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Carbon isotope geochemistry of the Santa Clara River

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Abstract. The Santa Clara River is a prototypical small mountainous river, with a headwater height greater than 1000 m and a basin area smaller than 10,000 m². Although individual small mountainous rivers export trivial amounts of sediment and carbon to the ocean, as a group these rivers may export a major fraction (as much as 50%) of the total global river sediment flux [Milliman and Syvitski, 1992], making their geochemistry relevant to the study of the ocean's carbon cycle. In addition, many small rivers export sediment in a few high flux events, causing massive, sporadic discharge of carbon onto coastal shelves, discharge conditions very different from those of large rivers. This class of rivers is an end-member of the river-ocean carbon exchange system, opposite the Earth's largest river, the Amazon. The carbon mass and isotopic properties of the Santa Clara River are significantly different from previously studied large rivers. During the 1997-1998 winter, all Santa Clara carbon pools were old, with flux-weighted average $\Delta^{14}\text{C}$ values of $-428 \pm 76\text{‰}$ for particulate organic carbon, $-73 \pm 31\text{‰}$ for dissolved organic carbon, and $-644 \pm 58\text{‰}$ for black carbon. The age of exported carbon is primarily due to the deep erosion of old soils and not to inclusion of fossil fuel carbon. Additionally, the $\delta^{13}\text{C}$ signatures of exported carbon pools were high relative to terrestrial carbon, bearing a signature quite similar to marine carbon (average particulate organic carbon (POC) $\delta^{13}\text{C} = -22.2 \pm 0.8\text{‰}$). The Santa Clara's estuary is small and drains onto the narrow eastern Pacific coastal margin, exporting this old soil organic matter directly into the ocean. If the Santa Clara export patterns are representative of this class of rivers, they may be a significant source of refractory terrestrial carbon to the ocean.

1. Introduction

Small, mountainous rivers have been recognized as a significant source of terrestrial sediment to the ocean [Milliman, 1995; Milliman and Syvitski, 1992]; however, because of their size and seasonal nature, the geochemistry of these rivers remains largely undescribed. The Santa Clara River is typical of this class of rivers, with a drainage basin of 4200 km² (Figure 1) and a headwater height > 1000 m [Milliman and Syvitski, 1992]. The Santa Clara River drains into the Pacific near Oxnard, California, and is within 100 km of Los Angeles. Although human impact on the landscape is visible, the Santa Clara has not experienced the major environmental alterations typical of southern California rivers, such as bed paving. The Santa Clara's small, seasonal estuary is undeveloped and contained within McGrath State Park in Oxnard, California, at 34°14'N, 119°16'W.

The Santa Clara drainage basin is among the five largest in southern California, preceded in size by the Tijuana and Santa Ana Rivers and followed by the Los Angeles/San Gabriel River and the much smaller Santa Margarita River [Brownlie

and Taylor, 1981]. Among these five, the Santa Clara is the largest river not located in a major metropolitan area. Additionally, the Santa Clara is the only one of these five with less than half of its drainage basin controlled by dams (37% of the basin is controlled) [Brownlie and Taylor, 1981].

The carbon isotope geochemistry of the Santa Clara River is relevant to understanding the ocean's particulate and dissolved organic carbon cycles (DOC and POC) and the controls on ocean sedimentary organic carbon sequestration. The burial of POC in oceans accounts for the presence of O₂ in the Earth's atmosphere and represents the final sink removing carbon (C) from rapid circulation between the atmosphere, biosphere, and the oceans [Berner, 1989; Hedges and Keil, 1995]. The oceanic DOC pool contains approximately as much carbon as the atmospheric CO₂ pool and the ~6000 year ¹⁴C age of deep Pacific DOC reflects slow exchange with the biosphere [Williams and Druffel, 1987]. As significant as these forms of carbon are, complete characterization of their sources remains elusive. Rivers export enough DOC to account for the ocean's entire DOC pool [Williams and Druffel, 1987] and enough POC to account for all of the carbon stored annually in ocean sediments [Hedges and Keil, 1995; Meybeck, 1982]. However, studies of tracers characteristic of organic matter derived from large rivers (like the Amazon) suggest that only small amounts of riverine

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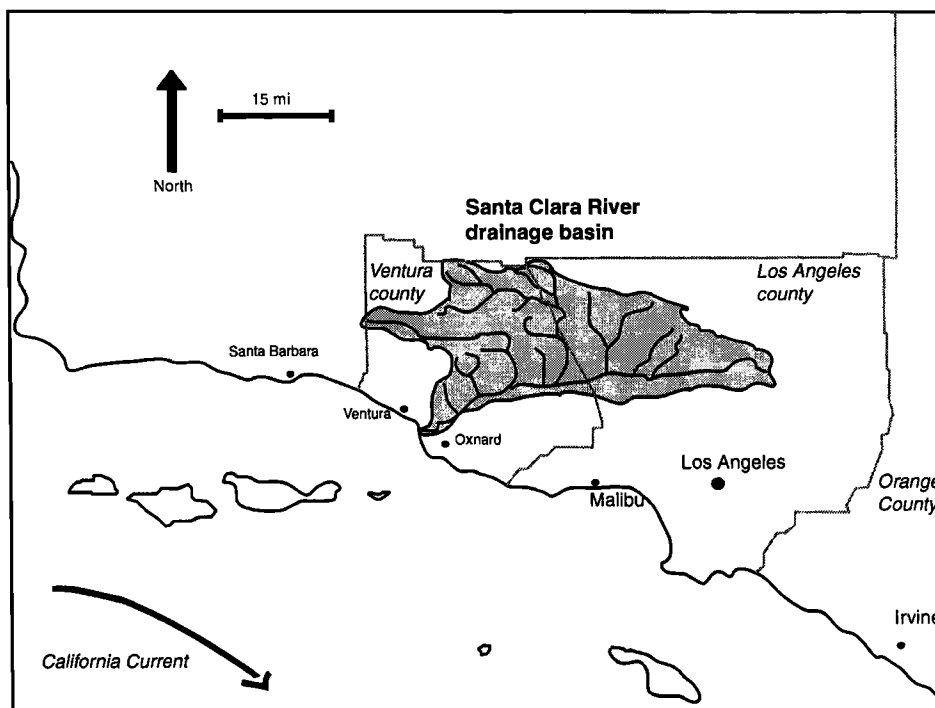


