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Changes in sediment and organic carbon accumulation in a highly-disturbed ecosystem: The Sacramento-San Joaquin River Delta (California, USA)

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ABSTRACT

We used the Sacramento-San Joaquin River Delta CA (Delta, hereafter) as a model system for understanding how human activities influence the delivery of sediment and total organic carbon (TOC) over the past 50–60 years. Sediment cores were collected from sites within the Delta representing the Sacramento River (SAC), the San Joaquin River (SJR), and Franks Tract (FT), a flooded agricultural tract. A variety of anthropogenic tracers including ^{137}Cs, total DDE ($\sum$DDE) and brominated diphenyl ether (BDE) congeners were used to quantify sediment accumulation rates. This information was combined with total organic carbon (TOC) profiles to quantify rates of TOC accumulation. Across the three sites, sediment and TOC accumulation rates were four to eight-fold higher prior to 1972. Changes in sediment and TOC accumulation were coincident with completion of several large reservoirs and increased agriculture and urbanization in the Delta watershed. Radiocarbon content of TOC indicated that much of the carbon delivered to the Delta is "pre-aged" reflecting processing in the Delta watershed or during transport to the sites rather than an input of predominantly contemporary carbon (e.g., 900–1400 years BP in surface sediments and 2200 yrs BP and 3610 yrs BP at the base of the SJR and FT cores, respectively). Together, these data suggest that human activities have altered the amount and age of TOC accumulating in the Delta since the 1940s.

1. Introduction

Anthropogenic activities including climate change influence connections between the hydrologic and carbon cycles as well as the exchange of materials between terrestrial and aquatic systems (Walling, 2006; Cole et al., 2007). Precipitation influences the delivery of water, suspended sediment and carbon, while construction of dams and reservoirs, water diversions, and changes in land use affect the flow paths, timing, and transport of sediment and associated materials to downstream environments. Since continued population growth in coastal regions and climate change will likely further modify these connections (Peters et al., 2008), it is important to understand how systems have responded to past alternations to water and sediment delivery and how these changes have influenced the amounts and composition of carbon delivered to downstream ecosystems. It is also important to understand potential interactions between anthropogenic activities and climate in order to evaluate whether historical changes can be used to predict future change.

The San Francisco Bay and its associated Delta is one of the most modified aquatic ecosystems (Nichols et al., 1986; Jassby and Cloern, 2000). In recent decades, the Delta and northern San Francisco Bay have experienced declines in productivity at the base of the food web. Phytoplankton chlorophyll-*a* concentrations decreased dramatically between 1969 and 1982 (Lehman and Smith, 1991; Lehman, 1992). Introduction of the Asian clam, *Potamocorbula amurensis*, in 1987 led to an 80% decrease in phytoplankton primary production (Alpine and Cloern, 1992), and many native fish species have become extinct, endangered, or have declined dramatically in abundance (Moyle et al., 1992; Jassby et al., 1995; Meng and Moyle, 1995; Jassby and Cloern, 2000; Sommer et al., 2007). Key components of the zooplankton and epibenthic invertebrate communities have also declined significantly (Kimmerer and Orsi, 1996; Orsi and Mecum, 1996), affecting food web dynamics.

Declines in native species and system productivity have been attributed to anthropogenic modifications to the Delta ecosystem. These include losses in Tule marsh, the once dominant habitat (Atwater et al., 1979), changes in the volumes of freshwater enter-

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ing the Delta from the Sacramento and San Joaquin Rivers and subsequent changes in sediment delivery (Arthur et al., 1996), introduction of and invasion by non-indigenous species (Cohen and Carlton, 1998), and inputs of contaminants (van Geen and Luoma, 1999; Venkatesan et al., 1999; Connor et al., 2007). Each of these factors has direct and indirect influences on the supply and quality of sediment and carbon delivered to downstream ecosystems. The progressive loss of wetlands in the Delta and conversion of land to agriculture have likely contributed to a loss of habitat as well as alterations to the delivery of sediment and associated materials such as organic carbon (Sickman et al., 2007). Alterations in freshwater flow due to water diversions as well as storage of water in dams and reservoirs likely influences the delivery of carbon from riverine algal production (Canuel and Cloern, 1996; Canuel, 2001) as well as sediment and soils from the surrounding watershed (Wright and Schoellhamer, 2004). Restoration in the Delta may (or may not) reverse some of these trends.

The goal of this study was to examine how anthropogenic activities in the Delta watershed have influenced the delivery of sediment and carbon to downstream environments over the past 50–60 years, a period of intense anthropogenic alteration. Sediment cores were collected from representative sub-habitats of the Delta including sites on the upper and lower Sacramento River (ES and SAC, respectively), San Joaquin River (SJR) and Frank's Tract (FT), a flooded agricultural tract. Downcore profiles of anthropogenic tracers representing the time period since the 1940s were used to determine sediment accumulation rates. This information was combined with sediment core profiles of total organic carbon (TOC) to quantify changes in the accumulation of carbon. Radiocarbon ages of TOC from surface sediments and downcore profiles in two of the cores were used to determine the age of carbon delivered to and stored in the Delta at present and whether there have been changes in the age of carbon delivered over this time period.

2. Methods

2.1. Core collection

Sediment vibra cores (80–280 cm in length (Table 1); 3 inch diameter) were collected using a gasoline-powered concrete vibrator adapted to couple with standard aluminum irrigation tubing. The coring sites represented sub-habitats of the Delta and ranged in water depth from ~1 to 3.6 m (Fig. 1, Table 1). Each core was split lengthwise immediately following collection and photographed digitally to record visual changes in color and texture. X-radiographs were produced using a Varian Paxscan® digital panel and a portable veterinary X-ray generator. This information indicated that the cores were not disturbed by bioturbation. One-half of each core was subsampled for the ^{137}Cs analyses while the other half was used for the organic analyses. Samples for organic analyses were stored on dry ice in the field and during transport to the laboratory where they were frozen at –80 °C until analyzed.

2.2. Total organic carbon and radiocarbon analyses

Sub-samples of frozen sediment were thawed and dried at 65 °C for several days to determine water content and in preparation for elemental and isotopic analyses. Water content and sediment density (2.65 g cm^{-3} for quartz) were subsequently used to calculate sediment mass accumulation. Dry sediment (20–40 mg) was weighed into pre-combusted (4 h at 450 °C) silver capsules and acidified using 10% high-purity hydrochloric acid to remove inorganic carbon (Hedges and Stern, 1984). We did not observe dolomite shell fragments. Total organic carbon (TOC) and total nitrogen (TN) were measured by high temperature combustion using a Fisons Flash EA (Model 1112). Duplicate analyses were performed for all elemental (TOC and TN) analyses.

Radiocarbon isotopic composition of sediment TOC was conducted at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility at the Woods Hole Oceanographic Institution using previously-published methods (Wakeham et al., 2004). Sediments were dried, ground, and prepared similarly to the preparation used for elemental analyses (see above). Delta-^{14}C values and errors reported for all samples were corrected for a combustion blank and stable carbon isotope composition (data not shown). Radiocarbon ages were calculated using the Libby half life of 5568 years.

