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2 **The nature of organic carbon in density-fractionated sediments in the**
3 **Sacramento-San Joaquin River Delta (California)**
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Technical corrections:

The technical corrections have been addressed as requested and are shown on the marked text below.

23 *Abstract*

24 Rivers are the primary means by which sediments and carbon are transported from the
25 terrestrial biosphere to the oceans but gaps remain in our understanding of carbon
26 associations from source to sink. Bed sediments from the Sacramento-San Joaquin River
27 Delta (CA) were fractionated according to density and analyzed for sediment mass
28 distribution, elemental (C and N) composition, mineral surface area, and stable carbon
29 and radiocarbon isotope compositions of organic carbon (OC) and fatty acids to evaluate
30 the nature of organic carbon in river sediments. OC was unevenly distributed among
31 density fractions. Mass and TOC were in general concentrated in mesodensity (1.6-2.0
32 and 2.0-2.5 g cm⁻³) fractions, comprising $84.0 \pm 1.3\%$ of total sediment mass and $80.8 \pm$
33 13.3% of total OC (TOC). Low density (<1.6 g cm⁻³) material, although rich in OC (34.0
34 $\pm 2.0\%$ OC) due to woody debris, constituted only $17.3 \pm 12.8\%$ of TOC. High density
35 (>2.5 g cm⁻³) organic-poor, mineral-rich material made-up $13.7 \pm 1.4\%$ of sediment mass
36 and $2.0 \pm 0.9\%$ of TOC. Stable carbon isotope compositions of sedimentary OC were
37 relatively uniform across bulk and density fractions ($\delta^{13}\text{C} -27.4 \pm 0.5 \text{‰}$). Radiocarbon
38 content varied from $\Delta^{14}\text{C}$ values of -382 (radiocarbon age 3800 yr BP) to $+94 \text{‰}$
39 (modern) indicating a mix of young and old OC. Fatty acids were used to further
40 constrain the origins of sedimentary OC. Short-chain $n\text{-C}_{14} - n\text{-C}_{18}$ fatty acids of algal
41 origin were depleted in ^{13}C ($\delta^{13}\text{C} -37.5 \text{‰}$ to -35.2‰) but were enriched in ^{14}C ($\Delta^{14}\text{C}$
42 >0) compared to long-chain $n\text{-C}_{24} - n\text{-C}_{28}$ acids of vascular plant origins with higher $\delta^{13}\text{C}$
43 (-33.0‰ to -31.0‰) but variable $\Delta^{14}\text{C}$ values (-180‰ and 61‰). These data
44 demonstrate the potentially complex source and age distributions found within river
45 sediments and provide insights about sediment and organic matter supply to the Delta.

1 Introduction

Rivers are the major conduits of sediment and organic carbon (OC) carried from upland erosional areas to lowland floodplains and estuaries and the coastal ocean (Milliman and Farnsworth 2011). During transport, sediment grains are eroded, remobilized, winnowed, and redeposited, resulting in the sorting or mixing of material from different sources and with different reactivities and ages (Prah, 1985; Hedges and Keil, 1995; Bianchi et al., 2007). Hydrodynamic sorting by particle size, shape and density influences transport of particles and associated materials in rivers, estuaries and continental margins. Density, grain size, mineralogy, and organic carbon characteristics of riverine sediment grains will determine whether they are eroded and transported as suspended or bed load or deposited, and how particles cycle between phases (Jepson et al., 1997; Hassanzadeh, 2012).

Interactions between minerals and OC influence the fate and distribution of organic materials in soils and aquatic sediments (Hedges and Keil, 1995; Hedges and Oades, 1997; Baldock and Skjemstad, 2000; Trumbore, 2006; Rühlmann and Berhe, 2014; Keil and Mayer, 2014). Evidence on organic matter-mineral associations from soils and marine sediments shows relationships between OC concentrations and compositions, mineral surface area, physical distributions of OC on minerals, and OC preservation (Keil et al., 1994a, b; Mayer, 1994a; Ransom et al., 1998; Mayer et al., 2004; Trumbore, 2006; Keil and Mayer, 2014). Particle size and density are also important characteristics when considering OM composition, reactivity and the fate of soil and sediment OC. In aquatic environments, OC associated with mineral grains strongly affects flocculation of suspended aquatic particles and the cohesion of bottom

70 sediments. OC that is intimately associated with the clay fraction is most extensively
71 altered diagenetically, whereas larger size or higher density mineral fractions are less
72 altered (e.g., Keil et al., 1994a; Bergamaschi et al., 1997; Wakeham et al., 2009). Trends
73 across size and density classes and between different depositional environments show
74 that a small fraction of the OC is present as distinct organic debris, but associations of
75 OC with mineral surfaces are consistent with selective partitioning of OC to mineral
76 surfaces (Keil et al., 1998; Keil and Mayer, 2014).

77 Chemical analysis of size-sorted sediments has been extensively used to show that
78 compositional differences between grain sizes are related to source, diagenesis and
79 mineralogy (e.g., Keil et al., 1998; Bergamaschi et al., 1997; Dickens et al., 2006).
80 Density fractionation, although much less widely utilized, takes advantage of density
81 differences between organic matter ($\sim 1 \text{ g cm}^{-3}$) and mineral grains ($\geq 2.5 \text{ g cm}^{-3}$) (Mayer
82 et al., 2004; Rühlmann et al., 2006) and by isolating organic-mineral aggregates having
83 different organic matter loadings offers a different view of relationships between OC and
84 particle grains. Densities of soils and sediments depend on the compositions and
85 proportions of both organic and mineral components. Mineral-rich/organic-poor soils
86 and sediments typically have densities the range of $\sim 2.4\text{-}2.9 \text{ g cm}^{-3}$; mineral-
87 poor/organic-rich soils and sediments have densities between ~ 1.0 and 1.5 g cm^{-3}
88 (Adams, 1973; Rühlmann et al., 2006).

89 Density fractionation has been widely used on soils to elucidate mechanisms of
90 how organic matter is physically and chemically associated with minerals and to estimate
91 stability, residence and turnover times of organic matter in soils (e.g., Golchin et al.,
92 1994; Hedges and Oades, 1997; Baldock and Skjemstad, 2000; Baisden et al., 2002a;

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94 Sollins et al., 2006; Rühlmann et al., 2006; Crow et al., 2007; Castanha et al., 2008;
95 Trumbore, 2009; Cerli et al., 2012; Kaiser and Berhe, 2014). The chemistry, stable and
96 radiocarbon isotopic compositions, and turnover times for isolated fractions is
97 particularly dependent on methodology. Protocols for dispersing soil aggregates as a
98 function of density for purposes of characterizing organic matter/mineral interactions and
99 ecological function differ considerably, from shaking to ultrasonication at varying energy
100 levels and with or without acid/base hydrolysis of the high density fraction(s). Overall,
101 soils tend to be compositionally (physically, chemically, and biologically) more complex
102 than sediments (Keil and Mayer, 2014).

