the 580-cm archive core from Frank's Wetland and the 726-cm archive core from Bacon Channel Island into 2-cm sections, splitting these sections in half, and then freezing the samples. Samples will be analyzed for Na, Sr, and other major and trace elements using ICP and atomic fluorescence methods at the USGS Trace Elements Laboratory in Boulder, CO, under the direction of Dr. Howard Taylor. A portion of the other half of the samples will be sent for $^{87}Sr/^{86}Sr$ analysis to Dr. Thomas Bullen at the USGS Isotope Laboratory in Menlo Park, CA. Strontium isotope ratios will be determined by thermal ionization mass spectrometry (TIMS). The resolution of the $^{87}Sr/^{86}Sr$ measurements by TIMS are ±0.00002 or better.

Relevance to the CALFED Science Program

This request for supplemental funding responds to a crucial need in the CALFED Science Program. The management of the Delta will undoubtedly change in the near future in response to Delta smelt litigation and the impending threat of levee failure. There are already several potential options for changing the water management regime of the Delta (e.g., Lund et al., 2007). Some of the many ideas for altering the Delta make sense ecologically and some are less beneficial for natural populations. Several of the proposed changes will potentially affect the salinity regime in the Delta. The salinity regime of the San Francisco Bay, particularly the 2 psu bottom salinity or X_2, has been strongly associated with the spring abundance and/or survival of several pelagic organisms including Delta smelt (Jassby et al.,1995, Kimmerer, 2002, 2004). When X_2

is located more than 85 km from the Golden Gate (approximately at the western boundary of the Delta), spring abundance and/or survival of several pelagic species plummet (Jassby et al., 1995).

The fact that we have cores from Brown's Island on the western boundary of the Delta as well as from Frank's Wetland and Bacon Channel Island in the central Delta (sites 4 and 10 on Figure 2) allows us to investigate the range of salinities that occurred before the Delta was reclaimed for agriculture and dams were built on most major tributaries. Knowing this variability will enable managers to better predict what changes in salinity will be ecologically tolerable to flora and fauna in the Delta of the future.

Our request represents value-added science at its best, because all we need are funds for laboratory analyses and data interpretation. Most of the work has already been done: (1) the study sites have already been selected; (2) the cores have already been collected and described; 3) several physical and chemical properties of the cores have already been measured including bulk density, % organic matter, and % carbon; and (4) the expensive process of determining the age of the peat through radiocarbon analysis has been completed. With just a little more lab work and interpretation of results on 3 cores, we will be able to make important statements about the salinity variability in the Delta over the past 7000 years.

New Project Staff and Qualifications

Dr. Charles N. Alpers joined the REPEAT team in 2007. His background is in trace metal fate and transport. He received his Ph.D. in Geology from UC Berkeley in 1986. He is a GS-14 Research Chemist who has worked as a Project Chief at the USGS California Water Science Center (formerly the California District Office) since 1991. His previous projects include analysis of trace metal transport in the Sacramento River, and several projects related to mercury transport and bioaccumulation in Sierra Nevada watersheds contaminated by mercury used in historical gold mining. Dr. Alpers has written or co-authored nearly 70 peer-reviewed publications in the fields of environmental geochemistry and mineral deposits. He has co-edited two books and one journal special issue. He currently serves on several technical advisory panels, including the U.S. EPA's Technical Advisory Committees for the Sulphur Bank Mercury Mine and Iron Mountain Mines Superfund sites. He is lead author and "model champion" for CALFED's DRERIP mercury conceptual model.

Budget and Justification

We anticipate this work to take two years. The details of the budget are shown in Table 1. The labor includes 25% time for Drexler and 12.5% time for Alpers over the two-year period. Laboratory analyses will be carried out during the first year. We will analyze samples in small batches so that we can learn as we go and only focus on depth intervals in the peat where there are the greatest changes in salinity. This will allow us to best manage our limited funds for analysis. The funds for laboratory analyses include approximately 220 peat samples (@ $200 gross/sample) for major and trace metals (or about 17 samples per meter of core) and approximately 65 peat and plant samples (@ ~$400 gross/sample) for Sr isotopes (or about 3-4 samples per meter of core). This number of analyses will enable us to gather enough information to adequately quantify salinity throughout the peat column. The supplies and shipping category includes costs for shipping samples to the appropriate USGS laboratories and the cost of EPA-certified clean jars for the samples.

