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Oceanic export of relict carbon by small mountainous rivers

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[1] Small mountainous rivers (SMR) export globally significant quantities of particulate organic carbon (POC) to the oceans, the composition of which may be distinct from POC delivered by major world rivers. To better constrain the controls on the $\Delta^{14}\text{C}$ signatures of POC suspended in SMR, we examined the temporal variability of $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of POC suspended in the Santa Clara River, a SMR in California, USA. Our data suggest mixing of bedrock and contemporary soil, which can be applied to other SMR in contrasting climate zones and with varying land cover. The data also suggest that chemical denudation is incomplete, but effective to the point that only the most recalcitrant moieties of the parent POC are exported. We further propose sediment yield as a potentially useful proxy for the $\Delta^{14}\text{C}$ of riverine POC. A preliminary analysis of the existing data for a spectrum of rivers supports this hypothesis. *INDEX TERMS*: 1030 Geochemistry: Geochemical cycles (0330); 1625 Global Change: Geomorphology and weathering (1824, 1886); 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4806 Oceanography: Biological and Chemical: Carbon cycling; 4825 Oceanography: Biological and Chemical: Geochemistry; *KEYWORDS*: shale, weathering, radiocarbon, organic, suspended, sediment. *Citation*: Komada, T., E. R. M. Druffel, and S. E. Trumbore (2004), Oceanic export of relict carbon by small mountainous rivers, *Geophys. Res. Lett.*, 31, L07504, doi:10.1029/2004GL019512.

1. Introduction

[2] Small mountainous rivers (SMR; basin area < 10,000 km², headwater height 1000–3000 m) have been projected to deliver as much as 40% of the global riverine sediment load due to their high erodibility [Milliman and Syvitski, 1992]. Correspondingly, 17–35% of the global riverine particulate organic carbon (POC) load has been attributed to SMR [Lyons *et al.*, 2002]. Compared to larger and/or lower-relief counterparts, POC suspended in SMR can be enriched in rock-derived organic carbon (OC), making SMR potentially significant sources of relict OC to the oceans [Kao and Liu, 1996; Masiello and Druffel, 2001; Blair *et al.*, 2003]. The riverine flux of relict OC is a key component of the marine and global C cycles, influencing our understanding of the source of ¹⁴C-depleted C in the oceans [Druffel *et al.*, 1992], as well as controls on atmospheric oxygen over geologic time [Berner, 1989]. However, the controls on the isotopic composition of POC suspended in SMR are not well understood.

[3] We report the temporal variability of $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of POC suspended in the Santa Clara River, one of many SMR in southern California, USA. Previous work has

shown that $\Delta^{14}\text{C}$ values of POC suspended in the Santa Clara can vary temporally, but on average, ~40% of the POC may be derived of ancient C [Masiello and Druffel, 2001]. In the present study, we examined the isotopic composition of POC suspended in recent storm events, and compared them to potential end-member POC sources to identify the major controls on POC isotopic composition. We present two models—weight-% POC and sediment yield models—to better understand the variability of $\Delta^{14}\text{C}$ signatures of POC suspended in rivers of different morphologies.

2. Study Sites and Methods

[4] The Santa Clara is a mixed land-use SMR (drainage area 4210 km²; headwater height 2900 m; Figure 1). Tectonic uplift, steep hillslopes, and friable bedrock promote physical denudation and attenuate soil development. Semi-arid climate fosters surface vegetation dominated by mixed chaparral and sage scrub [Scott and Williams, 1978]. Precipitation is largely limited to the months of November through March, during which storms trigger discharge events. Such events are responsible for the annual discharge of both sediment and water [Warrick, 2002].

[5] During the winter of 2002 to 2003, suspended sediment was collected under moderate to high flow conditions 0.3 km upstream of the river mouth using methods of Masiello and Druffel [2001]. The four events sampled accounted for 55% of the discharge for water year 2002 (Table 1). Samples were collected during low tide to avoid inclusion of marine POC, and stored on ice during transport to the laboratory. Within 24 hours of collection, suspended solids were concentrated from the river water by centrifugation. The solids were lyophilized, powdered, and stored frozen until analysis. Two samples collected in 1998 by Masiello and Druffel [2001] that had been stored frozen were also included in the current sample set (Table 1). Isotopic signatures reported by Masiello and Druffel [2001] are not used here, because of the possibility of incomplete carbonate removal (T. Komada, unpublished data, 2003).