103 Density fractionation has been applied less often to aquatic sediments. In the few
104 continental margin sediments that have been studied by density fractionation, most of the
105 mass and most of the OC is found in a so-called “mesodensity” fraction, roughly defined
106 operationally as between 1.6 and 2.5 g cm⁻³ (Bock and Mayer, 2000; Arnarson et al.,
107 2001, 2007; Dickens et al., 2006; Wakeham et al., 2009) that is rich in organic-mineral
108 aggregates. Lower density material is largely mineral-free organic detritus, whereas
109 higher density material is mostly organic-poor mineral grains. Chemical compositions
110 further distinguish these fractions (reviewed by Keil and Mayer, 2014). Amino acids that
111 are typically enriched in fine-grained and meso-density fractions point to preferential
112 association of nitrogenous material with clays and extensive alteration of organic matter.
113 Enrichment of carbohydrates in fine-grained fractions suggests that they help to hold
114 aggregates together. Lignin is typically associated with larger grains or low-density
115 material consistent with higher-plant origins.

River sediments, which are largely sourced from soils, are poorly represented among aquatic environments that have been investigated. Here we used density fractionation in a pilot study to examine relationships between organic matter and mineral grains in several river sediments. In particular, we wished to better understand whether and to what extent redistributions of OC, potentially via hydrodynamic sorting, occur between rivers and the ocean, at the river-ocean interface. We determined mass, elemental (C and N), and surface area distributions among density sorted fractions from five bed sediments within the Sacramento-San Joaquin River delta (hereafter termed the Delta). Stable carbon and radiocarbon isotopic compositions of bulk sediments, density fractions and isolated fatty acids were used to characterize the provenance and age of the OC in these sediments.

2 Methods

2.1 Study area and samples

The Sacramento-San Joaquin Delta is part of San Francisco Bay system. The Delta is a complex network of natural and man-made channels and islands, making it one of the 60 largest river deltas in the world, at $1.7 \times 10^5 \text{ km}^2$ and accounting for ~40% of California's land area (Herbold and Moyle, 1989; Jassby and Cloern, 2000; Schoellhamer et al., 2012). As such, it is one of the most highly modified and managed systems in the world (Jassby and Cloern, 2000) and is unique ecologically in North America (Herbold and Moyle, 1989). Precipitation (rainfall and snowmelt) in the Sierra Nevada Mountains contributes most of the freshwater delivered to the Delta, with the Coast Range dividing the water flow between the Sacramento River draining into the northern half of the

139 Central Valley and the San Joaquin River draining into the southern half. The
140 Sacramento and San Joaquin Rivers join in the Delta and flow into northern San
141 Francisco Bay. The Sacramento River contributes 80% of the freshwater delivered to
142 San Francisco Bay and the San Joaquin River adds an additional 15% (Conomos et al.,
143 1985). The Sacramento River presently delivers approximately seven times the sediment
144 load of the San Joaquin River, mostly as suspended sediment, but sediment loads are
145 highly episodic and significant transport of bed load occurs during floods. Sedimentation
146 in reservoirs behind the many dams has reduced overall sediment transport since the
147 1950's (Wright and Schoellhamer, 2004, 2005). The narrow mouth of the Delta enhances
148 deposition of sediments within the Delta, along the Sacramento River and in Suisun Bay,
149 rather than in the open waters of upper San Francisco Bay

150 In this study we investigate relationships between OC and density fractions in
151 river bed sediments at five sites in the Sacramento-San Joaquin Delta (Fig. 1) system
152 during a low freshwater discharge period in Summer 2005. Average freshwater
153 discharge on the Sacramento River at Freeport ranged from 546.5 to 600.3 m³s⁻¹ during
154 the sampling period and discharge on the San Joaquin River at Vernalis was 155.7 to
155 171.3 m³s⁻¹ (US Geological Survey). The sites were chosen to represent different sub-
156 habitats within the Delta (e.g., upper and lower Sacramento River (Elk Slough and
157 Horseshoe Bend, respectively), San Joaquin River (Potato Slough and Venice Cut) and
158 Suisun Marsh (Nurse Slough). Surface sediments (0-5 cm) were obtained by grab
159 sampling. Elk Slough, Venice Cut and Horseshoe Bend have contemporary
160 sedimentation rates of 1.1, 3.5 and 3.5 cm y⁻¹, respectively (Canuel et al., 2009). Nurse
161 Slough is a tidal slough in Suisun Marsh. Suisun Marsh consists of 240 km² of tidal and

managed brackish water wetlands and 120 km² of bays and sloughs and is the largest contiguous estuarine marsh remaining on the west coast of the U.S., constituting more than 10% of California's remaining natural wetlands.

2.2 Density fractionation

Sodium metatungstate solutions (Arnarson and Keil, 2001; Wakeham et al., 2009) with densities of 1.6, 2.0, and 2.5 g cm⁻³ were used sequentially to yield four density fractions: <1.6 g cm⁻³, 1.6 to 2.0 g cm⁻³, 2.0 to 2.5 g cm⁻³ and >2.5 g cm⁻³. These fractions have been used previously (Bock and Mayer, 2000; Arnarson and Keil, 2001, 2007) for studies of sediments. The fraction with density <1.6 g cm⁻³ is primarily organic-rich biogenic material, the >2.5 g cm⁻³ fraction is unaggregated mineral grains, and the middle density fractions are aggregates of organic matter and mineral grains. Roughly 20 g of wet sediment were dispersed in the 1.6 g cm⁻³ solution in 85 mL centrifuge tubes by gentle shaking on a shaker table for 30 min. Gentle shaking rather than sonication was used to minimize disaggregation of aggregates (note differences with investigations of soils as described below). Following shaking, solutions were centrifuged for 20 min at 20,000 relative centrifugal force. Particles at the surface of the solution were carefully removed by pipet, deposited on a 0.5 µm PTFE membrane filter and washed with distilled water. This process was repeated until no additional low density (<1.6 g cm⁻³) particles could be recovered (approximately 10 repetitions). The next solution, 2.0 g cm⁻³, was then added and the process repeated. Following each step, the collected particles were rinsed from the PTFE filter into 85 mL centrifuge tubes and washed repeatedly with distilled water to

remove any remaining sodium metatungstate. Fractionated sediments were freeze-dried for further analyses.

Most protocols employed to fractionate soils involve some degree of dispersion, usually ultrasonication, and generally yields a floating (light) fraction the contains mainly plant debris, an intermediate fraction of fine organic particles that has been released by disruption (e.g., ultrasonication with or without hydrolysis) of aggregates, and a heavy residual fraction of OC strongly bound to minerals (e.g. Golchin et al., 1994; Cerli et al., 2012; Kaiser and Berhe, 2014). The fractionation scheme we and others have used for sediments is less energetic or disruptive (at least in the latter stages) than commonly used for soils and these methodological contrasts need to be considered when comparing results.

Metatungstate solutions can solubilize organic matter from the soil/sediment grains (Shang and Tiessen, 2001; Crow et al., 2007; Castanha et al., 2008). OC solubilization apparently increases with the density of the metatungstate solution used and may range between 10 and 28% of bulk OC regardless of whether the treatment involved shaking with gravimetric settling or sonication and centrifugation. A slight yellowing of the solutions used here attests to dissolution of OC to some extent, but we did not specifically conduct mass balance measurements to quantify the extent of OC solubilization.