The second year of this supplemental work will involve analyzing the laboratory results and writing peer-reviewed journal articles. The total supplemental budget for this work is anticipated to be $283,063.

Table 1. Supplemental Budget for REPEAT Project

	Overhead and Assessments	Labor	Laboratory Analyses	Supplies and Shipping	Total Supplemental Funds
Year 1		$48,500	$70,000	$3,000	
Year 2		$48,500			
Total for project	$113,063	$97,000	$70,000	$3,000	
Total Supplemental Funds					**$283,063**

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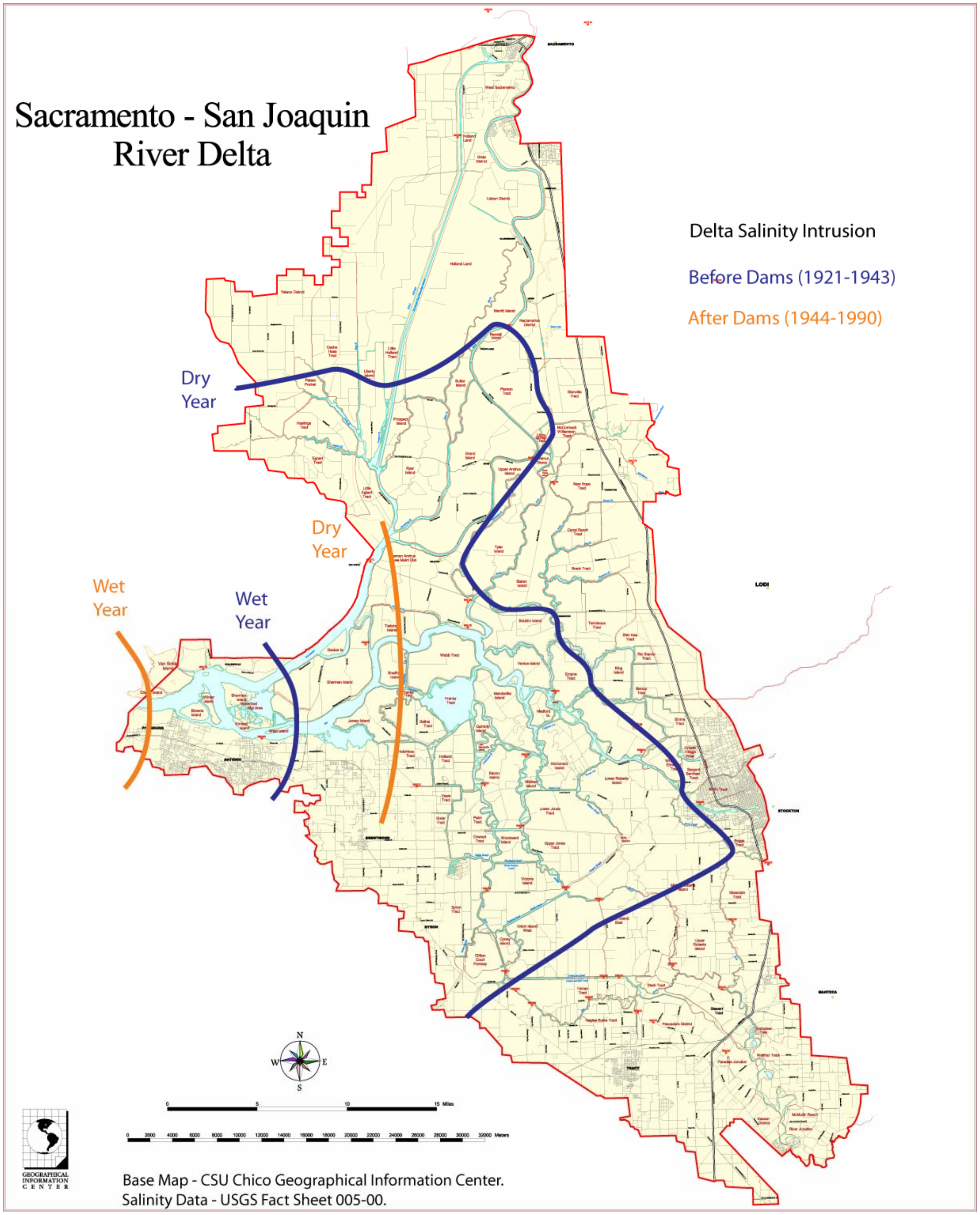