2.3. Organic contaminant analyses

Sediments were extracted with CH_2Cl_2:CH_3OH (2:1 v/v) using an ASE-200 Accelerated Solvent Extractor (Dionex®) at 80 °C and 1800 psi (2 × 10 min cycles) (Waterson and Canuel, 2008). Frozen sediments were thawed, homogenized and dried with hydromatrix (Varian®) prior to extraction. Extracts were partitioned into two phases and the lower organic phase collected. The aqueous phase was back-extracted into hexane and the combined organic phases sat over anhydrous Na_2SO_4 overnight to reduce traces of H_2O. The samples were concentrated to 1 ml (Zymark Turbo Vap 500). A portion of the extract was saponified using 1 N KOH in aqueous methanol (110 °C for 2 h). Neutral and acidic lipids were extracted into hexane from the saponified sample following Canuel and Martens (1993). The saponified neutral fraction was separated into lipid compound classes using silica gel columns. Fractions 1 and 2 were eluted with 10 ml hexane and 5 ml 25% toluene in hexane, respectively. The combined fractions included the *p,p* and *o,p* isomers of dichlorodiphenyldichloroethylene (DDE), primary degradation products of the pesticide dichlorodiphenyltrichloroethane (DDT), as well as the brominated diphenyl ether (BDE) congeners, a class of ubiquitous contaminants which are used as flame retardants. DDT was first used in the Central Valley CA in the 1940s (Hartwell, 2004; Connor et al., 2007; Mischke et al., 1996). DDT application increased from the 1940s through the late 1960s when use peaked, before being banned in 1973 (Table 2). BDEs were first introduced to the environment in the 1970s and use of this class of contami-

Table 1
Site descriptions and locations.

Site	Abbreviation	Environment	Water depth (m)	Core length (cm)	Latitude	Longitude	Radiocarbon age of surface sediment (y BP ± error)	F_{modern} (± error)
Elk Slough	ES	Upper Sacramento River	3.6	83	38° 21.498′ N	121° 33.714′ W	Modern	1.010 (0.003)
Horseshoe Bend	SAC	Lower Sacramento River	1.8	282	38° 05.248′ N	121° 42.683′ W	n/a	n/a
San Joaquin River	SJR	San Joaquin River	2.4	220	38° 02.886′ N	121° 31.392′ W	1410 (35)	0.839 (0.004)
Frank's Tract	FT	Flooded agricultural tract	1.5	225	38° 01.528′ N	121° 36.521′ W	980 (35)	0.885 (0.004)

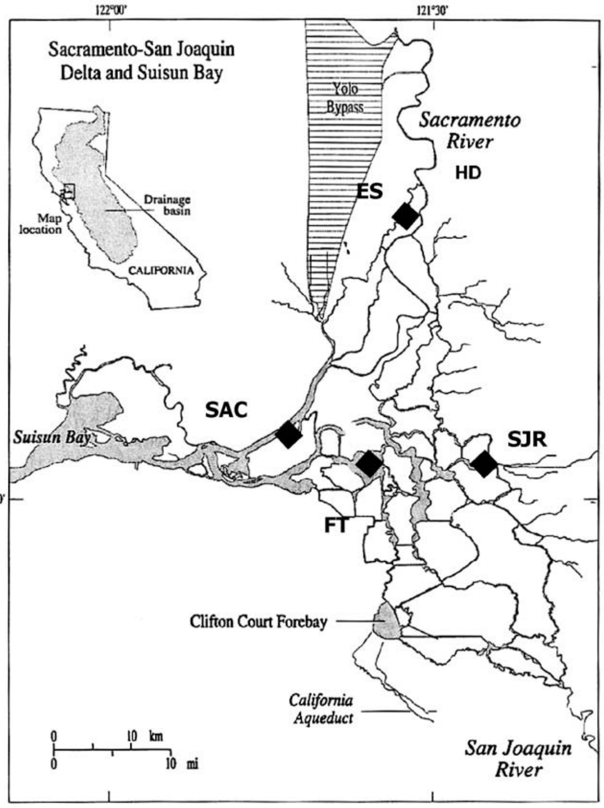

Fig. 1. Map of the Sacramento-San Joaquin River Delta, CA showing locations where sediments were collected for this study.

nants has increased exponentially over the past thirty years with a doubling time of approximately five years (Hites, 2004). These classes of contaminants were analyzed by gas chromatography–negative chemical ionization mass spectrometry as described elsewhere (Geisz et al., 2008) after the addition of deuterated-hexachlorocyclohexane as an internal standard.

2.4. ^{137}Cesium analyses

^{137}Cs activity was measured on whole ground sediment in a well-type intrinsic germanium gamma detector. Samples were dried, ground and placed in plastic vials to a uniform height of 4 cm to ensure a constant geometry among samples counted. Samples were counted for 90,000 seconds and specific activity (dpm g^{-1}) was determined from the peak intensity at 661.66 keV and the detector efficiency derived from a commercial ^{137}Cs standard. The depth of ^{137}Cs penetration was used to identify the sediment horizon corresponding to introduction of this isotope to the environment during atmospheric bomb testing in 1954 (Ritchie and McHenrey, 1990). The depth of maximum activity was also identified. This horizon corresponds to 1963, when activity peaked in the environment, just prior to the signing of the International Test Ban Treaty, which banned atmospheric testing of nuclear weapons. ^{210}Pb was also measured in some samples. This information is not included in this manuscript since Pb-210 derived rates could not be presented consistently for the three sites.

2.5. Uncertainty estimates

Several parameters contribute to uncertainty associated with linear and mass accumulation rates including the size of the sampling interval, uncertainty associated with the age of the horizon and errors and assumptions in porosity measurements when converting to mass. Since we were only to account for uncertainty associated with the sampling interval and this uncertainty most likely underestimates total uncertainty, measures of uncertainty associated with linear and mass accumulation rates are not presented here. We expect measures of uncertainty to be similar to those reported previously (e.g., 12 ± 6% uncertainty was observed in a study conducted by Lu and Matsumoto (2005). Uncertainty estimates for TOC accumulation rates were based on the standard deviation of the mean TOC content for intervals deposited within the same time window.

3. Results

Three anthropogenic tracers were employed to date the sediment cores used for this study: ^{137}Cs activity (initial activity and peak activity), appearance of and peak concentration of primary degradation products of the pesticide DDT ($\sum$DDE), and first appearance of a class of ubiquitous contaminants used as flame retardants, the BDEs (Table 2). In addition, a peat layer was observed between 50 and 120 cm in the FT core, which likely corresponds to the time period when this site was a marsh prior to the construction of levees and its subsequent conversion to an agricultural tract (late 1800s). This information was used to identify depths in the sediment cores corresponding to the known introduction and use patterns of these anthropogenic tracers in the environment. Sediment accumulation rates were calculated for time periods between these dated horizons assuming constant accumulation and were compared to average rates of sediment accumulation from the base of the core to the surface (corresponding to 2005 when the cores were collected).

3.1. Cesium-137

The activity of ^{137}Cs was measured in three sediment cores collected from the Delta (Fig. 2). In the SJR core, total ^{137}Cs activities ranged between 0.03 ± 0.025 at the base of the core (215–220 cm) and 0.62 ± 0.05 dpm g^{-1} at approximately 150 cm depth. Since ^{137}Cs activity was measureable to the base of the core, the SJR core likely represents accumulation since 1954. Relative to

Table 2
Description of tracers used to date sediment cores for this study. References are provided in the text.