2.3 Elemental analysis

Organic carbon (% OC) and total nitrogen (% TN) were measured using a Fisons CHN analyzer (Model EA 1108) (Waterson and Canuel, 2008). Freeze-dried sediments were

207 ground and acidified in pre-combusted silver capsules with 10% high purity HCl to
208 remove inorganic carbon.

209

210 **2.4 Specific surface area analysis**

211 Specific surface area (SA) of the mineral component of each sediment fraction was
212 measured by nitrogen adsorption using a five-point (Brunauer-Emmett-Teller (BET))
213 method in a Micromeritics Gemini V surface area analyzer (Waterson and Canuel, 2008).
214 Freeze-dried but unground sediments were heated at 350 °C for 12 h to remove organic
215 matter and then degassed for >2 h on a Micromeritics Flow Prep 060 degas station at
216 250 °C to remove water. SA ($\text{m}^2 \text{g}^{-1}$) and carbon:surface area ratios (OC:SA; mg OC m^{-2}) were obtained.

218

219 **2.5 Carbon isotope analysis**

220 Stable carbon ($\delta^{13}\text{C}$) and radiocarbon ($\Delta^{14}\text{C}$) analyses were conducted at the National
221 Ocean Sciences Accelerator Mass Spectrometer (NOSAMS) facility at Woods Hole
222 Oceanographic Institution. Ground and acidified sediment samples were combusted to
223 CO_2 at 850°C for 5 hours in Vycor tubes. A split of the purified and quantified CO_2 was
224 analyzed for $\delta^{13}\text{C}$ on a VG Micromass Optima isotope ratio mass spectrometer. The
225 remaining CO_2 was reduced to filamentous carbon (graphite) over either Fe or Co powder
226 and then analyzed for radiocarbon using standard NOSAMS procedures (McNichol et al.,
227 1994; von Reden et al., 1998).

228 Fatty acids (FA) were isolated from three of the bulk sediments and analyzed for
229 ^{13}C and ^{14}C isotope values. Lipid extracts obtained by accelerated solvent extraction

(ASE) using dichloromethane:methanol (9:1) were saponified, and the recovered FA were methylated with $\text{BF}_3\text{-MeOH}$. Two fatty acid methyl ester (FAME) composites were obtained by preparative capillary gas chromatography (Eglinton et al., 1997; Wakeham et al., 2006): short-chain FAME ($n\text{-C}_{14}$ – $n\text{-C}_{18}$) and long-chain FAME ($n\text{-C}_{24}$ – $n\text{-C}_{28}$). Compositions, purity and amounts of FAME isolates were checked by gas chromatography and analyzed subsequently for ^{13}C and ^{14}C . Corrections for the addition of carbon from the methyl group during methylation were made by mass balance.

3 Results

3.1 Density Fractionation

Particles in the 2.0 to 2.5 g cm^{-3} density range dominated four of the studied sediments (Potato Slough, Elk Slough, Venice Cut, and Nurse Slough), constituting ~75-80% of total dry mass (Fig. 2a), with a mean of $73.1 \pm 6.6\%$. Considering all five sediments, the 2.0 to 2.5 g cm^{-3} material accounted for between 26.5 and 80.1% of dry mass or a mean of $63.8 \pm 21.5\%$ (Fig. 3a). The Horseshoe Bend sediment contained the greatest proportion (~66%) of mass in the high density fraction, $>2.5 \text{ g cm}^{-3}$, whereas only ~30% of total mass was in the 2.0 to 2.5 g cm^{-3} fraction. The lowest density fraction of these sediments, $<1.6 \text{ g cm}^{-3}$ material, made-up the smallest proportion of total mass, never more than a few percent ($1.6 \pm 1.9\%$). The 1.6 to 2.0 g cm^{-3} fractions varied between 4 and 17% of mass ($11.6 \pm 6.1\%$), and the heaviest material ($>2.5 \text{ g cm}^{-3}$) was generally less than ~15% ($13.7 \pm 1.4\%$).

3.2 Elemental Compositions

253 Organic carbon (% OC) of all five bulk, unfractionated sediments ranged from 0.7% at
254 Horseshoe Bend to 2.9% at Venice Cut (Fig. 2b); mean $2.0 \pm 0.86\%$ (Fig. 3b). Total
255 nitrogen (% TN) ranged from 0.07 to 0.20% in bulk sediments (mean $0.15 \pm 0.05\%$). %
256 OC and % TN were well correlated with one another ($r^2=0.93$). Atomic C:N(a) ratios
257 ranged between 16.9 in Venice Cut to 11.9 in Elk Slough (Fig. 2c; mean $14.6 \pm 2.1\%$,
258 Fig. 3c). Low density fractions had the highest OC and TN concentrations; highest
259 density fractions had the lowest % OC and % TN. Low density $<1.6 \text{ g cm}^{-3}$ material
260 contained between 32 and 37 % OC ($34.0 \pm 2.1\%$) and from 1.5 to 2.7% TN ($1.9 \pm 0.6\%$;
261 data not shown). The 1.6 to 2.0 g cm^{-3} material contained 9-15 % OC ($12.4 \pm 2.2\%$) and
262 0.7-1.1 % TN ($0.8 \pm 0.2\%$); the 2.0 to 2.5 g cm^{-3} and $>2.5 \text{ g cm}^{-3}$ fractions both contained
263 $<1\%$ OC ($0.8 \pm 2.2\%$ and $0.2 \pm 0.1\%$, respectively) and $<0.1\%$ TN ($0.2 \pm 0.04\%$ and 0.09
264 $\pm 0.06\%$, respectively). C:N(a) ratios thus generally decreased with increasing particle
265 density (Fig. 2c, 3c): 24 for $<1.6 \text{ g cm}^{-3}$, 17 for 2.0 to 2.5 g cm^{-3} , 6.7 for 2.0 to 2.5 g to
266 3.1 for $>2.5 \text{ g cm}^{-3}$ fractions. Low C:N(a) ratios for the $>2.5 \text{ g cm}^{-3}$ fractions may be
267 artifacts arising from sorption of excess inorganic nitrogen onto these particles or blanks
268 associated with measuring low levels of nitrogen in these organic matter-poor samples.
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270 3.3 Specific Surface Area (SA) and OC:SA ratios

271 Specific surface areas (SA) of mineral grains in bulk Delta sediments ranged from ~ 14
272 $\text{m}^2 \text{ g}^{-1}$ (Horseshoe Bend) to $\sim 34 \text{ m}^2 \text{ g}^{-1}$ (Potato Slough) (Fig. 4a). SA was measured on
273 three density fractions for each sediment, but not on the $<1.6 \text{ g cm}^{-3}$ fractions because
274 they contained incompletely charred plant fragments which could confound
275 interpretations. SA decreased with increasing particle density. The 1.6 to 2.0 g cm^{-3}

279 material had the highest SA of the measured fractions and SA ranged from $\sim 65 \text{ m}^2 \text{ g}^{-1}$ at
280 Horseshoe Bend to $\sim 30 \text{ m}^2 \text{ g}^{-1}$ in Elk Slough. Thus in four out of five cases SA of 1.6 to
281 2.0 g cm^{-3} fractions was $\geq 50 \text{ m}^2 \text{ g}^{-1}$. SA's in the 2.0 to 2.5 g cm^{-3} fractions were ~ 25 - 30
282 $\text{m}^2 \text{ g}^{-1}$, and in the 2.5 g cm^{-3} fractions were ~ 5 - $10 \text{ m}^2 \text{ g}^{-1}$.