Figure 1. The landward movement of salinity incursions into the Delta before and after dams were built on inflowing rivers.

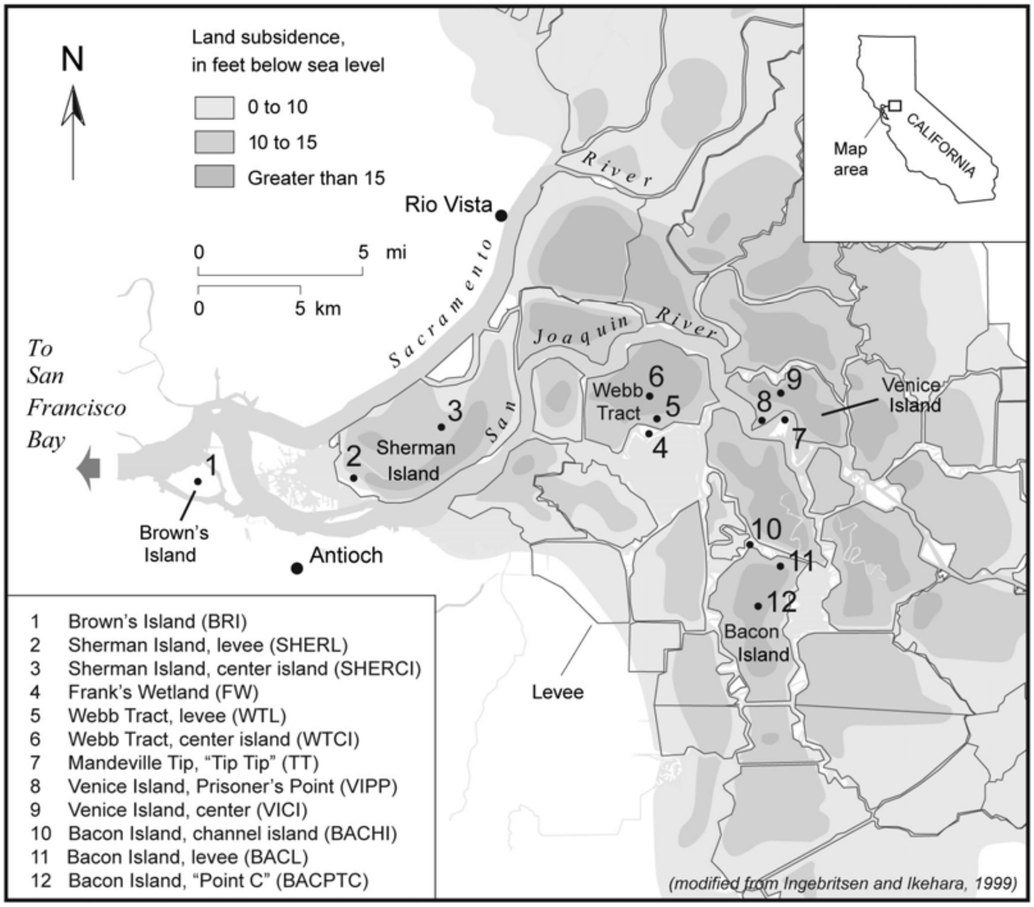

Figure 2. REPEAT coring sites in the Sacramento-San Joaquin Delta.