Tracer	Use	Year event	
^{137}Cs	Atmospheric weapons testing	1954	Initial use
		1963	Peak activity
ΣDDE	Pesticide	1944	Initial use
		Late 1960s	Peak use; DDT declared restricted material by CA Dept Food and Agriculture
		1973	DDT banned
BDE	Flame retardants	1972	Initial use
Peat layer		1880	Conversion from wetland to agricultural tract

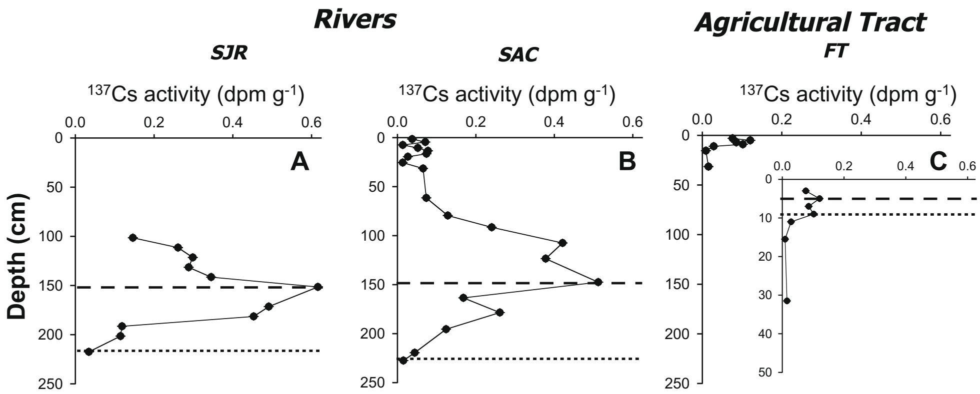

Fig. 2. ^{137}Cs profiles for sediment cores collected from the San Joaquin River (SJR), Sacramento River (SAC) and a flooded agricultural tract, Frank's Tract (FT), located in the Sacramento-San Joaquin River Delta. The dotted line identifies the first appearance of ^{137}Cs in 1954. The dashed line corresponds to 1963, when peak activities of ^{137}Cs occur. The insert provides a detailed profile of ^{137}Cs activity in the upper 50 cm of the FT core. ^{137}Cs activity was not measured for the upper sections of the SJR core. Activity concentrations in disintegrations-per-minute/gram (dpm g^{-1}) may be converted to Bequerels per kg (Bq/kg) by multiplying values by 16.66.

the SJR core, peak ^{137}Cs activity was somewhat lower in the SAC core, which was collected from the lower Sacramento River. ^{137}Cs activity in the SAC core ranged from <0.08 ± 0.04 dpm g^{-1} in the surface sediments (0–30 cm) and at the base of the core (below 220 cm) to peak ^{137}Cs activity (0.51 ± 0.04 dpm g^{-1}) at 146–149 cm (Fig. 2B). ^{137}Cs activity in the core collected from FT, the flooded agricultural tract, was lower than in the cores collected from the two river sites. The zone where ^{137}Cs activity was above background was restricted to the upper 12 cm, indicating that only sediments above this depth were deposited since 1954. ^{137}Cs activity ranged from 0.03 ± 0.02 at 10 to 12 cm to a peak activity of 0.12 ± 0.04 dpm g^{-1} at 4 to 6 cm depth, indicating that the upper 6 cm accumulated since 1963. Assuming constant accumulation between 1954 (initial ^{137}Cs activity) and 1963 (peak ^{137}Cs activity), rates of sediment accumulation were calculated to be 7.8 cm yr^{-1}, 8.3 cm yr^{-1} and 0.7 cm yr^{-1} for the SJR, SAC and FT cores, respectively, during this time period (Table 3). Correcting for water content and assuming a bulk density of 2.65 g cm^{-3} (density for quartz), these accumulation rates translate to mass accumulation rates of 9.9 g cm^{-2} yr^{-1}, 13.5 g cm^{-2} yr^{-1} and 2.1 g cm^{-2} yr^{-1}, for the SJR, SAC and FT cores, respectively (Fig. 3A; Table 3).

3.2. Total DDE (∑DDE)

∑DDE concentrations were above detection limits throughout the core collected from SJR, ranging from 2.9 to 15 ng g^{-1} dry weight sediment (Fig. 4A). Measurable levels of ∑DDE throughout the SJR core suggest that it represents accumulation since the 1940s, when DDT was first used in the Central Valley CA. Concentrations increased linearly from the base of the SJR core to approximately 130 cm, corresponding to increased use of DDT between 1944 and the late 1960s. Within the SJR core, there was relatively good agreement between the 1963 peak in ^{137}Cs activity at 150 cm and the peak in ∑DDE concentrations at 130 cm, corresponding to maximal use of DDT in the late 1960s. ∑DDE concentrations were variable between 20 and 130 cm with concentrations ranging between 3.8 and 15 ng g^{-1} dry weight and concentration peaks were also observed at 20 cm, 30 cm and 80 cm.

∑DDE concentrations in the SAC core were similar to concentrations measured in the SJR core (~2–20 ng g^{-1} dry weight) (Fig. 4B), though fewer analyses were conducted. ∑DDE was detected in the SAC core to 200 cm, suggesting that sediments above this depth reflect accumulation since the 1940s. The maximum ∑DDE concentration was measured at 150 cm, corresponding to the late 1960s, and declined linearly to levels below detection at 45 cm depth. There was a secondary peak in ∑DDE concentrations between 0 and 45 cm. Dating of the sediment horizons in SAC core was consistent whether based on peak ^{137}Cs activity or DDT peak concentration (i.e., 150 cm, corresponding to the 1960s).

In contrast to the cores collected from the river sites, ∑DDE in the FT core was confined to the surface sediments (Fig. 4C). Thus sedimentation at FT since the 1940s was considerably lower than at the river sites. There was good correspondence between peaks in ^{137}Cs activity and ∑DDE (~6 cm depth), proxies for sediments deposited during the 1960s.

Table 3
Linear sedimentation rates (LSR), mass accumulation rates and TOC accumulation rates.

Site	Time period	LSR cm yr^{-1}	Mass accumulation g cm^{-2} y^{-1}	TOC accumulation g OC cm^{-2} yr^{-1}
SAC	1944–1954	2.8	5.6	0.07
	1954–1963	8.3	13.5	0.21
	1963–1972	14.1	24.6	0.31
	1972–2005	0.7	1.3	0.01
	Avg 1944–2005	2.8	7.6	0.10
SJR	1944–1954	n/a	n/a	n/a
	1954–1963	7.8	9.9	0.41
	1963–1972	9.3	11.8	0.45
	1972–2005	2.0	1.9	0.05
	Avg 1954–2005	4.3	5.0	0.16
FT	1944–1954	0.6	1.3	0.33
	1954–1963	0.7	2.1	0.51
	1963–2005	0.1	0.3	0.07
	Avg 1944–2005	0.3	0.2	0.15