Figure 1. Map of the Santa Clara River drainage basin.

organic matter survive to reach the open ocean [Keil *et al.*, 1997; Opsahl and Benner, 1997].

It is also clear from studies of large rivers that the fates of DOC and POC are intertwined through suspended-dissolved carbon interconversion at the river-ocean margin. Keil *et al.* [1997] have shown that suspended mineral material experiences replacement of $\delta^{13}\text{C}$ -depleted terrestrial carbon with $\delta^{13}\text{C}$ -enriched marine material in transition from rivers to continental shelves. Estuarine and oceanic adsorption and desorption of mineral-associated C is influenced by the mineralogy of associated particles, the decompositional history of the organic matter, and the local estuarine dynamics [Hedges and Keil, 1999]. Tracer studies based on the physical, isotopic, and biomarker properties of very large rivers like the Amazon show that these adsorption/desorption processes work to enhance remineralization of terrestrial organic matter and inhibit its transport to the open ocean. However, this may not be the whole story: the physical and isotopic properties of OM exported by the Santa Clara are quite different from those of the Amazon, and combined, small mountainous rivers export much more of the global river sediment flux than the Amazon [Milliman and Syvitski, 1992]. Small river geochemistry is an important missing component in our understanding of the role of rivers in the ocean's carbon cycle.

The sediment transport processes at the mouth of the Santa Clara River are substantially different from those of larger rivers in terms of estuarine processes, shelf deposition, and the coupling between sediment discharge and coastal storage. Because the Santa Clara flows intermittently, it has created only a small, seasonal estuary. During the flood events responsible for over 90% of the Santa Clara's sediment export,

flow is massive and fast, delivering terrestrial organic matter directly to the Pacific Ocean without the benefit of the estuarine processing typical of larger rivers like the Amazon. The eastern rim of the Pacific lacks the broad, shallow shelf present in both the north and south Atlantic. Broad continental shelves such as those of the northwest Atlantic trap terrestrial sediments, allowing coastal reworking of organic matter and impeding sediment delivery to the deep ocean. However, because the Eastern Pacific shelf is much narrower, sediments borne by rivers like the Santa Clara are more likely to survive coastal processing and reach the deep ocean. Additionally, the Santa Clara's discharge events are caused by California's winter storms which concurrently impact the Pacific shelf, connecting river discharge to the offshore storms which mobilize coastal sediments [Cacchione *et al.*, 1994; Sherwood *et al.*, 1994]. The narrowness of the Pacific margin and the coupling between river discharge and coastal storms creates conditions ideal for the transport of river organic matter to the open ocean.

The 1997-1998 El Niño winter rains caused flooding in the south-central California area comparable only to the 1969 El Niño, which caused the largest floods recorded in the preceding 50 years. The extraordinary 1997-1998 winter flooding created the opportunity to study the geochemistry of a number of high-flux events from the Santa Clara in one year. Plate 1 (top) shows the Santa Clara under low-flow conditions and Plate 1 (bottom) shows the Santa Clara during one medium flow event (February 14, 1998).

Along with POC and DOC, we measured the concentration and isotopic signature of black carbon (BC) in the particulate carbon exported by the Santa Clara. BC is a class of solid, refractory carbon compounds produced during biomass



Plate 1.(top) View of the Santa Clara estuary, towards the Pacific from the Harbor Boulevard bridge This photo was taken under low-flow conditions in the summer of 1996 **(bottom)** As Plate 1 (top), on 2-14-98 during a medium-strength flood event

burning and fossil fuel combustion (for information on the BC cycle, see *Kuhlbusch* [1998]), making BC a tracer of terrestrial organic carbon. Where BC analyses have been performed, BC makes up a measurable component of C in most sediments [e.g., *Griffin and Goldberg*, 1975; *Gustafsson and Gschwend*, 1998; *Herring*, 1985; *Masiello and Druffel*, 1998; *Smith et al.*, 1973; *Verardo*, 1997], suggesting that terrestrial organic matter is a measurable component of sequestered carbon in at least abyssal ocean sediments. Radiocarbon measurements of BC extracted from deep-sea sediments point to rivers and/or the ocean's DOC pool as potential conduits transporting this terrestrial material to the deep ocean [*Masiello and Druffel*, 1998].

