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The role of effective discharge in the ocean delivery of particulate organic carbon by small, mountainous river systems

Robert A. Wheatcroft,[a,*] Miguel A. Goñi,[a] Jeff A. Hatten,[a,1] Gregory B. Pasternack,[b] and Jonathan A. Warrick[c]

[a] College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, Oregon
[b] Department of Land, Air and Water Resources, University of California–Davis, Davis, California
[c] United States Geological Survey, Western Coastal and Marine Geology, Santa Cruz, California

Abstract

Recent research has shown that small, mountainous river systems (SMRS) account for a significant fraction of the global flux of sediment and particulate organic carbon (POC) to the ocean. The enormous number of SMRS precludes intensive studies of the sort conducted on large systems, necessitating development of a conceptual framework that permits cross-system comparison and scaling up. Herein, we introduce the geomorphic concept of *effective discharge* to the problem of source-to-sink POC transport. This idea recognizes that transport effectiveness is the product of discharge frequency and magnitude, wherein the latter is quantified as a power-law relationship between discharge and load (the 'rating curve'). An analytical solution for effective discharge (Q_e) identifies two key variables: the standard deviation of the natural logarithm of discharge (σ_q), and the rating exponent of constituent i (b_i). Data from selected SMRS are used to show that for a given river Q_e-POC < Q_e-sediment, Q_e for different POC constituents (e.g., POC_{fossil} vs. POC_{modern}) differs in predictable ways, and Q_e for a particular constituent can vary seasonally. When coupled with the idea that discharge peaks of small rivers may be coincident with specific oceanic conditions (e.g., large waves, wind from a certain direction) that determine dispersal and burial, these findings have potentially important implications for POC fate on continental margins. Future studies of POC transport in SMRS should exploit the conceptual framework provided herein and seek to identify how constituent-specific effective discharges vary between rivers and respond to perturbations.

Delivery of particulate organic carbon (POC) from the land to the sea by rivers and its eventual burial in ocean sediments are critical processes in the global carbon cycle. Sequestration of POC in marine sediments is a major long-term sink of CO_2 and a net source of oxygen over millennial time scales (Berner 1982; Ludwig et al. 1998). The majority (> 80%) of the long-term POC burial in the oceans occurs on continental and insular margins, where terrestrially derived carbon is apt to be most significant (Hedges and Keil 1995). Despite much attention, fundamental, unresolved questions remain in regard to the flux and fate of terrigenous POC across the land–ocean interface (Hedges et al. 1997). For example, some studies suggest that most terrigenous POC is degraded efficiently and little is preserved in ocean margins (Keil et al. 1997; Aller et al. 2004). Conversely, other investigations show that terrigenous POC accounts for the majority of organic matter preserved on continental margins (Leithold and Hope 1999; Goñi et al. 2005). Uncertainty also surrounds the relative contributions of POC of different age, ranging from fossil to modern, which is transported by rivers. Current estimates of the fossil or 'petrogenic' content of riverine POC (i.e., POC derived from sedimentary rocks) range from < 10% to 75% and display extensive geographical and temporal variability among and within watersheds (Masiello and Druffel 2001; Blair et al. 2003; Hilton et al. 2008*b*). Because the sequestration of nonfossil biogenic POC in marine sediments is a major contributor to CO_2 drawdown, whereas the burial of petrogenic POC is not, it is important to assess which of these values is more representative.

Among river basins, small ones (< 2×10^4 km^2) with high relief (> 1000 m) account for a significant fraction of the global sediment flux to the ocean (Milliman and Syvitski 1992) and likely contribute a similar fraction of terrigenous POC flux (Lyons et al. 2002; Gomez et al. 2003; Coynel et al. 2005). These mountainous systems display high particulate yields (kg km^{-2} yr^{-1}) and behave quite differently from large rivers with vast inland storage that have been the focus of much prior research. For example, discharge by small, mountainous river systems (SMRS) is highly episodic, with most of it occurring during periods of elevated rainfall associated with storms that affect nearshore waters and river basins simultaneously. Thus, SMRS are coherent across the land–ocean boundary. In addition, SMRS (because they are small) are likely to be more easily perturbed by natural and anthropogenic forcings. In spite of its potential global importance, a quantitative understanding of riverine POC flux by SMRS and its effect on carbon burial on ocean margins is lacking. In this selective review we focus on the question of not how much POC is delivered by SMRS, but *when POC is delivered to the coastal ocean* (i.e., under what discharges). Further, we will show that the timing of POC delivery has potentially important implications for the oceanic fate of terrestrial carbon.