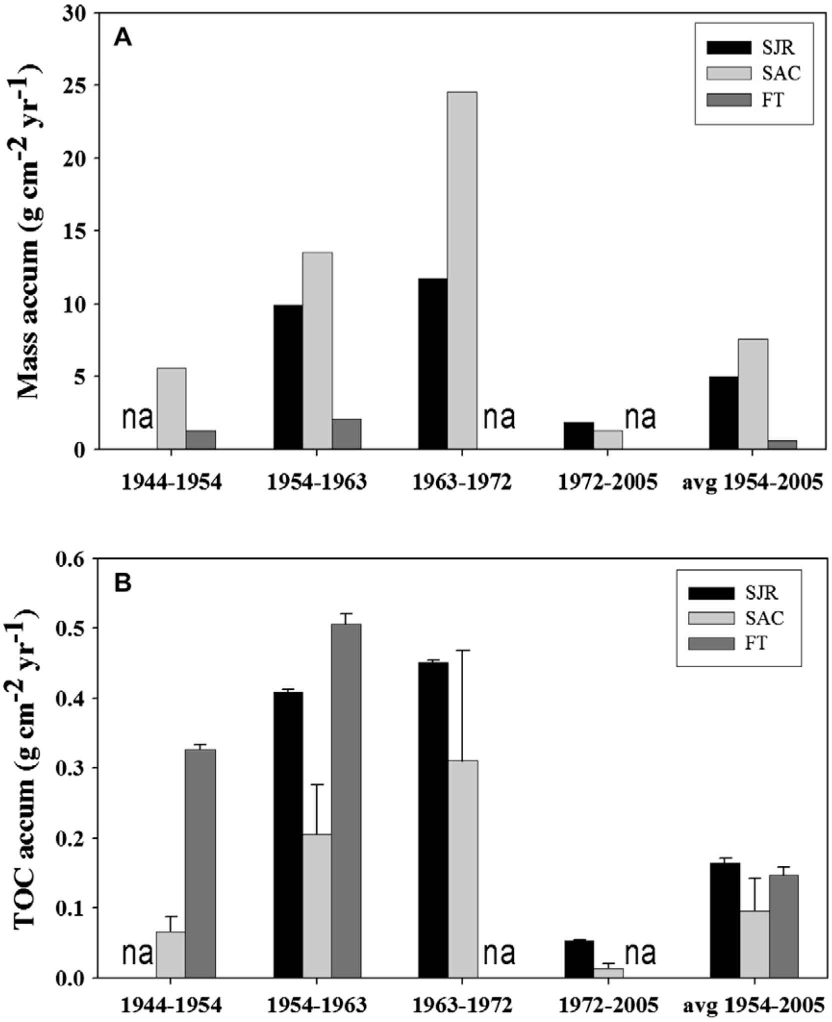

Fig. 3. Sediment mass accumulation rates (A) and TOC accumulation rates (B) for sediment cores collected from the Sacramento-San Joaquin River Delta. na = Not available (details provided in text).

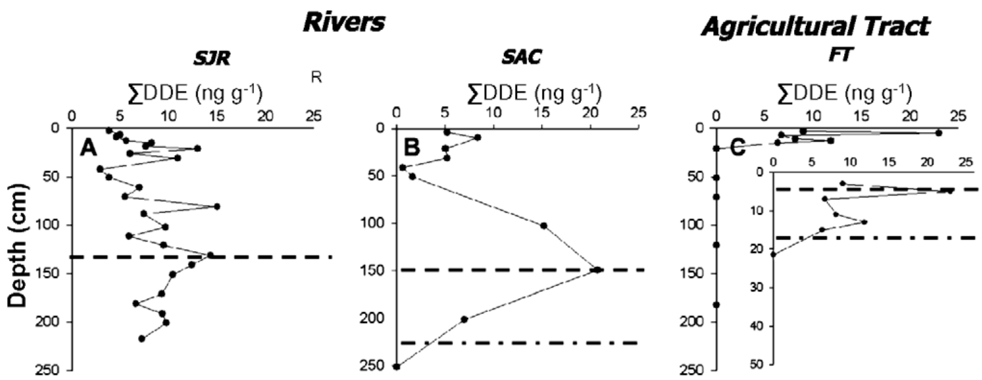

Fig. 4. Downcore profiles showing concentration of the primary degradation products of the pesticide DDT (∑DDE = p,p′-DDE + o,p-DDE) in sediment cores collected from the San Joaquin River (SJR), Sacramento River (SAC) and a flooded agricultural tract, Frank's Tract (FT). The dash-dot line identifies the onset of detectable levels of ∑DDE, which corresponds to its initial use in the Central Valley, CA during the 1940s. The presence of ∑DDE throughout the SJR core indicates that the entire core sequence represents accumulation post-1940s. The dashed line corresponds to the late 1960s, when DDT use peaked. The insert provides a detailed profile of ∑DDE concentrations in the upper 50 cm for the FT core.

3.3. Bromodiphenyl ethers (BDE)

At SJR, sediment concentrations of BDE increased from background levels (our laboratory blank was 0.15 ng g^{-1} dry weight) in sediments below 80 cm depth to peak concentrations (~3 ng g^{-1} dry weight) in surface sediments (Fig. 5A). At SAC, BDE concentrations were approximately an order of magnitude lower than at SJR (0.15–0.42 ng g^{-1} dry weight) and were only detected to 23 cm depth, suggesting lower rates of sediment accumulation since the 1970s than at SJR (Fig. 5B). We identified the sediment horizon

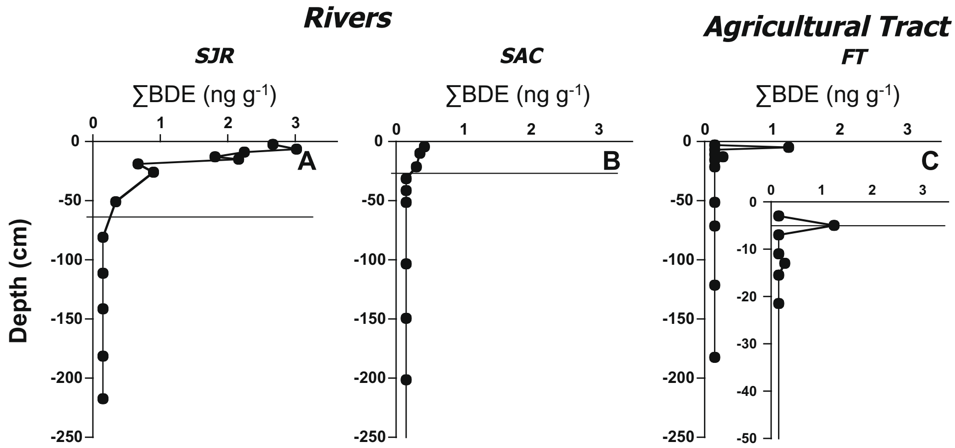

Fig. 5. Downcore profiles showing concentration of five brominated diphenyl ether (BDE) congeners (∑BDE = BDE28 + 47 + 99 + 100 + 153) in sediment cores collected from the San Joaquin River (SJR), Sacramento River (SAC) and a flooded agricultural tract, Frank's Tract (FT). The solid line identifies the first appearance of these contaminants in the environment in the early 1970s. The insert provides a detailed profile of BDE concentrations in the upper 50 cm for the FT core.

where BDE concentrations were first above background concentrations as corresponding to 1972 (Fig. 5). Assuming constant accumulation between 1972 and 2005, rates of mass accumulation since 1972 were calculated to be 2.0 cm yr^{-1} and 0.7 cm yr^{-1} for the cores collected from SJR and SAC, respectively (Table 3).