2. Methods and Research Site

Through the 1997-1998 season we measured the concentration, $\delta^{13}\text{C}$, and $\Delta^{14}\text{C}$ of organic carbon in three pools: DOC, POC, and black carbon in POC. Additionally, samples were collected for salinity to verify that there was no intrusion of ocean water during high-flow samples (see data in Table 1). We collected two low-flow samples, one on November 22, 1997, before the annual flooding began and one on January 2, 1998, after the winter rains had begun. Low-flow samples were taken to characterize the isotopic properties of the river at times most likely to be influenced by human and agricultural effluent. The rest of the samples were collected under flood conditions (December 5, 1997, January 28, 1998, February 14, 1998, February 24, 1998, and March

25, 1998). When the Santa Clara was flooding, samples were collected from the Harbor Boulevard bridge, which crosses the estuary ~0.3 km upstream of the Pacific. Care was taken to sample each time from the same central river site. Because the depth of the Santa Clara is highly variable, samples were collected from the upper 60 cm of water to avoid sampling bed load. The potential bias in this measurement technique is toward smaller, more easily suspended particulates. Under low flow conditions, samples were collected at a site slightly further downstream accessible by hiking. We waded into the southernmost fork of the estuary and submerged the sampling bottle in the portion of the water flowing toward the Pacific. The southernmost fork was selected because during low-flow conditions in the 1997-1998 winter, it was the fork flowing most consistently toward the Pacific. Samples were collected in a precombusted (550°C) glass bottle capped with a cleaned Teflon-lined lid and then transported on ice to the University of California Irvine (~2 hours), where they were shaken and then gently vacuum-filtered through precombusted (500°C) quartz fiber filters, which retained particles larger than 1 μm . Filtrate samples were frozen in amber bottles for DOC analysis and filters were frozen for POC and BC analysis. Two bottles were collected from each of the last two events sampled (February 24, 1998, and March 25, 1998). One was processed as described above, while the second was allowed to stand in a refrigerator for ~3 hours. The suspended liquid was pipetted out and filtered for suspended POC analysis, and the sediment which sank to the bottom of the bottle was saved for sinking POC analysis.

Table 1. Full Matrix of Data Collected During the 1997-1998 Water Year

analysis	Nov. 22, 1997	Dec. 5, 1997	Jan. 2, 1998	Jan. 28, 1998	Feb. 14, 1998	Feb. 24, 1998 total	Feb. 24, 1998 sink	Feb. 24, 1998 susp	Mar. 25, 1998 total	Mar. 25, 1998 susp	Mar. 25, 1998 sink
Salinity	2.5	0.3	7.1	0.4	0.4	0.1			0.4		
Event Weight		0.026		0.003	0.062	0.890			0.019		
mM POC	0.51	7.18	0.065	6.6	16.44	17.96	0.086	x	18.11	0.07	x
$\delta^{13}\text{C}$ POC, ‰	-33.3	-25.3	-21.7	-24	-19.7	-22.3	-24.7	x	-20.6	-23.5	x
$\Delta^{14}\text{C}$ POC, ‰	14	-139	x	-260.6	-657	-418	-167	x	-534	-644	x
%OC POC	x	3.557	x	1.604	0.737	1.153	x	0.84	1.22	x	1.11
%N POC	x	0.367	x	0.169	0.083	0.101	x	0.089	0.15	x	0.14
OC/N POC	6.7	9.69	x	9.49	8.88	11.42	x	9.44	8.13	x	7.93
mM BC	x	0.57	x	0.93	1.8	3.1	x	x	x	x	x
$\delta^{13}\text{C}$ BC, ‰	x	-26.1	x	-25.4	-24.2	-24.9	x	x	x	x	x
$\Delta^{14}\text{C}$ BC, ‰	x	-357	x	-489.9	-781	-643	x	x	x	x	x
mM DOC	0.561	0.944	0.358	0.417	0.319	0.394	x	x	0.443	x	x
$\delta^{13}\text{C}$ DOC, ‰	-26	-26.3	x	-26.1	-27.8	-25.6	x	x	-25	x	x
$\Delta^{14}\text{C}$ DOC, ‰	-220	-115	-221.1	-186	-180	-62	x	x	-125	x	x
DOC/POC	1.1	0.13	5.51	0.063	0.019	0.022	x	x	0.024	x	x
BC/POC	x	0.079	x	0.14	0.11	0.17	x	x	x	x	x

Here total = total material in sample, susp = suspended particulates in sample, and sink = sinking particulates in sample.