283 Measuring SA allows calculation of an organic carbon:surface area ratio (OC:SA)
284 widely used to express the loading of sedimentary OC onto mineral grains. OC:SA ratios
285 of bulk sediments ranged from 0.68 - $0.84 \text{ mg OC m}^{-2}$ (mean $0.72 \pm 0.13 \text{ mg OC m}^{-2}$; Fig.
286 4b). The 1.6 - 2.0 g cm^{-3} fractions consistently had the highest OC:SA ratios (1.6 - 5.1 mg
287 OC m^{-2} , Fig. 4b; mean $2.8 \pm 1.4 \text{ mg OC m}^{-2}$). OC:SA ratios decreased with density so
288 that for the $>2.5 \text{ g cm}^{-3}$ fractions OC:SA ranged from 0.21 - $0.32 \text{ mg OC m}^{-2}$ (0.26 ± 0.04
289 mg OC m^{-2}).

290

291 **3.4 Stable Carbon and Radiocarbon Isotopes**

292 Stable carbon isotope ($\delta^{13}\text{C}$) values for bulk OC were relatively uniform and ranged
293 between -27.5 and -26.5 ‰ ($-27.0 \pm 0.5 \text{ ‰}$; Table 1; Fig. 5a). $\delta^{13}\text{C}$ values for OC in the
294 density fractions of the three fractionated sediments (Elk Slough, Venice Cut, and Nurse
295 Slough) were somewhat more variable, but $\delta^{13}\text{C}$ values among density fractions were
296 always within $\pm \sim 1.5 \text{ ‰}$ (Fig. 5a, Table 1). $\delta^{13}\text{C}$ values for density fractions from Elk
297 Slough were lower than those from Venice Cut and Nurse Slough. Low density material
298 tended to have lower $\delta^{13}\text{C}$ values (~ 1 to 1.5 ‰ lower) than higher density fractions.

299 Radiocarbon compositions were quite variable, reflecting a wide range of carbon
300 ages (Fig. 5b; Table 1). $\Delta^{14}\text{C}$ is defined by Stuiver and Pollach (1977) and Stuiver (1980)
301 where $\Delta^{14}\text{C}$ values ≥ 0 are completely modern OC and reported as “modern”; $\Delta^{14}\text{C}$ values

302 < 0 indicate the presence varying proportions of old carbon. “Modern” is conventionally
 303 defined as 95% of the ^{14}C activity of an oxalic acid standard for AD 1950 (Karlen et al.,
 304 1964). The fraction of carbon in a sample that is modern, f_m , ranges from f_m values > 1 (if
 305 ^{14}C from atmospheric nuclear bomb testing is present) to 0 (containing no measurable
 306 ^{14}C). Ages are calculated using 5568 years as the half-life of radiocarbon. Bulk OC from
 307 Elk Slough was modern in age ($\Delta^{14}\text{C} +3.4\text{‰}$). Mesodensity (1.6 to 2.0 g cm $^{-3}$ and 2.0 to
 308 2.5 g cm $^{-3}$) fractions from Elk Slough were enriched in ^{14}C ($\Delta^{14}\text{C} +94\text{‰}$ and +89 ‰,
 309 respectively) relative to bulk sediment OC, whereas the >2.5 g cm $^{-3}$ material was depleted
 310 in ^{14}C (–25 ‰) relative to both OC and mesodensity material. In contrast, bulk OC from
 311 Venice Cut and Nurse Slough was depleted in ^{14}C ($\Delta^{14}\text{C} -151$ and –161 ‰, respectively),
 312 as were the density fractions. In both Venice Cut and Nurse Slough, >2.5 g cm $^{-3}$ fractions
 313 were highly depleted in ^{14}C ($\Delta^{14}\text{C} -339\text{‰}$ and –382 ‰ for Venice Cut and Nurse
 314 Slough, respectively), whereas the remaining density fractions and bulk sediment were
 315 remarkably uniform (average $\Delta^{14}\text{C}$ of $-156 \pm 39\text{‰}$).

316 Fatty acids (FA) were isolated from bulk (unfractionated) sediments and analyzed
 317 for stable carbon and radiocarbon content to help constrain the provenance and age of OC
 318 in the sediments. As constituents of many energy storage and structural membrane lipids
 319 in organisms, FA feature structural differences between compounds biosynthesized by
 320 algae, bacteria and higher plants that make them biomarkers for elucidating the origins
 321 and diagenetic fate of organic matter in sediments (Volkman, 2006; Wakeham et al.,
 322 1997). FA distributions in the Delta river sediments were bimodal: short-chain $n\text{-C}_{14} - n\text{-}$
 323 C_{18} compounds peaking at $n\text{-C}_{16}$ and long-chain $n\text{-C}_{24} - n\text{-C}_{28}$ FA peaking at C_{24} . Short-
 324 chain FA had lower $\delta^{13}\text{C}$ values (–37.5 ‰ to –35.2 ‰; Fig. 5c) compared to long-chain

325 FA (−33.0 ‰ to −31.0 ‰). FA were significantly depleted in ^{13}C relative to total OC
326 reflecting contributions from other organic compounds to OC such as amino acids and
327 carbohydrates that are enriched in ^{13}C compared to lipids. Short-chain FA in all three
328 fractionated sediments were modern ($\Delta^{14}\text{C} > 0$; Fig. 5d). While the radiocarbon age for
329 long-chain FA in Elk Slough was also modern (61 ‰), $\Delta^{14}\text{C}$ values in Venice Cut and
330 Nurse Slough were lower indicating that FA at these locations were older in age (−180 ‰
331 and −80 ‰, respectively).

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333 4 Discussion

334 4.1 Particle morphology

335 Previous studies have shown scanning electron microscopy (SEM) to be valuable
336 for examining particle morphology of density-fractionated sediments (photomicrographs
337 of density fractions are shown in Bock and Mayer, 2000; Arnarson and Keil, 2001, 2007;
338 Wakeham et al., 2009). We do not have SEM images of the density fractions in this
339 study but observations from the previous studies are relevant here. Low density $< 1.6 \text{ g}$
340 cm^{-3} fractions typically contain readily identifiable filaments and particles resembling
341 terrestrial wood fragments or aggregates containing plant debris. Aggregates of up to a
342 millimeter in size are common, as well as smaller-sized particles. The abundance of plant
343 material in low density material is borne out by the high OC concentrations and, when
344 measured, high lignin concentrations (Sampere et al., 2008; Wakeham et al., 2009;
345 Schreiner et al., 2013). Mesodensity (1.6 to 2.0 and 2.0 to 2.5 g cm^{-3}) fractions contain
346 aggregates that survived the density fractionation process, but the size and abundance of
347 aggregates decreases as density increases. The highest density ($> 2.5 \text{ g cm}^{-3}$) fractions are

primarily unaggregated mineral grains, often only a few micrometers in size. Arnarson and Keil (2001) also examined the mineral content of density fractions of a sediment from the oxygen minimum zone off the west coast of Mexico by X-ray photoelectron spectroscopy. Low density and OC-rich material was dominated by clay minerals whereas the high density OC-poor fraction was dominated by quartz and feldspars. It is impossible to rule out some alteration of particle morphology during the fractionation treatment, but Arnarson and Keil (2001) suggest that the degree of sample handling used here does not significantly disrupt the “organic glue” that holds aggregates together. Indeed, Bock and Mayer (2000) had previously proposed that removal of this organic binder, such as by the combustion step used in SA analysis, is required for organic-mineral particles to disaggregate.