[6] Of the various sedimentary rocks that outcrop within the watershed, three were targeted as potential POC sources based on their outcrop areas and friability: Pico (Tp; Plio-Pleistocene), Monterey and lower Monterey (Tm and Tml; Miocene), and Cozy Dell (Tcd, Eocene). Tp has been proposed as a major source of sediment to the Santa Clara due to its exceptional erodibility [Warrick, 2002]. The remaining formations are less friable, but outcrop widely. We collected two sets of Tm samples: a dark, less weathered sample (Tm-black), and a lighter, more weathered sample (Tm-white). All samples were collected from 10 to 20 cm beneath road-cut surfaces avoiding surface litter and soil. All samples were powdered, lyophilized, and stored frozen until analysis.

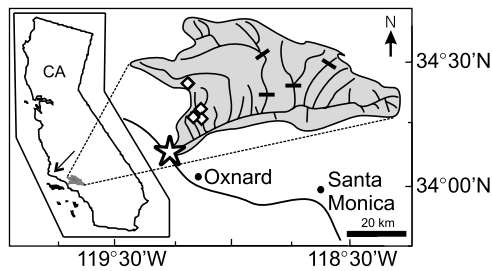


Figure 1. The Santa Clara basin showing suspended sediment (star) and shale (diamonds) sampling sites. Bars represent active dams. The arrow in the inset shows the location of the Sedgwick Reserve where surface soils were collected.

[7] Soil samples were collected in 1997 from the Sedgwick Reserve in the Santa Ynez basin approximately 100 km due east of our study area (Figure 1). We use the Sedgwick soil data to approximate soil geochemistry of the Santa Clara basin because the two regions lie within the same geologic province (the Transverse Ranges), have overlapping lithologies (Tm dominates the soil pit locations), and have similar precipitation patterns and surface vegetation [Scott and Williams, 1978]. Samples were collected from the uppermost 5 cm of the soil profile and separated by density using a 2.0 g ml^{-1} sodium polytungstate solution.

[8] Weight-% (wt%) POC and $\delta^{13}\text{C}$ of POC were determined with a Carlo Erba Elemental Analyzer interfaced with a Finnigan Delta Plus-Mass Spectrometer after decarbonation [Hedges and Stern, 1984]. The standard deviation of replicate measurements were $\pm 0.02\%$ and $\pm 0.1\%$ for wt% POC and $\delta^{13}\text{C}$, respectively. For $\Delta^{14}\text{C}$ analyses, samples were decarbonated [Hedges and Stern, 1984], dried, then combusted [Druffel et al., 1992]. The evolved CO_2 was purified, graphitized [Vogel et al., 1987], and analyzed at the Keck Carbon Cycle AMS Laboratory at

Table 1. Isotopic Values and wt% POC of Shales, Soils and Suspended POC

| Sample | UCI # | $\Delta^{14}\text{C}$ (‰) | $\delta^{13}\text{C}$ (‰) | POC (wt%) |
|----------------------------------|-------|---------------------------|---------------------------|------------------|
| Shale | | | | |
| Cozy Dell (Tcd) | - | N/A ^a | -24.5 | 0.33 |
| Pico (Tp) | - | N/A | -23.4 | 0.19 |
| Monterey-black (Tm) | D5334 | -995 | -21.7 | 4.29 |
| Monterey-white (Tm) | D5336 | -885 | -22.3 | 0.40 |
| Lower Monterey (Tml) | - | N/A | -21.1 | 0.50 |
| Soil | | | | |
| High density (pit 10) | T4120 | +45 | -27.0 | 4.0 ^b |
| Low density (pit 10) | T4121 | +122 | -27.9 | |
| High density (pit 19) | T4111 | +67 | -26.8 | 3.6 ^b |
| Low density (pit 19) | T4110 | +120 | -27.9 | |
| Santa Clara Suspended POC | | | | |
| 24-Feb-98 (20000) ^c | D6863 | -271 | -25.1 | 0.94 |
| 25-Mar-98 (3500) | D6430 | -437 | -24.2 | 1.11 |
| 08-Nov-02 (136) | D6864 | -232 | -25.2 | 3.44 |
| 12-Feb-03 (2730) | D6835 | -276 | -25.2 | 1.76 |
| 15-Mar-03 (3100) | D6834 | -544 | -24.4 | 1.01 |
| 03-May-03 (1270) | D6865 | -333 | -24.8 | 1.37 |

^aNot available.