Filters were acidified to pH 2 with 5% H₃PO₄ for 24 hours, dried, and then combusted with pre-fired CuO and Ag foil in quartz tubes at 850°C for 2 hours [Druffel *et al.*, 1992]. CO₂ for DOC concentration, δ¹³C and Δ¹⁴C measurements was produced by high energy ultraviolet (UV) irradiation [Druffel *et al.*, 1992]. BC was measured through a dichromate/sulfuric acid oxidation procedure [Wolbach and Anders, 1989], as modified for Δ¹⁴C analysis [Masiello, 1999; C.A. Masiello *et al.*, Radiocarbon measurements of black carbon in aerosols and ocean sediments, submitted to *Geochimica et Cosmochimica Acta*, 2000]. Four to six filters from each flow event were added to a Teflon tube and dissolved in hydrofluoric acid, releasing organic material for dichromate/sulfuric acid BC extraction. The precision of this BC analysis is ± 10% by mass and better than ± 14‰ Δ¹⁴C for a modern sample (or better than ± 7‰ when Δ¹⁴C = -500‰) [Masiello, 1999]. (Note that due to a lack of commonly accepted standards, it is currently only possible to report precision in BC analyses, not accuracy. For a review of BC measurement methods see Schmidt and Noack, [2000]). Total uncertainty for POC and DOC Δ¹⁴C measurements is ±6‰, and for δ¹³C is ± 0.1‰. For all types of samples, CO₂ was condensed to graphite through reaction with H₂ over a cobalt or iron catalyst [Vogel *et al.*, 1987] and then measured for Δ¹⁴C at either Lawrence Livermore National Laboratory Center for Accelerator Mass Spectrometry or the Woods Hole Oceanographic Institution National Ocean Sciences Accelerator Mass Spectrometry facility. For discussion of ¹⁴C terminology, see Stuiver and Polach [1977].

3. Results and Discussion

Figure 2a shows the water output from the Santa Clara in ft³/s for the period of active flow during the winter of 1997-1998. The filled circles on Figure 2a correspond to dates that samples were collected and also correspond to the sampling points on Figures 2b-2d. We sampled 5 of 8 high flow events in 1997-1998.

Although the U.S. Geological Survey (USGS) has discontinued direct measurements of the sediment exported by the Santa Clara, measured water discharge is still continuously monitored. It is possible to estimate the total suspended sediment load from water discharge by using a rating curve, an empirical relationship developed from previous USGS measurements. From 1969 to 1976, the USGS measured the high flow suspended sediment concentration at USGS station 11114000 at Montalvo, California (Montalvo is located ~2 km upstream from our sampling site and receives >99% of the Santa Clara's sediment load). Using this data, Brownlie and Taylor [1981] developed the empirical relationship

$$Q_{ss} = 24.4Q^{1.73}$$

($n=50$; $r^2 = 0.89$) where Q is average daily water discharge in m²/s and Q_{ss} is suspended load in metric tons/day [Brownlie and Taylor, 1981]. We used this equation, plus USGS data on daily water discharge [United States Geological Survey (USGS), 1999] to calculate that in 1997-1998 the Santa Clara exported ~1.07x10¹² L of water and 59 x 10⁶ tons of sediment, as compared to the annual average Santa Clara export of 6.0 x

10⁶ tons of sediment [Milliman, 1991]. For comparison, the Mississippi exports 210 x 10⁶ tons of sediment/yr [Milliman and Syvitski, 1992]. It is important to note that trivial amounts of water (< 1% of the total) and sediment are exported from the Santa Clara under low-flow conditions.

Figures 2b-2d show the concentration, δ¹³C, and Δ¹⁴C values of POC, DOC, and BC in the Santa Clara River during the 1997-1998 winter. The most obvious characteristic of the Santa Clara's output is its large variability in concentration and isotopic values for all carbon components measured. For example, the Δ¹⁴C of POC ranges from an initial low-flow value of +14‰ to a high flow value of -657‰ on 2-14-98, a shift of over 600‰. The amount exported during each event also varies substantially, with the event centered around February 24, 1998 accounting for 56% of the annual export and the March 25, 1998 event accounting for 1.2%. Consequently, for each property we have chosen to report both the flux-weighted average (± 1 standard deviation, reported in the text and Table 2) and the data range (highest value - lowest value for high flow events, reported in Table 2). Flux-weighted averages were calculated for each event by assigning a weight to each event calculated as weight = $L_{event}/L_{totalmonitored}$, where L_{event} = the number of liters of water exported during the event and $L_{totalmonitored}$ = the total number of liters exported during all events measured in this study. We measured events corresponding to 1.07 x 10¹² L, or 63% of the total 1.70 x 10¹² L exported in 1997-1998. Weights were 0.026 for the December 5, 1997 event, 0.003 for the January 28, 1998 event, 0.062 for the February 14, 1998 event, 0.89 for the February 24, 1998 event, and 0.019 for the March 25, 1998 event. In addition, the full matrix of 1997-1998 Santa Clara data is reported in Table 1.

Figure 2b shows the concentration of POC, DOC, and BC in the Santa Clara River during each storm event at the time of sampling. The average high flow DOC concentration ranged from 0.32 mM to almost 1 mM, with a weighted mean value of 0.41 ± 0.09 mM, or approximately twice the DOC concentration of the Amazon river at low flow [J.E. Bauer *et al.*, The cycling of carbon in a transect from the mouth of the Amazon River to the Atlantic Ocean, submitted to *Limnology and Oceanography*, 2000] and 7-14 times that of the open ocean. During flood conditions, the POC concentration exceeded that of the DOC concentration by a factor of 7-50, reflecting the extraordinarily large sediment load characteristic of small mountainous rivers. The suspended sediment load was 17.23 g/L for the sample taken during the March 25, 1998 event. During both low-flow sample periods, however, DOC and POC were closer in concentration. BC was only measured during flood conditions because there was not enough material recovered to allow BC extraction during low-flow conditions. BC made up 8-17% of the POC exported during the events measured.