4.2 Organic carbon among density fractions

In previous studies, bed sediments of the Lower Sacramento River were found to have a mean OC content of 0.55% (range 0.14%-2.1%) and in the lower San Joaquin River a mean OC of 0.68% (0.26-1.38%) (Reed, 2002; Nilsen and Delaney, 2005). The bulk sediments in our study had somewhat higher TOC contents (mean $2.0 \pm 0.9\%$, range 0.7-2.9%). TOC of the density fractions were lower than bulk sediments for high density fractions ($0.8 \pm 0.2\%$ OC for $2.0\text{-}2.5 \text{ g cm}^{-3}$ and $0.2 \pm 0.07\%$ OC for $>2.5 \text{ g cm}^{-3}$ fractions, respectively) and higher for low density fractions ($34.0 \pm 2.1\%$ OC for $<1.6 \text{ g cm}^{-3}$ and $12.4 \pm 2.1\%$ OC for $1.6\text{-}2.0 \text{ g cm}^{-3}$ fractions). The 1.6 to 2.0 g cm^{-3} fractions therefore made-up the greatest proportions of TOC (44-65%; mean $53.7 \pm 8.8\%$ of TOC; Figs. 2d and 3d), reflecting the high proportion this density fraction contributed to total

sediment mass despite low OC concentrations. The 2.0 to 2.5 cm⁻³ fractions contained 13-37% of TOC (mean 27.1 ± 10.3% of TOC). Collectively, mesodensity material (1.6 to 2.0 g cm⁻³ plus 2.0 to 2.5 g cm⁻³ fractions) constituted the highest proportions of TOC, 63-96% (mean 80.8 ± 13.3% of TOC).

This dominance of mesodensity material, in terms of both mass and OC content, is common among river (lower Mississippi River) and coastal sediments (Mississippi Margin, Washington Margin, Mexico Margin) that have been investigated by density fractionation (Bock and Mayer, 2000; Arnarson et al., 2001; Dickens et al., 2006; Wakeham et al., 2009). The Sacramento-San Joaquin Delta sediments therefore were generally consistent with previous studies in coastal regions. The Horseshoe Bend sediment was somewhat different from the other four sediments studied here in that OC-poor high density >2.5 g cm⁻³ material (65 % of mass but only 4 % of TOC) was most abundant, with only 30 % of mass and 37% of TOC in the mesodensity fractions. This sediment is similar to sediments off the Eel River on the California Margin and in the Colville River Delta in the Alaskan Beaufort Sea where erosive hydrodynamic winnowing leaves behind greater proportions of denser, sandy material (Wakeham et al., 2009; Schreiner et al., 2013). Horseshoe Bend flows along the eastern and southern edges of Decker Island, and is the original Sacramento River channel. Higher density sediments with low OC content at Horseshoe Bend are consistent with hydrodynamic winnowing by Sacramento River flow and/or tidal currents from San Francisco Bay.

4.3 Physical character of sediment particles

Sediment transport through the Delta, and deposition in the upper San Francisco Bay estuary, has varied considerably over the past century. The high sediment loads from hydraulic mining during the later 1800s and early 1900s (up to a 9-fold increase over the pre-mining period) have dropped significantly due to water management projects such as dams, levees and bypass channels (Schoellhamer et al., 2012) and adjustment to a regime of decreasing sediment supply during the 20th century (Schoellhamer et al., 2013). Bed sediments in channels of the lower Sacramento River are 8-50 % (mean 19%) fines (<63 µm) and in the San Joaquin River are 15-79% (mean 48%) fines (Schoellhamer et al., 2012), and as noted above TOC contents are 0.14-2.1%. Larger floods and increased winnowing of fine grains from the bed sediments in the Sacramento River are the probable cause for differences between the two rivers. During large floods, the sand content of bed sediments often approaches 100% in the Sacramento River, whereas during intervals between floods, sediments become finer.

4.4 Specific surface area OC loadings on sediment grains

Sediment grain size, particle shape, density, mineralogy and organic carbon content determine how particles behave in rivers and on coastal margins (Bridge and Bennett, 1992; Dade and Friend, 1998; Hassanzadeh, 2012) and their nutritional value to organisms (Mayer et al., 1993). Specific mineral surface area (SA) of sediment particles is often thought of as an approximate (inverse) proxy for grain size (Horowitz and Elrick, 1987; Keil et al., 1994a; Bergamaschi et al., 1997). In general, as grain size decreases, SA and % OC increase. But this relationship is probably simplistic since surface roughness of mineral particles may cause SA to be considerably higher than predicted by

grain size alone (Weiler and Mills, 1965; Mayer, 1994a,b), and SA measured after combustion that may destroy larger organic particles or organic-mineral aggregates likely under-represents the true size of the original aggregates. Inorganic coatings, notably Fe and Mn oxides, also help to cement fine-grained particles into water-stable aggregates of larger size (Horowitz and Elrick, 1987), decreasing effective SA. In the present study, SA was measured on all five bulk sediments and three density fractions of each sediment to evaluate the degree of OC loading (OC:SA) onto different density fractions, analogous to the more common measurements of SA and OC:SA of sediment particles of different grain sizes. SA decreased with increasing particle density (Fig. 4a), suggesting that higher density fractions were characterized by larger particle grain sizes (the $<1.6 \text{ g cm}^{-3}$ fractions being exceptions). Higher SA for the intermediate density fractions (e.g., 1-6 to 2.0 g cm^{-3}) are similar to previous observations (Arnarson and Keil, 2001, 2007; Wakeham et al., 2009) and might result from rough three-dimensional structures of aggregated clay grains (Hodson et al., 1998). In contrast, quartz and feldspar grains that dominate the high-density fractions have low SA.