^bBulk values.

^cDaily mean discharge in cubic feet per second from the US Geological Survey: <http://waterdata.usgs.gov/ca/nwis/si>; site number 11114000.

the University of California, Irvine. Total uncertainty for the $\Delta^{14}\text{C}$ values [Stuiver and Polach, 1977] was ± 6 to 20‰, which included uncertainties arising from sample processing and AMS measurement.

3. Results and Discussion

3.1. Sources of POC to the Santa Clara

[9] Spatial and temporal fluctuations in the isotopic values of riverine POC has been attributed to variations in autochthonous and allochthonous POC sources [e.g., Mook and Tan, 1991]. However, in small turbid rivers such as the Santa Clara, allochthonous POC input may dominate the isotopic signal, because light limitation and short transit times curb in situ production. Furthermore, rapid physical denudation should promote transport of sediment derived from poorly weathered rocks, while maintaining soil development at a minimum [Stallard, 1995; Petsch et al., 2000].

[10] We determined the isotopic values of shale and surface soils to identify possible allochthonous POC sources to the Santa Clara. The $\delta^{13}\text{C}$ values of the shales ranged from -24.5% (Tcd, terrigenous and marine [Slatt and Thompson, 1985]) to -21.1% (Tml, predominantly marine [Katz and Elrod, 1983]; Table 1). While ^{14}C was undetectable in Tm-black (-995%), it was detectable in Tm-white (-885% ; Table 1) possibly from microbial activity [Petsch et al., 2001] and dissolved organic matter input from the surface. Relative to the shales, surface soils were depleted in ^{13}C (-27.9 to -26.8%), and enriched in ^{14}C ($+45$ to $+122\%$; Table 1). The isotopic signatures of POC suspended in the Santa Clara varied temporally, and indicated mixing between a ^{13}C -enriched ancient, and a ^{13}C -depleted modern end-member (Figure 2). $\Delta^{14}\text{C}$ values ranged from -544 to -232% , and $\delta^{13}\text{C}$ values decreased linearly with increasing $\Delta^{14}\text{C}$. These isotopic signatures are consistent with surface soils and poorly weathered shales as being the two key POC sources to the river.

3.2. $\Delta^{14}\text{C}$ of Suspended POC: wt% POC Model

[11] The apparent dominance of allochthonous POC in the Santa Clara (Figure 2) combined with high rates of mass wasting in SMR [Milliman and Syvitski, 1992] suggest that POC transfer from source to the river mouth may be highly

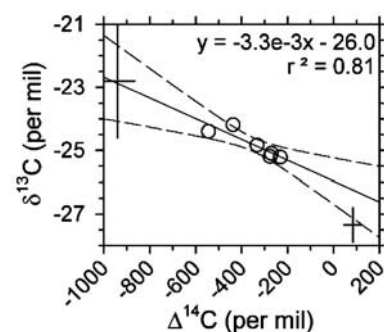


Figure 2. $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of shales and soils (upper left and lower right crosses, respectively, showing total ranges) and Santa Clara suspended POC (circles; Table 1). Linear regression and 95% confidence limits are for suspended POC only.

efficient in these systems. If so, it may be possible to model the $\Delta^{14}\text{C}$ values of POC suspended in SMR regardless of land cover/use and climate. Hence, we model the isotopic composition of POC suspended in SMR by adopting a mixing scheme analogous to *Stallard* [1995] and *Blair et al.* [2003], with surface soil and shale as contemporary and ancient sources, respectively:

$$C_{\text{tot}} * M_{\text{tot}}^{-1} = C_{\text{soil}} * M_{\text{tot}}^{-1} + C_{\text{rock}} * M_{\text{tot}}^{-1} \quad (1)$$

$$\Delta_{\text{tot}} * C_{\text{tot}} * M_{\text{tot}}^{-1} = \Delta_{\text{soil}} * C_{\text{soil}} * M_{\text{tot}}^{-1} + \Delta_{\text{rock}} * C_{\text{rock}} * M_{\text{tot}}^{-1} \quad (2)$$

where C is POC, M is mass of solids, Δ is the $\Delta^{14}\text{C}$ of POC, and subscripts *tot*, *soil* and *rock* represent the total river suspended load, and its components originating either from surface soil or shale, respectively. Combining equations (1) and (2) and solving for δ_{tot} gives:

$$\Delta_{\text{tot}} = [(\Delta_{\text{rock}} - \Delta_{\text{soil}}) * C_{\text{rock}} * M_{\text{tot}}^{-1}] * C_{\text{tot}}^{-1} * M_{\text{tot}} + \Delta_{\text{soil}} \quad (3)$$