The δ¹³C of exported carbon showed large variations, with the POC δ¹³C, for example, ranging from -33.3‰ under the first, low-flow conditions, to -19.7‰ during the February 14, 1998 flood event (Figure 2c). The weighted mean high-flow POC δ¹³C was -22.2 ± 0.8‰ ($n=5$). DOC and BC δ¹³C varied less, giving weighted high-flow means of -25.8 ± 0.6‰ for DOC δ¹³C ($n=6$) and -24.9 ± 0.3‰ for BC δ¹³C ($n=4$). Measurement uncertainty for δ¹³C is ± 0.1‰, and data points are larger than error bars in Figure 2c.

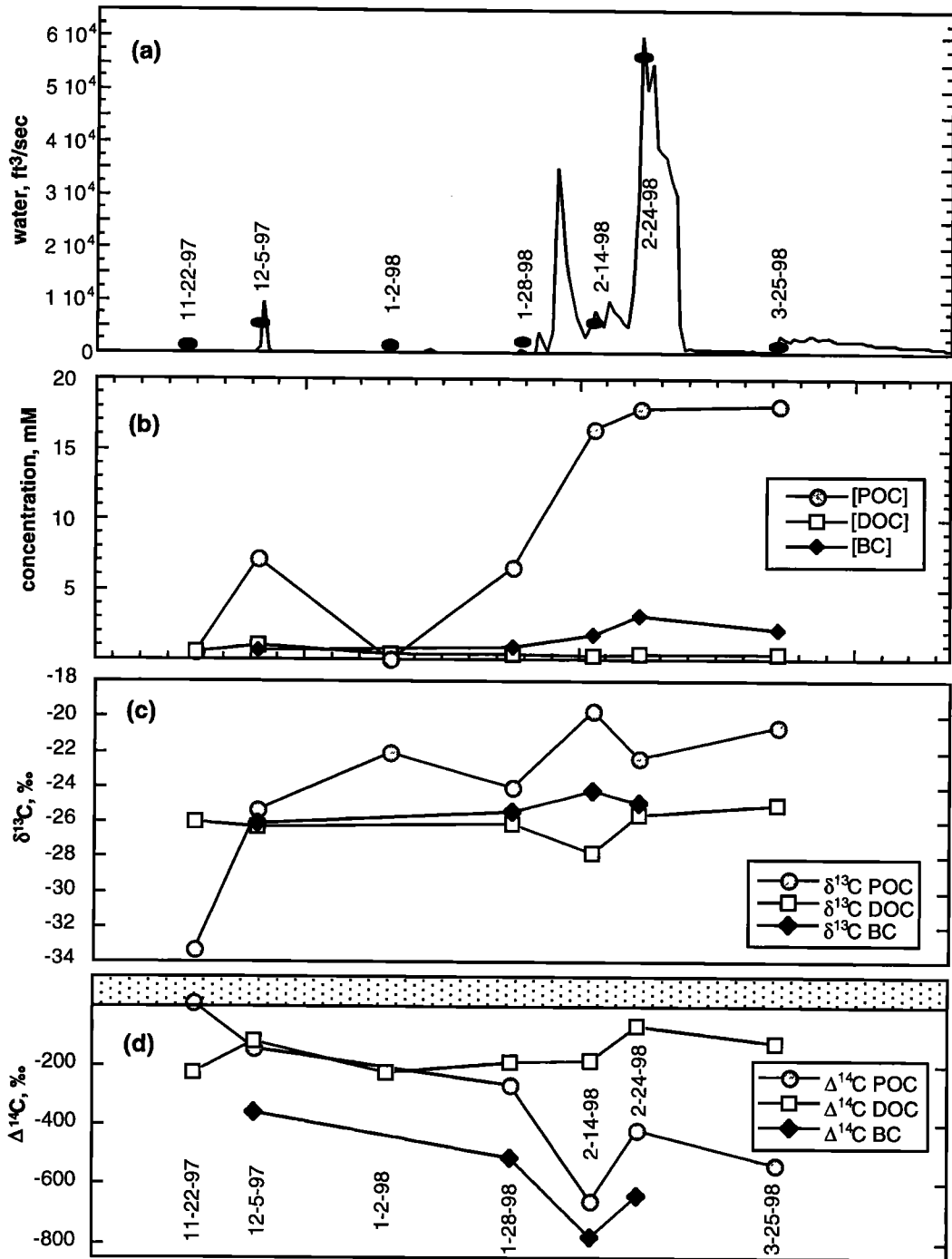


Figure 2. (a) Water output from the Santa Clara River during the 1998 water year, USGS public data courtesy of Henry Miyashita. (b) Concentration of carbon pools transported by the Santa Clara. (c) $\delta^{13}\text{C}$ of Santa Clara carbon pools. (d) $\Delta^{14}\text{C}$ of Santa Clara carbon pools. Points within the stippled region contain detectable amounts of bomb carbon.