BDE concentrations ranged between 0.15 and 1.24 ng g^{-1} dry weight) in the FT core (Fig. 5C). Peak BDE concentrations were observed in the 4–6 cm horizon and background levels (0.15 ng g^{-1} dry weight) were measured at depths below 15 cm. Unfortunately, our sample resolution did not provide the ability to differentiate between sediment horizons corresponding to detectable levels of BDE and peak ∑DDE (Figs. 3C and 4C). As a result, sediment accumulation rates were calculated for the FT core based on peak ^{137}Cs activity (6 cm; corresponding to 1963) and detectable concentrations of ∑DDE (15 cm; post 1944) (Table 3; Fig. 4C). Peak ^{137}Cs activity was used to calculate accumulation rates for 1963–2005. This approach yielded accumulation rates of 0.14 cm yr^{-1} (Table 3), providing a somewhat more conservative measure of recent sediment accumulation for the FT core than rates based on initial detectable levels of BDE.

3.3.1. Total organic carbon accumulation and radiocarbon age

Downcore profiles of TOC were measured for each of the sediment cores (Fig. 6). In the SJR core, TOC content ranged from 2.1% to 4.6% with mean (± s.d.) values of 3.25 ± 0.7%. TOC profiles in the SJR core display a general trend of decreasing TOC content from 1963 to the present ($r^2 = 0.61$, $p < 0.001$; Fig. 6A). TOC content was significantly lower in the SAC core than the SJR core (paired t-test; $p < 0.001$) with %TOC content ranging from 0.7% to 2.7% and overall values averaging 1.3 ± 0.6% TOC (Fig. 6B). Overall, the TOC content in the FT core was significantly higher than that found in either the SAC or SJR cores (mean ± s.d. = 26.7 ± 16.5% TOC; ANOVA; $p < 0.001$) with the highest TOC content within the peat layer between 50 and 120 cm, where values reached 40% to 48% (Fig. 6C).

Mass accumulation rates were multiplied by %TOC to calculate TOC accumulation rates over the time horizons identified in each sediment core (Fig. 3B). TOC accumulation rates averaged over the entire core (1940s-present) were similar at the three study sites: 0.16 g OC cm^{-2} yr^{-1} at SJR, 0.10 g OC cm^{-2} yr^{-1} at SAC, and 0.15 g OC cm^{-2} yr^{-1} at FT. However, when horizons representing specific time periods were examined individually, there were differences in the TOC accumulation rates for different time periods and between the sites. Similar to sediment mass accumulation rates, the highest TOC accumulation rates were found between 1954–1963 and 1963–1972 for the cores collected from SJR and SAC, with an appreciable decrease in TOC accumulation since 1972 (Fig. 3B; Table 3). At FT, rates of TOC accumulation were highest between 1944–1954 and 1954–1963. This likely reflects marsh

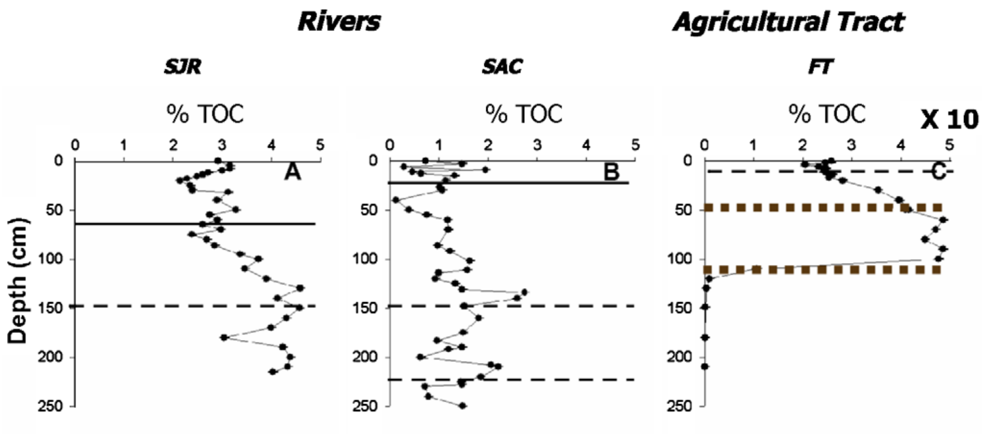

Fig. 6. %TOC content for sediment cores collected from the Sacramento-San Joaquin River Delta. The dashed line corresponds to peak activities of ^{137}Cs (1963), the solid line identifies the first appearance of BDE (1972), the dash-dotted line corresponds to detectable levels of ∑DDE (1944). The thick dotted lines shown on the FT profile define the peat layer. Note that the scale for the FT core is ten-fold higher than for SJR and SAC.

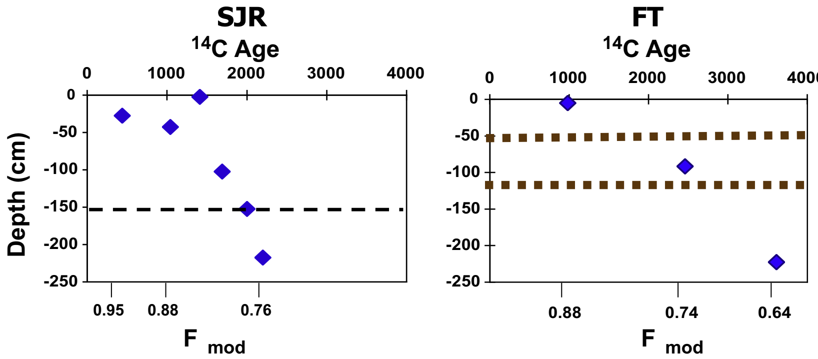

Fig. 7. Downcore profiles showing radiocarbon ages (upper axis) and fraction modern carbon (lower axis) of sediment TOC in cores collected from SJR and FT. The dashed line identifies the depth corresponding to peak ^{137}Cs activity in 1963 activity in the SJR core. A peat layer, likely corresponding to the transition from wetland to agriculture in the late 1800s, is noted with the dashed lines on the profile for FT. For both cores, radiocarbon ages are substantially older than corresponding sediment accumulation rates suggesting that much of the carbon delivered to these locations is pre-aged.

accretion, which is consistent with the high %TOC content of these sediments, since rates of sediment accumulation were low during this time period (Fig. 3A; Table 3).

Radiocarbon ages for bulk TOC in surface sediments ranged from modern at the upper Sacramento River site (ES) to 1410 years before present (yrs BP, hereafter) at FT (Table 1). Modern radiocarbon ages for TOC in the surface sediments of ES suggest that this site is dominated by inputs from recent production, reflecting contemporary aquatic algae and/or land plants. In contrast TOC associated with newly deposited sediments at SJR and FT contains an older component, yielding radiocarbon ages of ~1000 years BP or more.

In both cores, radiocarbon ages of TOC increase with depth but are considerably older than what would be predicted based on sediment accumulation rates (Fig. 7). The presence of ∑DDE throughout the SJR core indicates that the entire core was deposited since the 1940s. However, sediments at the base of the core had radiocarbon ages of 2200 yrs BP and a fraction of modern carbon (F_{modern} carbon) of 0.76. Similarly, sediments from within the peat layer at FT, which likely represent accumulation when this system was a wetland before its conversion to agriculture in the late 1800s, had radiocarbon ages of 2460 yrs BP, corresponding to F_{modern} carbon of 0.74. Similarly, radiocarbon ages at the base of the FT core were 3610 yrs BP with F_{modern} carbon of 0.64 (Fig. 7).