Thousands of SMRS discharge into the coastal ocean (Vörösmarty et al. 2000); therefore, studying all of these

* Corresponding author: raw@coas.oregonstate.edu

[1] Present address: Department of Forestry, Mississippi State University, Starkville, Mississippi

dispersal systems in detail is not feasible. As an alternative, general principles that explain the export of POC by SMRS and its subsequent fate on ocean margins should be identified and tested. Herein, we propose that the concept of *effective discharge*, a well-established principle in geomorphology (Wolman and Miller 1960), has tremendous heuristic value when considering source-to-sink transfer of POC. According to this principle, the effectiveness of a geomorphic process depends on both its magnitude and frequency, which are interdependent. That is, an event that occurs frequently is typically of low magnitude and vice versa. For many natural functions, including sediment flux from a watershed, high-frequency events transport too little material to be effective, while low-frequency events do not occur often enough to be effective. Based on this recognition, Wolman and Miller (1960) postulated that events of intermediate frequency and magnitude would be most important for transporting sediment and, therefore, shaping the landscape.

In the roughly 50 yr since the original idea, the concept of effective discharge has been applied in a host of studies that have demonstrated its tremendous utility (Andrews 1980; Nash 1994; Doyle et al. 2005). It has now been shown that the most effective discharge for any particular process does not have to be an intermediate value, but depends on the type of process under consideration, the climate, and the spatiotemporal scale of interest. For example, ecological functions (e.g., incubation of fish embryos in riverbeds; Vadas 2000) that depend on persistent stability of the landscape have relatively low effective discharges. Functions with high thresholds of initiation, such as coarse sediment transport in mountainous rivers, have relatively higher effective discharges (Grant et al. 1990) or multiple ones (Lenzi et al. 2005).

The challenge of source-to-sink POC transport

Source-to-sink transfer of POC involves a complex set of linked atmospheric, terrestrial, and oceanic processes that operate over a wide range of time and space scales (Blair et al. 2004; Cole et al. 2007). Despite the scope of these processes, two terms are most important in determining delivery of POC to the ocean: river discharge and constituent load.

River discharge—The volume flux of water ($m^3 s^{-1}$)—discharge—measured at some point along a river, is determined by the production and routing of freshwater across and within the landscape. Because of its obvious role in determining flood potential and the management of water resources, this topic has received much study. The space–time variability of precipitation exerts important controls on the frequency distribution of discharge. Patterns of precipitation amount and intensity vary over event (Ralph et al. 2006), seasonal (Leung et al. 2003), decadal (Cayan et al. 1998), and millennial (Knox 2000) timescales. Similarly, precipitation amount and intensity varies spatially over kilometer (Anders et al. 2007) to continental scales. At the small and short ends of the space–time continuum, there is clear coupling in precipitation variability that is caused orographically, whereby subtle shifts in wind direction relative to mountain topography can exert first-order control on precipitation rate and amount (Roe 2005). At the basin scale, the source of precipitation, whether convective or cyclonic, will determine its spatial extent, with the former resulting in smaller scales of variation (Smith et al. 2004). Coupling also occurs at larger and longer scales via teleconnections and consequent shifts in storm tracks. For example, precipitation along the west coast of North America has a close relationship with the phase of the El Niño–Southern Oscillation and the Pacific Decadal Oscillation (PDO; Cayan et al. 1999; Neal et al. 2002).

An additional complicating factor that is particularly important at the event scale is the phase of the precipitation; that is, rain vs. snow or ice. In mountainous river basins, small fluctuations in the height of the snowline can have marked effects on subsequent runoff rate, leading to so-called rain-on-snow events that are often responsible for severe flooding (McCabe et al. 2007). Because of the obvious role of temperature in determining the form of precipitation, changes in regional to global climate will have important implications for water budgets (Mote 2006; Feng and Hu 2007).