Figure 2d shows the $\Delta^{14}\text{C}$ values of POC, DOC, and BC measured during this study. Error bars are $\pm 6\text{‰}$ for both POC and DOC and $\pm 14\text{‰}$ for BC. In Figure 2d all data symbols are larger than the error bars. The stippled region at the top of Figure 2d delineates $\Delta^{14}\text{C}$ values $> 0\text{‰}$, which indicates the presence of carbon fixed since atmospheric nuclear weapons tests in the late 1950s and early 1960s. Only one POC

sample (11-22-97, collected under low-flow conditions) had a postbomb signature ($+14\text{‰}$). This is the sample most likely influenced by human and agricultural run-off, since it was collected prior to the 1997-1998 rainfall season. No other sample contained detectable amounts of bomb carbon. The weighted mean POC $\Delta^{14}\text{C}$ was $-428 \pm 76\text{‰}$, the weighted mean DOC $\Delta^{14}\text{C}$ was $-73 \pm 31\text{‰}$, and the weighted mean BC

Table 2. Weighted Mean Values and High-Flow Ranges for Properties Measured in the Santa Clara River

	Weighted Mean	± Standard Deviation	Range of Data
mM POC	17.6	1.8 (n=7)	11.5
$\delta^{13}\text{C}$ POC, ‰	-22.2	0.8 (n=7)	5.6
$\Delta^{14}\text{C}$ POC, ‰	-428.4	75.9 (n=6)	518
%OC	1.2	0.4 (n=5)	2.8
%N	0.11	0.04 (n=5)	0.29
C/N	11.2	0.8 (n=6)	3.3
mM DOC	0.41	0.09 (n=7)	0.62
$\delta^{13}\text{C}$ DOC, ‰	-25.8	0.6 (n=6)	2.8
$\Delta^{14}\text{C}$ DOC, ‰	-73	30.5 (n=7)	124
DOC/POC	0.025	0.02 (n=7)	0.11
mM BC	2.9	0.5 (n=4)	2.5
$\delta^{13}\text{C}$ BC, ‰	-24.9	0.3 (n=4)	1.9
$\Delta^{14}\text{C}$ BC, ‰	-644	58.1 (n=4)	424

Data range is for high-flow samples only.

$\Delta^{14}\text{C}$ was $-644 \pm 58\text{‰}$. In all flood-stage samples the Santa Clara's DOC was younger than the POC, on the average by 270‰, suggesting a shorter residence time of soluble carbon (DOC) in soils. For all four samples measured, BC was older than POC on average by 170‰.

The $\Delta^{14}\text{C}$ values reported here differ markedly from previous $\Delta^{14}\text{C}$ measurements made in the Amazon river but are similar to POC $\Delta^{14}\text{C}$ measurements made in another small mountainous river. Bomb carbon has been detected in every Amazon organic carbon $\Delta^{14}\text{C}$ measurement reported, and in the 1980s, Amazon River fulvic acids reached +344‰ [Hedges *et al.*, 1986]. Because of the presence of bomb carbon in these samples, their $\Delta^{14}\text{C}$ was 770‰ greater than the average Santa Clara $\Delta^{14}\text{C}$ POC value and more than 1000‰ higher than the oldest Santa Clara POC $\Delta^{14}\text{C}$ (-657‰).

However, the average $\Delta^{14}\text{C}$ for the Santa Clara River POC is heavier (younger) than almost all of the $\Delta^{14}\text{C}$ measurements made previously for the Lanyang Hsi River in Taiwan, a small mountainous river heavily impacted by human-induced erosion, with a much higher precipitation regime [Kao and Liu, 1996]. The Lanyang Hsi $\Delta^{14}\text{C}$ values approach -875‰ (12.6% modern, or ~16,600 ^{14}C years) and as much as 70% of the POC from this system may be eroded bedrock, much of it mobilized due to recent road construction [Kao and Liu, 1996].

Using the total volume of water exported by the Santa Clara in 1997-1998 and mean weighted average values (Table 2), we can extrapolate the amount and isotopic signatures of carbon transported to the ocean. In 1997-1998 the Santa Clara delivered to the ocean 3.6×10^5 tons of POC with a weighted mean average $\Delta^{14}\text{C}$ of $-428 \pm 76\text{‰}$ and a $\delta^{13}\text{C}$ of $-22.2 \pm 0.8\text{‰}$, of which 5.9×10^4 tons were particulate BC with a $\Delta^{14}\text{C}$ of $-644 \pm 58\text{‰}$ and a $\delta^{13}\text{C}$ of $-24.9 \pm 0.3\text{‰}$. The Santa Clara also exported 8.4×10^3 tons of DOC with a $\Delta^{14}\text{C}$ of $-73 \pm 31\text{‰}$ and a $\delta^{13}\text{C}$ of $-25.8 \pm 0.6\text{‰}$.

Santa Clara flood events typically last ~3 days. Because the residence time of sediment in the river is so short, it is unlikely that in-river biological processes (such as degradation or photosynthesis) change the isotopic signature of the transported carbon. Most likely, the isotopic signatures of carbon pools reflect their source: eroded soils, resuspended sediments, and bedrock from the Santa Clara drainage basin. The lack of river-estuary processing and the highly erosive nature of this class of rivers are the likely causes of the difference between the age of Santa Clara carbon pools and that of larger rivers.