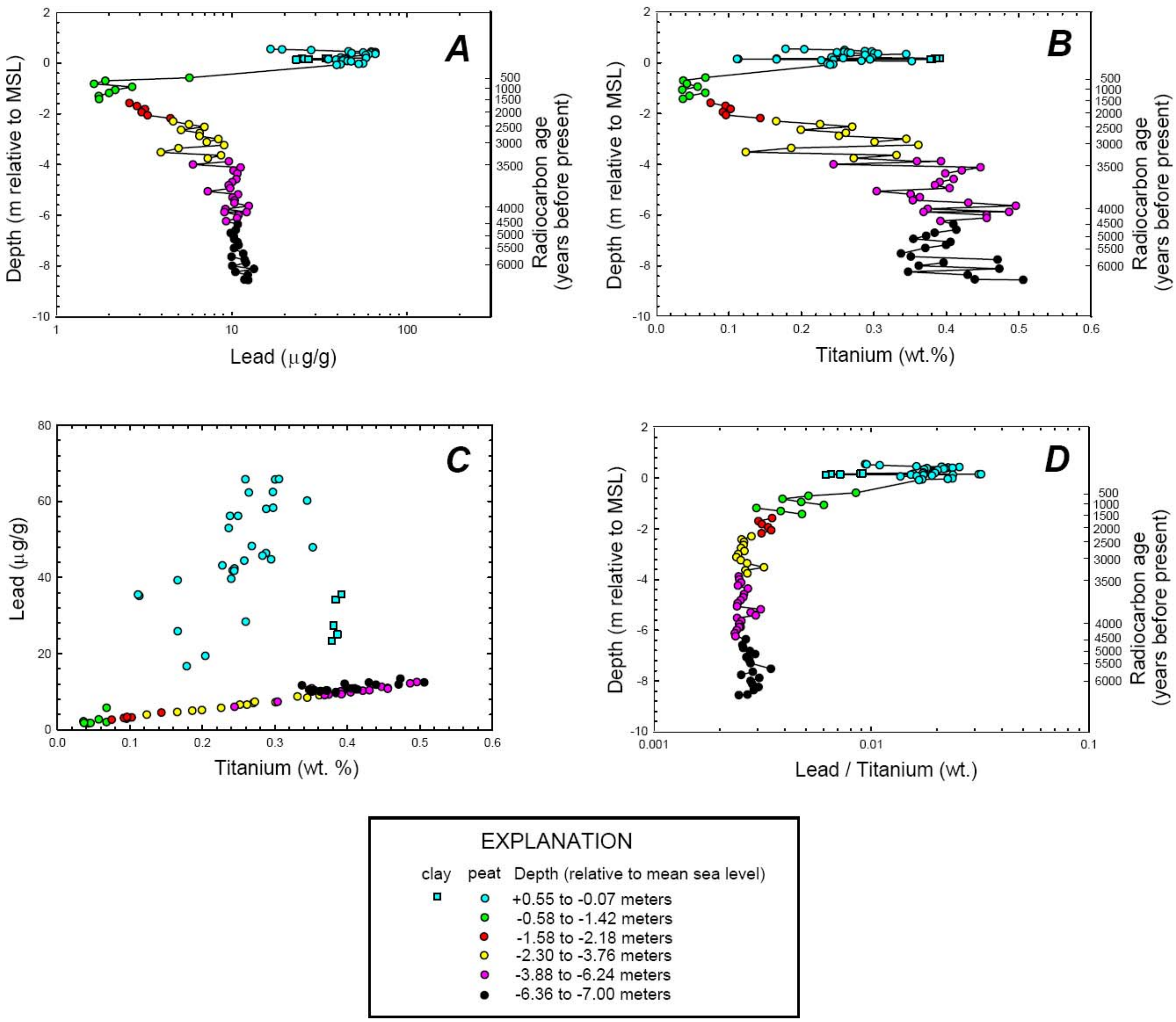

Figure 3. Metal content of peat from Brown's Island: (a) lead (Pb) (logarithmic scale) vs. depth, (b) titanium (Ti) vs. depth, (c) Ti vs. Pb, (d) Pb/Ti (logarithmic scale) vs. depth.