[12] To test this model, we plotted the inverse of wt% POC ($C_{\text{tot}}^{-1} * M_{\text{tot}}$) against the $\Delta^{14}\text{C}$ of POC (Δ_{tot}) suspended in the Santa Clara and other SMR that are currently available in the literature. These SMR span a range of climate zones: Mediterranean (Eel River, California; N. Blair, personal communication, 2003), humid subtropical (Lanyang Hsi, Taiwan [*Kao and Liu*, 1996]), and tropical monsoon (five small Papua New Guinea rivers [*Raymond*, 1999]). The Eel drains mainly conifer forests and grasslands underlain by Jurassic-Tertiary shale-rich melange [*Blair et al.*, 2003]. The Lanyang Hsi drains a subtropical forest underlain by Tertiary sediments [*Kao and Liu*, 2000]. Export of ancient C from this system has been attributed to enhanced erosion from human disturbance [*Kao and Liu*, 1996]. The Papua New Guinea rivers drain Cenozoic marine carbonates and sandstones [*Raymond*, 1999, and references therein].

[13] The data set produces a linear trend indicating bimodal mixing between C-rich modern and C-poor ancient sources (Figure 3a). The observed linearity also implies that the amount of POC in the suspended load originating from the ancient source ($C_{\text{rock}} * M_{\text{tot}}^{-1}$) is largely invariant (equation 3). Extrapolation of equation (3) to $\Delta_{\text{tot}} = -1000\text{‰}$ shows that ~ 0.5 wt% of rock-derived POC may be amenable for export in all four drainage regions (Figure 3a). This supports an earlier observation of *Blair et al.* [2003] who examined an overlapping but smaller data set (Eel, Lanyang Hsi, Santa Clara). Although not extensive, wt% POC values that are currently reported for the basement rocks in these watersheds vary by at least an order of magnitude: 1.1 wt% in the Eel [*Leithold and Blair*, 2001], 0.44 wt% in the Lanyang Hsi [*Kao and Liu*, 2000], 0.2 to >4 wt% in the Santa Clara (Table 1), and predominance of carbonates and sandstones in the Papua New Guinea rivers [*Raymond*, 1999, and references therein]. Therefore, the close agreement of $C_{\text{rock}} * M_{\text{tot}}^{-1}$ among these drainage regions is not due to similarities in wt% POC of the source material. Rather, a potential explanation is that a constant component of rock POC is exceptionally resistant to degradation, possibly due to association with clay minerals, and/or to molecular structure.

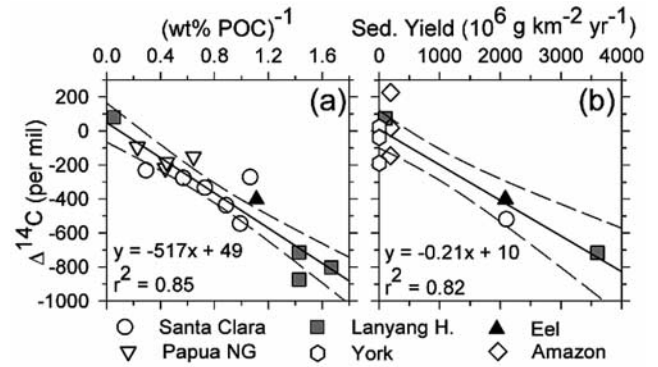


Figure 3. $\Delta^{14}\text{C}$ values of suspended POC against the inverse of wt% POC (a) and sediment yield (b). All $\Delta^{14}\text{C}$ values are for discrete samples from different dates or from different locations of the basin, except for the Santa Clara in (b), which is a discharge-weighted annual mean (-519‰). $\Delta^{14}\text{C}$ values of the Lanyang Hsi were calculated from % modern values of *Kao and Liu* [1996] following *Stuiver and Polach* [1977]. Dashed lines are 95% confidence limits.