The standard deviation of Santa Clara $\Delta^{14}\text{C}$ POC data ($\pm 76\text{‰}$) is far greater than that attributable to analytical uncertainty ($\pm 6\text{‰}$). Changes in $\Delta^{14}\text{C}$ POC do not correlate to changes in flow, as expected if harder, longer rains eroded deeper into the soil column. Although the $\Delta^{14}\text{C}$ of POC from the highest flood event of the season (2-24-98) was low (-418‰), a smaller event earlier in the season (2-14-98) exported POC that was -657‰, lower by more than 200‰. Changes in $\Delta^{14}\text{C}$ POC correlate well with changes in $\delta^{13}\text{C}$ POC ($r^2=0.994$, $P=0.001$), as shown in Figure 3. The oldest POC sample (-657‰) had the highest $\delta^{13}\text{C}$ value (-19.7‰). Although this is a marine-like $\delta^{13}\text{C}$ signature, salinity measurements indicate that this sample and all other high-flow samples were fresh (salinity < 0.4). The excellent correlation between $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ of POC suggests mixing of two end-members, one ^{14}C -enriched (modern) and $\delta^{13}\text{C}$ -depleted, and the other ^{14}C -depleted (old) and $\delta^{13}\text{C}$ -enriched.

Measurements of soil organic carbon $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ made close to the Santa Clara watershed at the University of California Sedgewick Ranch Preserve show a $\delta^{13}\text{C}$ increase with depth, from -27.9‰ at the surface to -24.5‰ at >200 cm deep (average = $-25.9 \pm 1.1\text{‰}$, $n=19$) and also show a $\Delta^{14}\text{C}$ decrease from +120‰ at the surface to -640‰ at >200 cm (average = $-206 \pm 243\text{‰}$, $n=19$), (S.E. Trumbore and O.A. Chadwick, unpublished data, 1998). The soil $\Delta^{14}\text{C}$ values observed at depth at Sedgewick Ranch are as old as the oldest POC exported by the Santa Clara and show the same

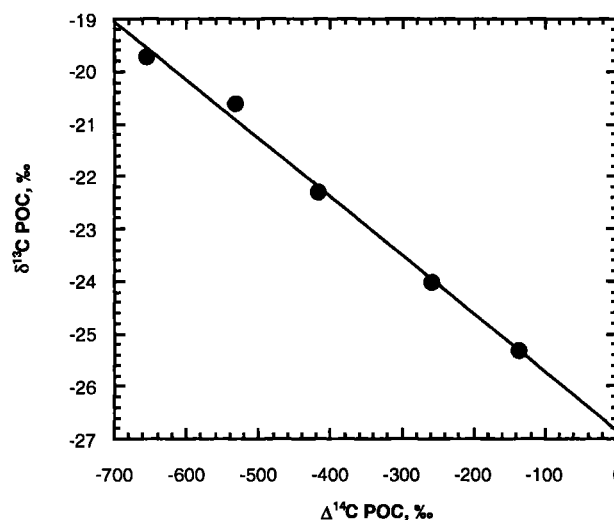


Figure 3. $\delta^{13}\text{C}$ of POC vs $\Delta^{14}\text{C}$ of POC in the Santa Clara during high flow events.

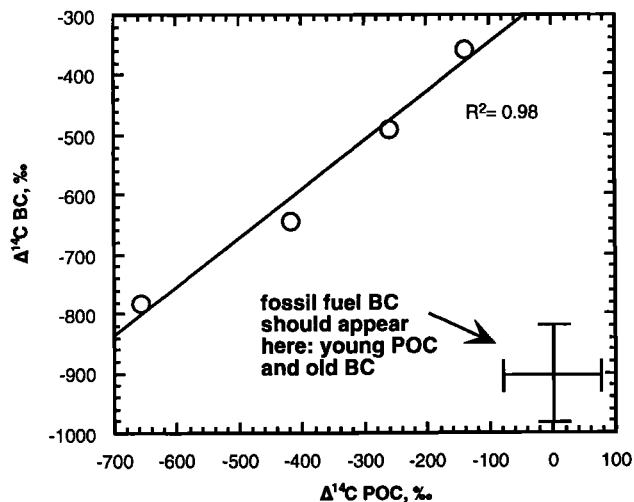


Figure 4. $\Delta^{14}\text{C}$ of BC vs $\Delta^{14}\text{C}$ of POC in the Santa Clara during high flow events.

relationship between $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ observed in Figure 3. However, soils alone cannot account for the very heavy $\delta^{13}\text{C}$ signature of some of the Santa Clara POC events (for example, -19.7‰ on February 14, 1998). The source of this old, $\delta^{13}\text{C}$ -enriched C is not resuspension of recently deposited marine carbon; tidal fluxes do not extend nearly far enough upstream to deposit a significant amount of marine C in the basin. To explain these heavy $\delta^{13}\text{C}$ values, the Santa Clara's exported POC must include some fraction of marine bedrock, and the $\delta^{13}\text{C}$ value of -19.7‰ for POC exported on February 14, 1998 is within the $\delta^{13}\text{C}$ range of kerogens [Whiticar, 1996]. The bedrock underlying Santa Clara drainage basin soils was formed as shallow marine terraces during past stands of high sea-level, and the $\delta^{13}\text{C}$ of the organic carbon preserved in this bedrock and exported as eroded POC in the Santa Clara River presumably reflects this marine source.