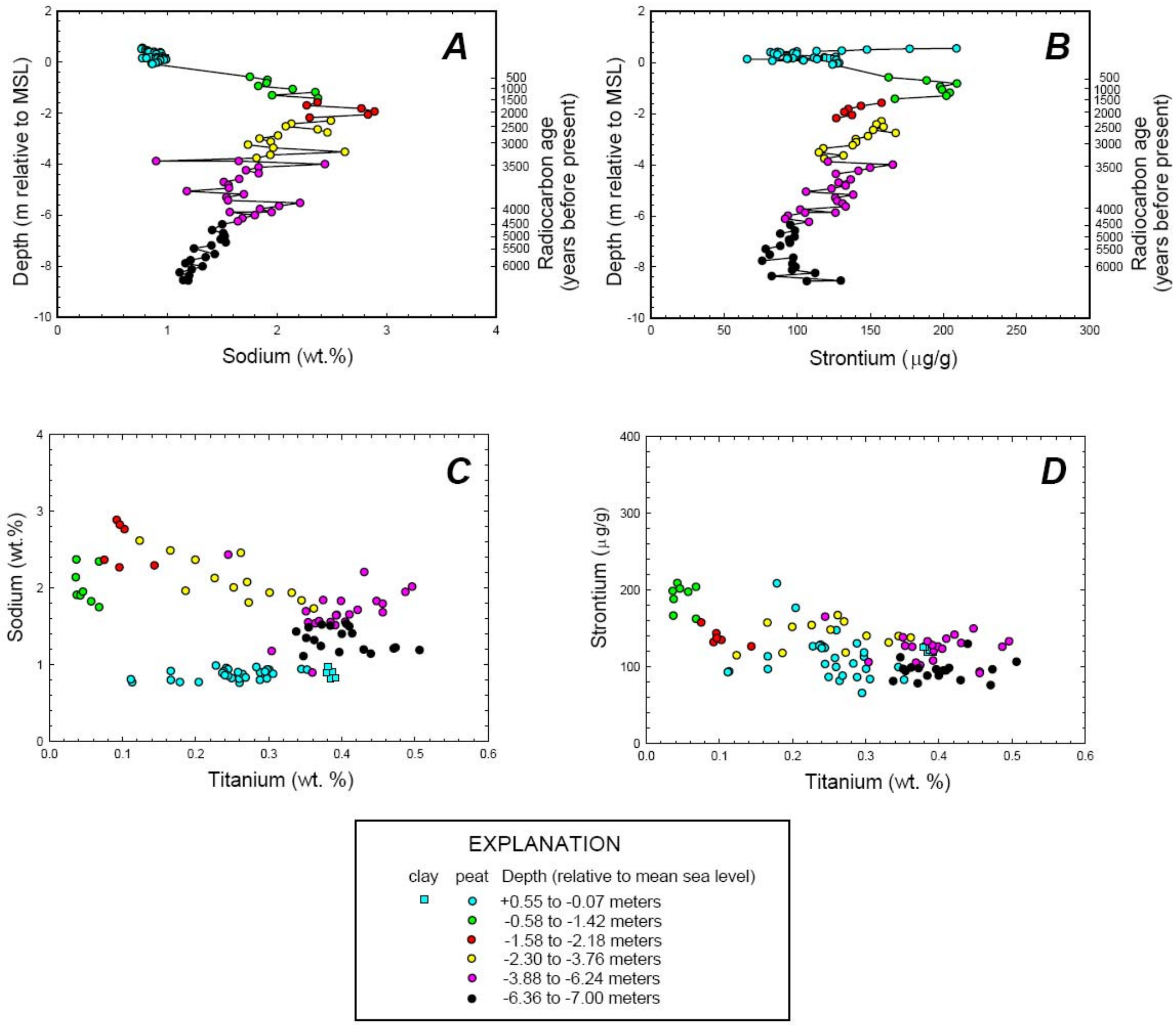

Figure 4. Concentrations of elements in peat at Brown's Island. (a) sodium (Na) vs. depth, (b) strontium (Sr) vs. depth, (c) Ti vs. Na, (d) Ti vs. Sr.