[14] Under this scenario, the currently available data may be explained as follows. The persistence of rock-derived POC in these SMR is consistent with the “weathering-limited” denudation regime [*Stallard*, 1995] where the rate of physical denudation is greater than that of chemical denudation, resulting in export of incompletely weathered material. Nevertheless, chemical weathering is still effective to the extent that only the most recalcitrant components survive downstream export. Further studies examining the alteration of POC during exposure and disintegration of bedrock are required to evaluate this point.

3.3. $\Delta^{14}\text{C}$ of Suspended POC: Sediment Yield Model

[15] We further investigate the controls on the $\Delta^{14}\text{C}$ values of riverine POC through an examination of sediment yield. Sediment yield, defined as the sediment discharge normalized to the drainage area, is a function of both the rate of physical erosion and the basin’s sediment storage capacity. Hence, export of poorly weathered material may be enhanced under increased sediment yield, assuming that the rate of chemical weathering remains relatively constant. Compared to rivers of other morphologies, SMR exhibit high sediment yields because steep hillslopes and small basin sizes enhance physical erosion while limiting sediment storage [*Milliman and Syvitski*, 1992]. SMR should hence be efficient exporters of rock-derived POC according to this model. Where possible, we scale the sediment yield to exclude areas that produce limited sediment and POC (e.g. regulated by dams, or underlain by crystalline rocks). This facilitates comparison of sediment yields and corresponding $\Delta^{14}\text{C}$ signatures of suspended POC across dissimilar watersheds, including those that fall outside the SMR classification [*Milliman and Syvitski*, 1992].

[16] We also believe that the use of sediment yield to describe $\Delta^{14}\text{C}$ values complements our wt% POC model. In our wt% POC model, two of the six data points in the Papua New Guinea data set (not shown) exhibited anomalously low wt% POC, especially following a local rain event [*Raymond*, 1999] which may have mobilized OC-poor bedrock. In contrast, because our sediment yield model is

free of parameters with units of concentration, it should be less susceptible to dilution by detrital minerals.

[17] Seven rivers of contrasting morphologies were selected: a small low-relief river (York [Raymond and Bauer, 2001]), three SMR (Lanyang Hsi [Kao and Liu, 1996], Eel (N. Blair, personal communication, 2003), Santa Clara (this study)), and a large high-mountain river (Amazon [Hedges et al., 1986; Druffel et al., manuscript in preparation]). Sediment yields were from Milliman and Syvitski [1992] for the Amazon and Eel, Langland et al. [1998] for the York, and Kao and Liu [1996] for the Lanyang Hsi. Sediment yield for the Santa Clara was derived using data from Warrick [2002]. Additional rivers whose $\Delta^{14}\text{C}$ values of POC exist in the literature, but could not be included in the data set, are: Papua New Guinea rivers [Raymond, 1999] and the Parker [Raymond and Bauer, 2001], due to unavailability of sediment yield data; and the Hudson [Raymond and Bauer, 2001], because samples were collected within the tidal freshwater portion of the river downstream of a dam that regulates ~60% of the drainage basin (P. Raymond, personal communication, 2003).

[18] Consistent with the predictions, our preliminary results show a drop in $\Delta^{14}\text{C}$ of suspended POC by >600‰ as sediment yield increases from $0.01 \times 10^6 \text{ g km}^{-2} \text{ y}^{-1}$ (York) to $3600 \times 10^6 \text{ g km}^{-2} \text{ y}^{-1}$ (Lanyang Hsi; Figure 3b). Although the correlation is driven by SMR data, the Amazon and York data do not deviate from the trend; sediment yield may therefore be a useful proxy for the $\Delta^{14}\text{C}$ signatures of POC suspended across a wide range of rivers. POC of river suspended load has long been known to converge to ~0.5 wt% with increasing turbidity [e.g., Meybeck, 1982; Ludwig et al., 1996]. The cause of the convergence is still unclear, but bedrock [Meybeck, 1993] and soil [Ludwig et al., 1996] erosion have been proposed. Assuming that turbidity increases with increasing sediment yield, our findings support a decrease in the $\Delta^{14}\text{C}$ value of suspended POC with increasing turbidity (Figure 3b) as a result of greater contribution of the ancient rock-derived source having ~0.5 wt% POC (Figure 3a).

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