BC and POC $\Delta^{14}\text{C}$ values show that the age of POC exported by the Santa Clara cannot be explained by inclusion of a significant amount of carbon from fossil fuel combustion. Carbon in deep California soils can easily reach one radiocarbon half-life (5730 ^{14}C years old, or -500‰) and because humans have been burning fossil fuels only during the last ~ 150 years, fossil BC would not appear in deep soils. The fossil BC isotopic signature ($\Delta^{14}\text{C} = -1000\text{‰}$) should only be present in surface soils (total organic $\Delta^{14}\text{C} \geq 0$). If fossil fuel carbon were a significant component of exported carbon, we would expect the oldest BC samples to occur in a matrix of young soil organic carbon. Similarly, the $\delta^{13}\text{C}$ of older POC samples should reflect input from low $\delta^{13}\text{C}$ (about -29‰) fossil fuel carbon. Neither of these conditions are met. The $\delta^{13}\text{C}$ of the oldest POC samples is heaviest (see Figure 3), and BC $\Delta^{14}\text{C}$ is well-correlated ($r^2 = 0.98$, $P=0.02$) with POC $\Delta^{14}\text{C}$; older BC samples occur in conjunction with older POC samples (see Figure 4). Fossil-fuel derived BC would appear on Figure 4 in the lower right corner, with POC $\Delta^{14}\text{C} \sim$ modern, and BC $\Delta^{14}\text{C} \sim -1000\text{‰}$. The largest possible perturbation of the bulk SOM age by inclusion of a dead BC component can be calculated through mass balance to be

-70‰ , (17% BC at -1000‰ + 83% SOM at 120‰), within the cross drawn on Figure 4.

The results of this study raise the question: what if the isotopic and mass properties of the 9.5×10^9 tons sediment/year estimated to come from small, mountainous rivers [Milliman and Syvitski, 1992] resemble those of the Santa Clara? Before commenting on this, it is important to note first, that the data set in this study is certainly not large enough to use to reevaluate the Earth's river carbon budget; a number of multiyear studies on many small rivers will be needed before revisions can be made. Second, the samples here were collected during an El Niño event and cannot be assumed to be representative of this river generally. Third, although the Santa Clara is not a heavily perturbed watershed, it is not pristine. Some of the old carbon exported by the Santa Clara may have been mobilized recently by construction, although it is important to note that the annual sediment export by the Santa Clara has, if anything, decreased with time (USGS records cited by Milliman [1991]). Finally, 37% of the Santa Clara basin is controlled by dams, and this has been shown to decrease the Santa Clara's sediment yield by 10-20% [Brownlie and Taylor, 1981].

Scaled up, the $\sim 9.5 \times 10^9$ tons of sediment estimated to come from small mountainous rivers [Milliman and Syvitski, 1992], at 1.2% C would yield 1.1×10^8 tons of carbon or 0.11 Gt. This is 73% of the global riverine POC load of 0.15 Gt [Meybeck, 1982], suggesting that 0.15 Gt C/year from rivers may be an underestimate, and/or that small mountainous rivers are a major component of river particulate carbon flux to the ocean. Of this POC, 16.4% or 0.019 Gt would be BC. This is $\sim 20\%$ of the carbon stored annually in ocean sediments and at the upper end of the 5-20% BC percentage observed in coastal California sediments [Masiello, 1999]. In the 1997-1998 winter season the DOC/POC ratio of the Santa Clara was 0.025, scaling up to 2.8×10^5 tons DOC, or 0.1% of the global river DOC load [Meybeck, 1982], suggesting that small rivers are not a major direct source of DOC to the ocean, although DOC-POC interconversion may occur in the estuary and coastal regions.

Previous studies suggest that transport to the open ocean is a major fate of sediments discharged from small mountainous rivers, studies such as the STRATAFORM study on the Eel River. The Eel is also a small, mountainous river discharging onto the narrow, active North American western margin, and it has been shown that on century timescales, less than 20% of the Eel's terrestrial sediment load is trapped on the upper slope, and at least 60% is transported beyond the shelf-slope break [Sommerfield and Nittrouer, 1999]. The long-range transport of old, $\delta^{13}\text{C}$ enriched terrestrial organic carbon from small mountainous rivers is consistent with the results of Bauer and Druffel [1998], who showed that continental margins (including the Eastern North Pacific) are a source of ^{14}C -depleted DOC and POC to the deep ocean.

Not only does this class of rivers have the potential to transport carbon effectively off-shore, but it is also the smaller clay and silt-sized minerals that are preferentially exported [Sommerfield and Nittrouer, 1999]. This is significant because some of the biochemical markers used to detect terrestrial organic matter in sediments, such as lignins [Goñi and Hedges, 1995; Prah et al., 1994] are poorly retained on

clays. This suggests that small, episodic rivers like the Santa Clara may be exporting C that is difficult to detect in the ocean by some forms of biomarker analyses. Some biochemical markers, such as n-alkanes, have been shown to be transported with silt and clay-sized particles [Prahl *et al.*, 1994], and measurements of these markers (along with lignins) in rivers would add substantially to our understanding of the processes which move carbon from soils to the deep ocean via continental margins.

The isotopic signatures of the Santa Clara's carbon pools point toward a different understanding of the fate of terrestrial carbon in the open ocean. The highly erosive conditions and effective coastal dispersion characteristic of rivers on active margins, coupled with the ^{14}C age and refractivity of C observed in the Santa Clara suggest that more information on the geochemistry of small mountainous rivers may be needed to understand the role of rivers in the ocean's carbon cycle. Further measurements will be necessary to understand the fate of old carbon exported by this class of rivers.

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