4. Discussion

4.1. Sediment and carbon accumulation since the 1940s

Results from the SJR core show four- to five-fold decreases in sediment and TOC accumulation since 1972, relative to the time period between 1954 and 1972 (Fig. 3A and B; Table 3). Trends were even more pronounced in the SAC core where we observed order-of-magnitude decreases in sediment and TOC accumulation for sediments deposited since 1972 (e.g., mass accumulation rates in 1954–1963 were 13.5 g cm^{-2} yr^{-1} while mass accumulation rates were 1.3 g cm^{-2} yr^{-2} for 1972 to present; Fig. 3A). For the FT core, we did not have sufficient sampling resolution to distinguish 1963 (peak ^{137}Cs) from 1972 (initial detection of BDE), thus we were only able to calculate rates for pre- vs. post-1963. The sediment accumulation rate for the FT core decreased approximately four-fold since 1963 (~0.6 cm yr^{-1} in pre-1963 sediments to 0.14 cm yr^{-1} in sediments deposited since 1963; Table 3). Mass accumulation and TOC accumulation also declined correspondingly. Potential mechanisms for the observed changes in sediment and TOC accumulation include changes in climate that altered precipitation patterns and the delivery of freshwater and sediment, population growth and associated demands for freshwater, increased conversion of land from wetlands and grasslands to agricultural and urban uses, and increased storage of sediments in dams and reservoirs. It is important to note that while increased precipitation can increase delivery of sediment due to erosion of soils, it can also decrease sediment accumulation if floods wash sediment away.

We investigated relationships between climate and accumulation rates using precipitation as a proxy. Over the timescale represented by our sediment cores, we found positive relationships between rainfall and discharge ($r^2 = 0.70$; $p < 0.0001$) as well as rainfall and total suspended solids ($r^2 = 0.59$; $p < 0.001$) for the Sacramento River. Similar relationships between rainfall and discharge ($r^2 = 0.73$; $p < 0.0001$) and rainfall and total suspended solids ($r^2 = 0.74$; $p < 0.0001$) were observed for the San Joaquin River. However, we did not find any correlation between rainfall (or discharge) and %TOC content, sediment accumulation and TOC accumulation rates at either SJR or SAC. The lack of a relationship is not particularly surprising since net sediment accumulation is influenced by a number of variables, including sediment supply, hydrodynamics, grain size and bathymetry (Wright and Nittrouer, 1995). It may also be difficult to identify a direct relationship between our sediment core chronology and events in the watershed since we assumed linear accumulation rates between the time horizons we identified while delivery may have occurred episodically. We also investigated the influence of episodic events by examining relationships with time periods identified as El Niño or flood years but did not find any statistically significant relationships. Together, these data suggest that anthropogenic activities in the watershed likely exerted a larger influence on the delivery of sediment and carbon than climate over the time frame of this study.

Peaks in ∑DDE concentration in the SJR core at 20 cm, 30 cm and 80 cm (Fig. 3A) suggest remobilization of legacy sediments or soils since DDT was banned in 1973 (Connor et al., 2007). Similarly, there was a secondary peak in ∑DDE concentrations between 0 and 45 cm in the SAC core (Fig. 4B), consistent with remobilization of legacy sediments and soils. Erosion of legacy sediments and soils could reflect increased conversion of land to agriculture during the study period (Wright and Schoellhamer, 2004; Sickman et al., 2007).

Radiocarbon ages of TOC in the surface sediments collected from FT and SJR were consistent with the delivery of "pre-aged" carbon. These older ages are similar to those observed for TOC in the water column of the Sacramento River, which were found to be >2000 yrs BP (Sickman et al., 2007). Sediment organic carbon in aquatic environments is known to be a mixture of modern (recent biogenic) carbon and older "pre-aged" material (Eglinton et al., 1997; Blair et al., 2003, 2004; Wakeham et al., 2004; White et al., 2007). "Pre-aged" carbon could include biogenic organic carbon from aquatic and terrigenous sources that has resided in soils or sediments for a period of time before being remobilized and redeposited within the Delta, along with petrogenic (fossil) inputs from petroleum hydrocarbons or weathered shales derived from the watershed.

Interestingly, radiocarbon ages for bulk TOC at SJR were older at the surface (0–5 cm) than in the sub-surface (25–30 cm), i.e., OC in most recently accumulated sediments contains, on average, more "old" carbon than previously-deposited sub-surface sediments. This may indicate increased remobilization of older soils and sediments from the Delta watershed in recent years, similar to observations for TOC in the Sacramento River (Sickman et al., 2007) and in a sediment core collected from Lake Washington (Wakeham et al., 2004). An alternative explanation for the "older" radiocarbon ages observed in surface vs. sub-surface sediments collected from SJR could be lower ^{14}C levels for the post-bomb portion of the TOC. Plant tissues synthesized during the 1980s, for example, would have lower contributions of "modern carbon" (F_{modern} = 1.1–1.2) relative to plants synthesized during the 1960s (F_{modern} = 1.7–1.8).

4.2. Dam and reservoir construction

Population growth in the city of Sacramento and its suburbs increased from $\sim 755 \times 10^3$ in 1972 to 1895×10^3 in 2007 (http://recenter.tamu.edu/data/popm/pm6920.htm), with marked growth in the last two decades. Coincident with these population increases, land has been converted from wetlands and grasslands to agriculture, grazing land, and urban uses (Jassby and Cloern, 2000; Sickman et al., 2007). Increased use of the watershed for agriculture and livestock grazing has the potential to increase the amounts of sediment delivered to the Delta through soil tillage and livestock disturbance and subsequent erosion. In addition to changes in land use, population growth has also increased demands for freshwater both to support drinking water needs and agriculture. Diversions of freshwater by the State Water Projects (SWP) increased dramatically over the time period reflected by our cores. Water exports from the Delta were 3500 cubic feet per second (cfs) with 920 cfs from SWP during water years 1969 to 1971, while during water years 1972 to 1974 exports increased to 5270 cfs with 2090 cfs from SWP (http://www.iep.ca.gov/dayflow/index.html).

Reduced inflow of freshwater water could also reduce sediment delivery to the Delta system. Consistent with our observations, recent studies have shown that suspended sediment loads in the Sacramento River have declined since the 1950s (Wright and Schoellhamer, 2004; Ganju et al., 2008). Wright and Schoellhamer (2004) investigated potential mechanisms responsible for these declines in suspended sediment. While shorter-term, climate driven changes were apparent, such as those reflecting wet and dry years (e.g. droughts in 1976–1977 and 1987–1992, and wet El Niño years), their analysis did not reveal significant trends in either annual flow or the variability of the flow record over the period 1957–2001.

Wright and Schoellhamer (2004) considered the processes that influence sediment delivery to the Sacramento River and identified two that could contribute to declining sediment yield: trapping of sediments in reservoirs and riverbank alteration for minimizing erosion. While their analysis did not rule out the role of riverbank alteration, they provide compelling evidence that sediment accumulation in reservoirs in the Sacramento River watershed could more that account for the declining suspended sediment loads. Using suspended sediment records for the Sacramento River, Wright and Schoellhamer (2004) showed a decrease in annual average suspended sediment yields from 2–3 Mt in 1957 to 1–2 Mt in 2001. Assuming the decrease in annual sediment loads was approximately linear, they calculated a decrease in total sediment yield of $\sim$25 Mt over this time period. Sediment accumulation in three of the large reservoirs in the Sacramento River watershed (Oroville, Folsom and Englebright) is estimated at 25, 46, and 25 Mt, respectively, suggesting that sediment accumulation in these reservoirs could easily account for the observed declines in suspended sediment for the Sacramento River (Wright and Schoellhamer, 2004). Similarly, the time period where our sediment cores record large decreases in sediment and TOC accumulation (post-1972) coincides with the completion of several large reservoir projects on CA rivers that began in the 1940–1950s such as the Oroville, Folsom and Englebright Dams in the Sacramento River watershed, as well as the Friant Dam on the San Joaquin River.