Organo-mineral associations affect OC reactivity and OC sorbed onto mineral grains is protected from degradation (Mayer, 1999; Hedges and Keil, 1995; Keil and Mayer, 2014). Lower OC:SA ratios in deltaic ($\sim 0.3 \text{ mg OC m}^{-2}$) and deep sea sediments ($\sim 0.15 \text{ mg OC m}^{-2}$) indicate desorption or losses of OC from mineral grains due to microbial decomposition whereas higher OC:SA ratios ($\geq 2 \text{ mg OC m}^{-2}$) occur typically in anoxic, marsh, and estuarine sediments where OC is preserved because supply exceeds decomposition (Keil et al., 1997). Among the river sediments discussed here, OC:SA ratios of bulk sediments were relatively invariant, between 0.54 and $0.84 \text{ mg OC m}^{-2}$,

similar to OC loadings in the Amazon and Mississippi Rivers but lower than adjacent marsh and estuary sediments and higher than adjacent continental shelf sediments (Keil et al., 1997; Gordon and Goñi, 2004; Waterson and Canuel, 2008). Among density fractions in this study, OC:SA ratios were higher for 1.6 to 2.0 g cm⁻³ fractions than for bulk sediments (2.75 ± 1.4 vs. 0.72 ± 0.13 mg OC m⁻², respectively) indicating more OC was associated with mineral material. In contrast, OC:SA were lower for the 2.0 to 2.5 and >2.5 g cm⁻³ fractions (0.31 ± 0.06 vs. 0.26 ± 0.04 mg OC m⁻², respectively) than bulk sediment, where less OC was associated with mineral phases.

4.5 Provenance of OC in the Sacramento-San Joaquin Delta

Sources of OC to river sediments in the Delta are diverse (Canuel, 2001). Autochthonous sources include phytoplankton (80% of annual TOC input), higher aquatic plants (18% of TOC) and benthic macroalgae (<2%); seagrasses and seaweeds are absent (Jassby and Cloern, 2000). Allochthonous contributions, much of which is soil-derived, from riparian zones within the rivers' watersheds may come from tributaries (81% of TOC), agriculture (11%), tidal marsh export (4%), and wastewater (4%) and urban discharges (1%). Relative contributions of each depend on river flow, which itself is seasonally variable. However, taken together, autochthonous inputs account for only about 15% of annual TOC input to the Delta, whereas allochthonous sources dominate at 85%. The Jassby and Cloern (2000) model further indicates that ~90% of TOC supply to Suisun Bay and northern San Francisco Bay is delivered by the Delta rivers, in stark contrast to south San Francisco Bay where ~90% of TOC is autochthonous.

C:N_(a) ratios of bulk sediments confirm the importance of vascular plant OC and minor input of algal material to the Delta river sediments. Among density fractions, increasing C:N_(a) ratios with decreasing density point to the importance of vascular plant OC in lower density fractions. Results from a wide-ranging investigation of elemental and isotope compositions of aquatic and terrestrial plants in the Delta system by Cloern et al (2002) and studies of suspended POM (Canuel, 2001) support this conclusion.

There was considerable variability in ¹³C isotopic composition among the plants analyzed by Cloern et al. (2002) in the Delta, with differences reflecting carbon source and carbon fixation pathway (Hayes, 2001; Pearson, 2010). Among plants fixing carbon dioxide from the atmosphere, C₄ marsh plants were relatively enriched in ¹³C (~ -17 to -12 ‰) whereas C₃ salt marsh, floating vascular and terrestrial plants were, by comparison, depleted in ¹³C (~ -31 to -22 ‰). Aquatic filamentous algae, phytoplankton and submerged vascular plants that utilize dissolved CO₂ had highly variable δ¹³C values covering most of the range given above, usually depleted in ¹³C compared to marine phototrophs due to different isotope systematics between freshwater and marine systems (Oana and Deevey, 1960). Isotope values for soils within the Delta reflect land use, ranging from ~ -20 ‰ in a corn (C₄) field to (~ -27 to -24 ‰) in an uncultivated grassland (C₃). Since the range of δ¹³C values in the bulk Delta sediments we analyzed was small (-27.4 ± 0.5 ‰) and seasonal and species variability is high (Cloern et al., 2002), it is difficult to conclusively infer the dominant OC source, except perhaps to say that inputs from C₄ plants are minor. Nonetheless, the consistently lower values for δ¹³C in the lower density fractions (Fig. 6a) suggest greater proportions of vascular plant OC in those fractions.

Natural-abundance radiocarbon measurements ($\Delta^{14}\text{C}_{\text{OC}}$ or fraction modern f_m) add the dimension of “age” to the character of organic matter and help define the residence time and redistribution of OC in rivers and estuaries (Raymond and Bauer, 2001a, b; Blair et al., 2003; Griffith et al., 2010; Lu et al., 2014; McIntosh et al., 2015). In our study, radiocarbon ages of OC of bulk and most density fractions at Elk Slough are modern [$\Delta^{14}\text{C} \geq 0 \text{ ‰}$ ($f_m \sim 1$)], whereas high density $>2.5 \text{ g cm}^{-3}$ material is depleted in ^{14}C reflecting a more aged character (Fig. 6a). OC in Venice Cut and Nurse Slough, however, is considerably more depleted in ^{14}C . Bulk OC and <1.6 , 1.6 to 2.0 , and 2.0 to 2.5 g cm^{-3} fractions are similar in radiocarbon isotope values ($\Delta^{14}\text{C} -247$ to -114 ‰) but high density $>2.5 \text{ g cm}^{-3}$ fractions are highly ^{14}C depleted ($\Delta^{14}\text{C} -339$ and -382 ‰ , for Venice Cut and Nurse Slough, respectively) and hence the oldest (3,300 and 3,800 yr BP, respectively). Radiocarbon ages of sediments that are “too old” to reflect deposition of recently-biosynthesized (“young”) OC require contributions from old OC (often termed “pre-aged” OC) from terrestrial soil or fossil (rock) OC (Drenzek et al., 2009; Griffith et al., 2010; Blair and Aller, 2012; Douglas et al., 2014; Galy et al., 2015) and/or anthropogenic (petrogenic or fossil fuel combustion) sources (Mitra et al., 2002; Masiello, 2004). Rivers are an important mechanism for redistributing old terrestrial OC (Raymond and Bauer, 2001b; Masiello and Druffel, 2001; Blair and Aller, 2012). In the Rhine and Meuse Rivers, the Ems-Dollard estuary, and the southern North Sea, ^{13}C and ^{14}C compositions of size fractionated suspended particulate matter showed seasonal variations in a mix of OC sources and that a greater proportion of old terrestrial material was associated with coarse ($>20 \text{ }\mu\text{m}$) material ($\delta^{13}\text{C} \sim -26 \text{ ‰}$; $\Delta^{14}\text{C} \sim -500 \text{ ‰}$) than fine fractions ($\delta^{13}\text{C} \sim -23 \text{ ‰}$; $\Delta^{14}\text{C} \sim -200 \text{ ‰}$) (Megens, et al. (2001, 2002)). In the present

509 study, the relatively unimpacted Elk Slough, which lies north of the city of Sacramento,
 510 contains mostly recently-biosynthesized OC whereas Venice Cut and Nurse Slough
 511 contained higher proportions of older OC. Interestingly, the Nurse Slough site in Suisan
 512 Marsh that is little influenced by anthropogenic activities had $\Delta^{14}\text{C}$ values indicating
 513 sources of aged carbon that could reflect erosion or scouring of deeper marsh sediments
 514 or mixing with “older” sources from the surrounding watershed. Overall, there is a
 515 progression from $\Delta^{14}\text{C}$ -enriched (young) but $\delta^{13}\text{C}$ -depleted OC (bulk and density
 516 fractions) in Elk Slough to generally more $\Delta^{14}\text{C}$ -depleted (older) and $\delta^{13}\text{C}$ -enriched OC in
 517 Venice Cut and Nurse Slough.