Interestingly, the Wright and Schoellhamer (2004) study observed gradual trends of declining sediment discharge whereas our sediment cores appear to show a sudden drop in sediment accumulation. Wright and Schoellhamer (2004) attributed the gradual trend to erosion of large but declining volumes of mine tailings stored on the Bear River floodplain and projected that depletion of such deposits as the rivers adjust to dynamic equilibrium would result in a decrease in sediment yield with time. In contrast, our data indicate a sudden decrease in sediment accumulation since 1972. This difference might be attributed to the method we used for quantifying sediment and TOC accumulation (assigning sediment horizons to dates and assuming linear rates of sediment accumulation between these time periods). It is also important to note that the methods we use calculate *net* accumulation rates, which depend on both sediment delivery to, and retention within, the Delta. Our study sites may also be influenced by local processes (e.g., resuspension, hydrodynamics, sediment trapping) that accentuate the gradual trends in declining sediment yield observed for the Sacramento River.

A second interesting finding is that we observed similar trends in declining sediment and TOC accumulation not only in the core collected from the lower Sacramento River (SAC) but also in cores collected from the San Joaquin River (SJR and FT). This suggests that decreasing sediment delivery is not unique to the Sacramento River but may reflect a larger, system-wide disturbance to sediment supply, resulting from dam and reservoir construction on both rivers as well as other perturbations to the Delta watershed. This is further supported by a recent study in San Pablo Bay CA, a sub-system of northern San Francisco Bay, into which the Delta drains. Similar to our observations for the Delta, San Pablo Bay experienced a net loss of sediment between 1951 and 1983, which was attributed to reductions in sediment delivery from the Sacramento and San Joaquin Rivers due to damming of rivers, riverbank protection, and alterations in land use (Jaffe et al., 2007).

Similar to observations of reduced sediment loads in the Sacramento River, historical data for the lower Mississippi River indicate that suspended sediment loads have been declining since perhaps as far back as 1900 (Kesel, 2000). The decline has been attributed to dam construction on the Upper Mississippi, Missouri, and Arkansas tributaries, soil conservation practices instituted beginning in the 1930s, and elimination of overbank flooding and bank caving by artificial levee construction and channel shortening (1928–1942; (Kesel, 2000; Keown et al., 1986). Recent work has shown that the timing of decreasing mass accumulation rates at two Louisiana shelf stations is synchronous with the timing of decreasing river particulate loads established from historical river records.

Reductions in the suspended loads, from dam and reservoir construction, in many rivers around the world, have also resulted in increased light availability and consequently greater phytoplankton production/biomass (Thorp and Delong, 1994; Humborg et al., 1997, 2000; Ittekkot et al., 2000; Sullivan et al., 2001; Duan and Bianchi, 2006). Future studies should focus on investigating the role of dams and reservoirs in changing the delivery of carbon and sediment to the Delta ecosystem as well as other study systems.

5. Conclusions

Overall, results from this study document changes in the amount of sediment and carbon delivered to the Delta over the time period from the 1940s to present, with a marked reduction in sediment and carbon accumulation since the 1970s. Much of the carbon delivered to the Delta over this timeframe is "pre-aged" with average ages of 1000–1400 years BP and includes contaminants likely derived from legacy sediments and soils. Over the timeframe represented by our sediment cores, it appears that anthropogenic activities in the watershed exerted a larger influence on the delivery of sediment and carbon than climate. This is not surprising since this time period coincides with population growth in the Delta watershed, changes in land use, and the completion of several large reservoir projects on CA rivers that began in the 1940–1950s. Findings from this study should be considered in efforts to restore the Delta since the supply of sediment and organic carbon has important implications for marshes and levees as well as carbon and energy flow in downstream ecosystems.

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References

Alpine, A.E., Cloern, J.E., 1992. Trophic interactions and direct physical effects control phytoplankton biomass and production in an estuary. Limnology and Oceanography 37, 946–955.

Arthur, J.F., Ball, M.D., Baughman, S.Y., 1996. Summary of federal and state water project environmental impacts in the San Francisco Bay-Delta Estuary, California. In: Hollibaugh, J.T. (Ed.), San Francisco Bay: The Ecosystem. Pacific Division American Association for the Advancement of Science, San Francisco, CA, pp. 445–495.

Atwater, B.F., Conrad, S.G., Dowden, J.N., Hedel, C.W., MacDonald, R.L., Savage, W., 1979. History, landforms and vegetation of the estuary's tidal marshes. In: Conomos, T.J. (Ed.), San Francisco Bay: The Urbanized Estuary. Pacific Division American Association for the Advancement of Science, San Francisco, CA, pp. 347–385.

Blair, N.E., Leithold, E.L., Ford, S.T., Peeler, K.A., Holmes, J.C., Perkey, D.W., 2003. The persistence of memory: the fate of ancient sedimentary organic carbon in a modern sedimentary system. Geochimica et Cosmochimica Acta 67, 63–73.

Blair, N.E., Leithold, E.L., Aller, R.C., 2004. From bedrock to burial: the evolution of particulate organic carbon across coupled watershed-continental margin systems. Marine Chemistry 92, 141–156.

Canuel, E.A., 2001. Relations between river flow, primary production and fatty acid composition of particulate organic matter in San Francisco and Chesapeake Bays: a multivariate approach. Organic Geochemistry 32, 563–583.

Canuel, E.A., Cloern, J.E., 1996. Regional differences in the origins of organic matter in the San Francisco Bay ecosystem. Evidence from lipid biomarkers. In: Hollibaugh, J.T. (Ed.), San Francisco Bay: The Ecosystem. Pacific Division American Association for the Advancement of Science, San Francisco, CA, pp. 305–324.

Canuel, E.A., Martens, C.S., 1993. Seasonal variations in the sources and alteration of organic matter associated with recently-deposited sediments. Organic Geochemistry 20, 563–577.

Cohen, A.N., Carlton, J.T., 1998. Accelerating invasion rate in a highly invaded estuary. Science 279, 555–558.

Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Downing, J.A., Middelburg, J.J., Melack, J., 2007. Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. Ecosystems 10, 171–184.

Connor, M.S., Davis, J.A., Leatherbarrow, J., Greenfield, B.K., Gunther, A., Hardin, D., Mumley, T., Oram, J.J., Werme, C., 2007. The slow recovery of San Francisco Bay from the legacy of organochlorine pesticides. Environmental Research 105, 87–100.

Duan, S.W., Bianchi, T.S., 2006. Seasonal changes in the abundance and composition of plant pigments in particulate organic carbon in the lower Mississippi and Pearl Rivers (USA). Estuaries and Coasts 29, 427–442.

Eglinton, T.I., Benitez-Nelson, B.C., Pearson, A., McNichol, A.P., Bauer, J.E., Druffel, E.R.M., 1997. Variability in radiocarbon ages of individual organic compounds from marine sediments. Science 277, 796–799.

Ganju, N.K., Knowles, N., Schoellhamer, D.H., 2008. Temporal downscaling of decadal sediment load estimates to a daily interval for use in hindcast simulations. Journal of Hydrology 349, 512–523.

Geisz, H.N., Dickhut, R.M., Cochran, M.A., Fraser, W.R., Ducklow, H.W., 2008. Melting glaciers: a probable source of DDT to the Antarctic marine ecosystem. Environmental Science and Technology 42, 3958–3962.

Hartwell, S.I., 2004. Distribution of DDT in sediments off the central California coast. Marine Pollution Bulletin 49, 299–305.

Hedges, J.I., Stern, J.H., 1984. Carbon and nitrogen determinations of carbonate-containing solids. Limnology and Oceanography 29, 657–663.

Hites, R.A., 2004. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. Environmental Science and Technology 38, 945–956.

Humborg, C., Ittekkot, V., Cociasu, A., 1997. Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure. Nature 386, 385–388.

Humborg, C., Conley, D.J., Rahm, L., 2000. Silicon retention in river basins: far-reaching effects on biogeochemistry and aquatic food webs in coastal marine environments. Ambio 29, 45–50.

Ittekkot, V., Humborg, C., Schafer, P., 2000. Hydrological alterations and marine biogeochemistry: a silicate issue? Bioscience 50, 776–782.

Jaffe, B.E., Smith, R.E., Foxgrover, A.C., 2007. Anthropogenic influence on sedimentation and intertidal mudflat change in San Pablo Bay, California: 1856–1983. Estuarine, Coastal and Shelf Science 73, 175–187.

Jassby, A.D., Cloern, J.E., 2000. Organic matter sources and rehabilitation of the Sacramento-San Joaquin Delta (California, USA). Aquatic Conservation Marine and Freshwater Ecosystems 10, 323–352.

Jassby, A.D., Kimmerer, W.J., Monismith, S.G., Armor, C., Cloern, J.E., Powell, T.M., Schubel, J.R., Vendlinski, T.J., 1995. Isohaline position as a habitat indicator for estuarine populations. Ecological Applications 5, 272–289.

Keown, M.P., Dardeau, E.A., Causey, E.M., 1986. Historic trends in the sediment flow regime of the Mississippi River. Water Resources Research 22, 1555–1564.

Kesel, R.H., 2000. Human modification to the sediment regime of the lower Mississippi River flood plain. Geomorphology 56, 325–334.

Kimmerer, W.J., Orsi, J.J., 1996. Changes in the zooplankton of the San Francisco Bay Estuary since the introduction of the clam Potamocorbula amurensis. In: Hollibaugh, J.T. (Ed.), San Francisco Bay: The Ecosystem. Pacific Division American Association for the Advancement of Science, San Francisco, CA, pp. 403–424.

Lehman, P.W., 1992. Environmental factors associated with long-term changes in chlorophyll concentration in the Sacramento-San Joaquin Delta and Suisun Bay, California. Estuaries 15, 335–348.

Lehman, P., Smith, R.W., 1991. Environmental factors associated with phytoplankton succession for the Sacramento-San Joaquin Delta and Suisun Bay Estuary, California. Estuarine Coastal Shelf Science 32, 105–128.

Lu, X., Matsumoto, E., 2005. Recent sedimentation rates derived from Pb-210 and Cs-137 methods in Ise Bay, Japan. Estuarine, Coastal and Shelf Science 65, 83–93.

Meng, L., Moyle, P.B., 1995. Status of splittail in the Sacramento-San Joaquin Estuary. Transactions of the American Fisheries Society 124, 538–549.

Mischke, T., Brunetti, K., Acosta, V., Weaver, D., Brown, M., 1996. Agricultural sources of DDT residues in California's environment. Environmental Hazards Assessment Program, Sacramento CA.

Moyle, P.B., Herbold, B., Stevens, D.E., Miller, L.W., 1992. Life history and status of the Delta smelt in the Sacramento-San Joaquin Estuary, California. Transactions of the American Fisheries Society 121, 67–77.

Nichols, F.H., Cloern, J.E., Luoma, S.N., Peterson, D.H., 1986. The Modification of an Estuary. Science 231, 567–573.

Orsi, J.J., Mecum, W.L., 1996. Food limitation as the probable cause of a long-term decline in the abundance of Nemysis mercedis the opossum shrimp in the Sacramento-San Joaquin Estuary. In: Hollibaugh, J.T. (Ed.), San Francisco Bay: The Ecosystem. Pacific Division American Association for the Advancement of Science, San Francisco, CA, pp. 375–401.

Peters, D.P.C., Groffman, P.M., Nadelhoffer, K.J., Grimm, N.B., Collins, S.L., Michener, W.K., Huston, M.A., 2008. Living in an increasingly connected world: a framework for continental-scale environmental science. Frontiers in Ecology and the Environment 6, 229–237.

Ritchie, J.C., McHenrey, J.R., 1990. Application of radioactive fallout cesium-137 for measuring soil erosion and sediment accumulation rates and patterns: a review. Journal Environmental Quality 19, 215–233.

Sickman, J.O., Zanoli, M.J., Mann, H.L., 2007. Effects of urbanization on organic carbon loads in the Sacramento River, California. Water Resources Research 43, W11422.

Sommer, T., Armor, C., Baxter, R., Breuer, R., Brown, L., Chotkowski, M., Culberson, S., Feyrer, F., Gingras, M., Herbold, B., Kimmerer, W., Mueller-Solger, A., Nobriga, M., Souza, K., 2007. The collapse of pelagic fishes in the Upper San Francisco Estuary. Fisheries 32, 270–277.

Sullivan, B.E., Prahl, F.G., Small, L.F., 2001. Seasonality of phytoplankton production in the Columbia River: a natural or anthropogenic pattern? Geochemica Cosmochimica Acta 65, 1125–1139.

Thorp, J.H., Delong, M.D., 1994. The river production model: an heuristic view of carbon sources and organic processing in large river ecosystems. Oikos 70, 305–308.

van Geen, A., Luoma, S.N., 1999. The impact of human activities on sediments of San Francisco Bay, California: an overview. Marine Chemistry 64, 1–6.

Venkatesan, M.I., de Leon, R.P., van Geen, A., Luoma, S.N., 1999. Chlorinated hydrocarbon pesticides and polychlorinated biphenyls in sediment cores from San Francisco Bay. Marine Chemistry 64, 85–97.

Wakeham, S.G., Forrest, J., Masiello, C.A., Gelinas, Y., Alexander, C.R., Leavitt, P.R., 2004. Hydrocarbons in Lake Washington sediments. A 25-Year Retrospective in an Urban Lake. Environmental Science and Technology 38, 431–439.

Walling, D.E., 2006. Human impact on land-ocean sediment transfer by the world's rivers. Geomorphology 79, 192–216.

Waterson, E.J., Canuel, E.A., 2008. Sources of sedimentary organic matter in the Mississippi River and adjacent Gulf of Mexico as revealed by lipid biomarker and [delta] 13CTOC analyses. Organic Geochemistry 39, 422–439.

White, H.K., Reddy, C.M., Eglinton, T.I., 2007. Relationships between carbon isotopic composition and mode of binding of natural organic matter in selected marine sediments. Organic Geochemistry 38, 1824–1837.

Wright, L.D., Nittrouer, C.A., 1995. Dispersal of river sediments in coastal seas: six contrasting cases. Estuaries 18, 494–505.

Wright, S.A., Schoellhamer, D.H., 2004. Trends in the sediment yield of the Sacramento River, California, 1957–2001. San Francisco Estuary and Watershed Science 2, 1–14.