518 Biomarkers shed additional light on the sources and diagenetic state of river
 519 sediment OC. Among the fatty acids analyzed here, short-chain ($n\text{-C}_{14} - n\text{-C}_{18}$) FA are
 520 biosynthesized by all plants but they are major lipids in freshwater microalgae (Cranwell
 521 et al., 1988, 1990; Volkman et al., 1998) and freshwater macroalgae (Dembitsky et al.,
 522 1993; Rozentsvet et al., 1995; 2002). Long-chain ($n\text{-C}_{24} - n\text{-C}_{28}$) FA are components of
 523 epicuticular waxes of terrestrial higher plants (Cranwell et al., 1987; Volkman, 2006) and
 524 are abundant in soils. FA compound distributions in Delta sediments – a mix of short-
 525 chain and long-chain compounds – confirm heterogeneous sources. Stable carbon
 526 isotope values of FA in Delta sediments were lower than TOC, by ~8.1 to 10.4 ‰ for the
 527 short-chain FA but by ~3.6 to 5.5 ‰ for the long-chain FA (Fig. 6b). All sites showed
 528 the same ^{13}C trend: $\delta^{13}\text{C}_{\text{short FA}} > \delta^{13}\text{C}_{\text{long FA}} > \delta^{13}\text{C}_{\text{OC}}$. The offset of $\delta^{13}\text{C}_{\text{FA}}$ relative to
 529 $\delta^{13}\text{C}_{\text{OC}}$ reflects the 4-8 ‰ isotope fractionation common during autotrophic biosynthesis
 530 of acetogenic lipids (in this case FA) vs primary biomass (here represented by TOC)
 531 (Hayes, 2001; Pearson, 2010), but the difference between $\delta^{13}\text{C}_{\text{short FA}}$ and $\delta^{13}\text{C}_{\text{long FA}}$

532 indicates a source distinction. A higher proportion of seston with low $\delta^{13}\text{C}$ values (Cloern
 533 et al., 2002) may contribute to the ^{13}C -depletion of the short-chain FA pool. Radiocarbon
 534 values of FA are more complex and $\Delta^{14}\text{C}_{\text{short FA}}$ indicate predominately modern OC while
 535 $\Delta^{14}\text{C}_{\text{long FA}}$ in Venice Cut and Nurse Slough indicate substantial proportions of old OC
 536 (Fig. 6b). Short-chain FA could originate from either aquatic or terrestrial plants; the
 537 narrow range of $\delta^{13}\text{C}$ does not provide a distinction. Long-chain, vascular plant FA
 538 likely reflect storage in soils for some time, but probably do not derive from fossil
 539 sources since functionalized lipids like FA, though present at low levels, are mostly lost
 540 during diagenesis (Rullkötter and Michaelis, 1990; de Leeuw and Largeau, 1993). Our
 541 findings are consistent with isotope compositions of FA in bulk sediments from the Eel
 542 Margin and in lower Mississippi River and Mississippi Margin sediments (Wakeham et
 543 al., 2009) and in the Delaware Estuary (McIntosh et al., 2015). Long-chain FA in Eel
 544 sediments had lower ^{13}C values compared to short-chain FA ($\delta^{13}\text{C}$ -32 ‰ and -25 ‰,
 545 respectively). In sediments of the Mississippi River/Margin, the opposite was found:
 546 long-chain FA had higher $\delta^{13}\text{C}$ values than short-chain FA (-31 ‰ vs -37 ‰,
 547 respectively). However, like the Sacramento-San Joaquin Delta sediments, short-chain
 548 FA in both the Eel and Mississippi River/Margin were modern in age ($\Delta^{14}\text{C}$ $+49$ ‰ and
 549 $+47$ ‰, for Eel and Mississippi, respectively) whereas long-chain FA were older ($\Delta^{14}\text{C}$ $-$
 550 109 and -91 ‰ for Eel and Mississippi, respectively). This trend is the reverse of that of
 551 FA of particulate organic matter in the Delaware Estuary, where short-chain FA were
 552 older than long-chain FA, indicating that the riverine algae that are the source of the
 553 short-chain FA fix aged dissolved organic carbon (McIntosh et al., 2015). Long-chain
 554 FA used to evaluate OC transport from the Himalayan Mountains and Tibetan Plateau

555 through the Ganges-Bramaputra river system were younger ($\Delta^{14}\text{C}$ –160 to –3 ‰) than
556 bulk terrestrial biospheric OC ($\Delta^{14}\text{C}$ –878 to –63 ‰) (Galy et al., 2008; Galy and
557 Eglinton, 2011).

558 Modern carbon in river sediments and sediments at river-ocean margin interfaces
559 must derive from recently biosynthesized aquatic or terrestrial plant biomass. Land
560 plants that fix atmospheric CO_2 may have ^{14}C values that are completely modern due to
561 inclusion of post-bomb carbon. The radiocarbon content of freshwater plants varies
562 depending on the reservoir effect of freshwater dissolved inorganic carbon, either CO_2 or
563 bicarbonate. If old, dissolved inorganic carbon (e.g., bicarbonate leached from carbonate
564 or evaporitic deposits) is present in freshwater systems, reservoir ages may be longer than
565 in marine systems (Broecker and Walton, 1959; Phillipsen, 2013; Lu et al., 2014;
566 McIntosh et al., 2015) and aquatic plants may be ^{14}C -depleted relative to biomass that
567 fixed atmospheric CO_2 .

568 Most old carbon in sediments originates from ^{14}C -deficient OC remobilized from
569 terrestrial soils or fossil OC from ancient sediments, and much of this export is driven by
570 erosion (e.g., Galy et al., 2015). Soil OC is highly variable in ^{14}C age depending on soil
571 ecosystem and horizon depth, carbon cycling and residence time, land use, and the
572 proportions of modern and fossil carbon, with ages ranging from modern in litterfall and
573 upper horizons to thousands of years in deeper horizons (Richter et al., 1999; Ewing et
574 al., 2006; Trumbore, 2009). In the case of the Delta, surface alluvial soil horizons from
575 grasslands of the Central Valley are modern ($\Delta^{14}\text{C} > 0$) whereas deeper horizons are
576 significantly older ($\Delta^{14}\text{C}$ –800 to –600 ‰) depending on whether or not they have been
577 cultivated (Baisden et al., 2002a,b; Ewing et al., 2006). Soil OC typically consists of a

578 rapidly cycling (5-20 yr) low density fraction of relatively unaltered vascular plant
579 material and a more abundant but slowly cycling mineral-associated component with a
580 mean residence time >200 yr (Trumbore et al., 1989; Baisden et al., 2002a,b; Ewing et
581 al., 2006; Castanha et al., 2008; Trumbore, 2009; Cerli et al., 2012). The lower region of
582 the Delta, at the confluence of the Sacramento and San Joaquin Rivers, also contains
583 large tracts of peat. Bulk densities of the peat range from 0.2-0.7 g cm⁻³ and their
584 radiocarbon contents ranged from -560 to -225 ‰ (Ewing et al., 2006; Canuel et al.,
585 2009). Fossil carbon sources include OC remobilized from ancient rocks (kerogen) and
586 black carbon (BC). Kerogen is an amorphous network of degraded, polymerized and
587 crosslinked biomolecules generated during diagenesis (Derenne et al., 1997; de Leeuw
588 and Largeau, 1993; Stankiewicz et al., 2000); BC is a carbon-rich, highly aromatized and
589 heterogeneous material that derives from biomass or fossil fuel combustion and
590 sedimentary metamorphism (where alteration of OC has proceeded beyond the kerogen
591 stage) (Masiello, 2004; Dickens et al., 2004), and thus may have modern (biomass) or
592 fossil (ancient sediment) radiocarbon signatures. In lake and marine sediments (Dickens
593 et al., 2004; Veilleux et al., 2009), BC is concentrated in a <1.6 g cm⁻³ density fraction.
594 Mitra et al. (2002) estimated that ~27% of the BC load, or up to 25% of OC, of the
595 Mississippi River is fossil fuel combustion-derived. Because both kerogen and BC are
596 highly refractory with respect to chemical or biological degradation they may cycle
597 between fluvial and sediment/soil environments during their transport through drainage
598 basins, especially in environments characterized by rapid channel migration and flooding
599 (Dunne et al., 1998; Aalto et al., 2003; Blair and Aller, 2012). Most particles in rivers are

thought to have spent time in soils, floodplain alluvial deposits or wetlands (Reneau and Dietrich, 1991; Gomez et al., 2003; Leithold et al., 2006; Hoffmann et al., 2009).

The age of OC in rivers also varies with the nature of the river and its watershed, and consequently with sediment load (e.g., Raymond and Bauer, 2001b; Leithold et al., 2006; Blair et al., 2003). Small rivers (<10,000 km² watersheds) draining high relief, mountainous (1000 – 4000 m elevation) areas where thin soils/sedimentary rocks are continuously eroded and there is minimal sediment storage capacity export substantial amounts of old, refractory organic matter. Rivers with lower relief but watersheds that include long-term carbon storage environments such as forests, grasslands, and wetlands can also deliver significant amounts of old OC. In contrast, rivers that integrate large watersheds with diverse geology and land cover/use and with extensive lowland sediment storage areas and floodplains that are dominated by chemical weathering (e.g., the Mississippi-Atchafalaya River System (Gordon and Goñi, 2003; Rosenheim et al., 2013) carry generally younger and less degraded OC. Because the Sacramento and San Joaquin Rivers begin as steep-gradient, high energy streams in the Sierra Nevada Mountains but gradually become larger as numerous tributaries join the mainstems, including those from the Coast Range, they become more quiescent as they flow through the Central Valley and a range of OC sources contributes to the observed elemental and isotopic compositions of river sediments in the Delta.

5 Conclusions

Bed sediments in the Sacramento-San Joaquin Rivers contain organic matter unevenly distributed among density fractions, similar to other river and continental

margin sediments. In general, mass and TOC are concentrated in mesodensity fractions, whereas both low density material that is rich in woody debris and high density material that is OC-poor mineral grains are relatively unimportant. At the Elk Slough site, OC is mostly derived from contemporary vegetation, but in both Venice Cut in the San Joaquin River and Nurse Slough in Suisan Marsh substantial amounts of old carbon OC are present, especially in the OC-poor, mineral-rich highest density material. Low river flow, such as during our study period, allows bed sediments to accumulate all density fractions: low density but coarse-grained material consisting of young discrete plant debris, older mesodensity organic-mineral aggregates, and still older organic-poor high density mineral material. But even under low flow/low turbulence conditions, some hydrodynamic sorting may occur whereby the mesodensity fractions become predominant. Overall, this work identifies differences in the source and age composition of organic matter associated with different sediment density fractions in rivers and reveals some of the complex interactions between organic matter and sediments that arise from watershed, hydrology and hydrodynamic features.

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1021 Figure Captions

1022

1023 Fig. 1. Map of sampling locations in the Sacramento-San Joaquin River Delta.

1024

1025 Fig. 2. Distributions of (a) mass, (b) organic carbon content, (c) atomic C:N ratio, and
1026 (d) percent of total organic carbon for the Delta sediment bulk and density fractions.

1027

1028 Fig. 3. Mean and standard deviations of distributions of (a) mass, (b) organic carbon
1029 content, (c) atomic C:N ratio, and (d) percent of total organic carbon for each density
1030 fractions across the five study sites.

1031

1032 Fig. 4. Surface area (SA) (following combustion) (a) and organic carbon/surface area
1033 ratio (OC/SA) (b) for Delta bulk sediment and density fractions.

1034

1035 Fig. 5. $\delta^{13}\text{C}$ (a) and $\Delta^{14}\text{C}$ (b) values for OC in Delta bulk sediment and density fractions
1036 and $\delta^{13}\text{C}$ (c) and $\Delta^{14}\text{C}$ (d) values for fatty acids in bulk sediments.

1037

1038 Fig. 6. Cross plots of (a) $\delta^{13}\text{C}$ vs. $\Delta^{14}\text{C}$ for OC in Delta bulk sediment and density
1039 fractions: black symbols = Elk Slough; white symbols = Venice Cut; gray symbols =
1040 Nurse Slough and (b) $\delta^{13}\text{C}$ vs. $\Delta^{14}\text{C}$ for fatty acids in bulk sediments: black symbols
1041 = bulk OC; white symbols = long-chain FA; gray symbols = short-chain FA.

1042

Table 1. Stable and radiocarbon isotope data for OC in density fractions, bulk OC and fatty acids for Elk Slough, Venice Cut and Nurse Slough sediments.

	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	<i>fm</i>	<i>fm</i> error	Age (yr BP)	Age Error
Elk Slough						
<1.6	-28.2	10	1.017	0.0039	modern	
1.6-2.0	-28.2	94	1.101	0.0043	modern	
2.0-2.5	-28.0	89	1.097	0.0034	modern	
>2.5	-27.4	-25	0.982	0.0042	150	35
bulk	-27.5	3.4	1.010	0.0031	modern	
Short FA	-36.3	91	1.100	0.0072	modern	
Long FA	-33.0	61	1.069	0.0091	modern	
Venice Cut						
<1.6	-27.3	-147	0.859	0.0027	1220	25
1.6-2.0	-27.8	-152	0.854	0.0028	1270	25
2.0-2.5	-27.2	-114	0.892	0.0037	920	35
>2.5	-26.8	-339	0.666	0.0029	3270	35
bulk	-27.1	-151	0.854	0.0037	1260	35
Short FA	-37.5	90	1.099	0.0097	modern	
Long FA	-31.0	-180	0.825	0.0097	1840	100
Nurse Slough						
<1.6	-27.3	-247	0.758	0.0029	2230	30
1.6-2.0	-27.1	-135	0.871	0.0027	1110	25
2.0-2.5	-26.9	-144	0.862	0.0033	1190	30
>2.5	-26.6	-382	0.622	0.0026	3810	30
bulk	-27.1	-161	0.845	0.0032	1350	30
Short FA	-35.2	19	1.027	0.0056	modern	
Long FA	-31.6	-80	0.927	0.0097	915	85