Once delivered to the landscape, either as snowmelt or rain, water is subject to an additional set of complex processes and characteristics that collectively determine runoff in its broadest sense and, hence, river hydrographs. For example, vegetation type and density have been shown to affect runoff, either directly, via canopy interception and subsequent evapotranspiration (Peel et al. 2002), or indirectly through their effects on soil characteristics such as infiltration rate and microtopography (Dunne et al. 1991). Independent of any vegetation effects, the underlying geology of a catchment will also influence runoff patterns and amounts (Dietrich et al. 1992). Coupled to this spatial variability is the important role of temporal variability, whereby antecedent moisture conditions or seasonal vegetation cover may affect infiltration and runoff. Thus, identical rainfall amounts early vs. late in a rainy season may result in markedly different hydrographs. Equally important, human activities such as deforestation and urbanization can dramatically influence the rainfall-runoff relationship (Bowling et al. 2000; Warrick and Rubin 2007).

Space–time variation of rainfall and snowmelt is acted upon by the filtering capacity of a watershed to produce temporal variability in river discharge. Variability of SMRS discharge is illustrated by considering the Alsea (865 km^2) and Saco (3350 km^2) Rivers, two representative, albeit temperate, small, mountainous rivers in western Oregon (U.S.A.) and New England (U.S.A.), respectively. First, both rivers, but especially the Alsea, are event-dominated, characterized by rapid and short-lived peaks in discharge that can be $>$ 30 times the mean discharge, but last for only 1–2 d (Fig. 1A). This short response time is an important characteristic of SMRS that links them to conditions in the coastal ocean. Second, the number and magnitude of discharge peaks may be distributed throughout the year (Saco) or be clustered in a rainy season (Alsea;

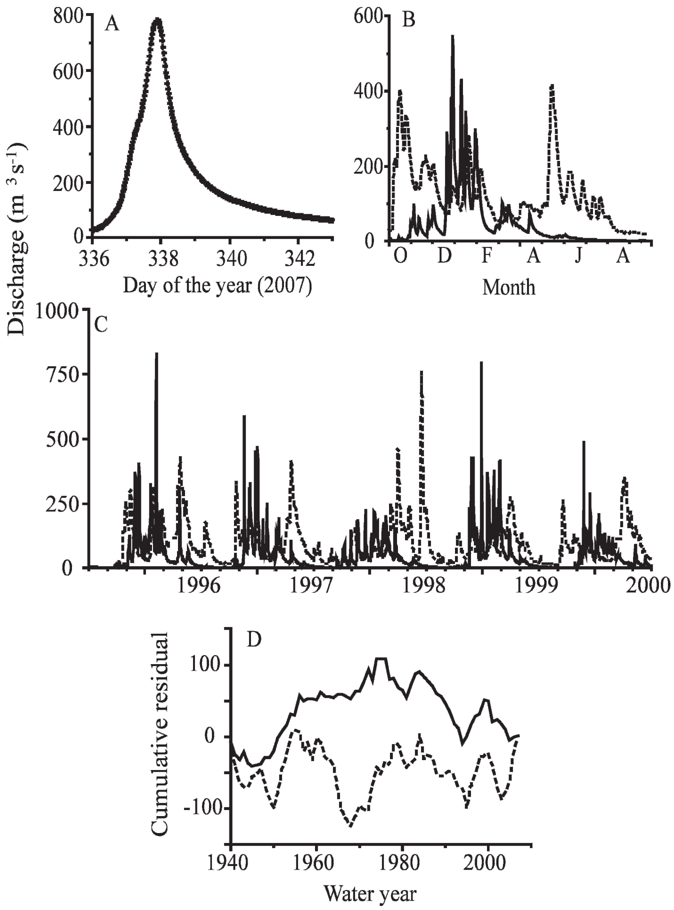

Fig. 1. Examples of temporal variability in the discharge of the Alsea River, central Oregon Coast Range, U.S.A. (solid lines), and the Saco River, northern Appalachian Mountains, U.S.A. (dashed lines) on time scales of (A) event (Alsea only), (B) annual (water year 2006), (C) inter-annual (water years 1996–2000), and (D) inter-decadal (1940 to present). Data were collected by the U.S. Geological Survey at gauging stations 14306500 (Alsea) and 01066000 (Saco).

Fig. 1B,C). Although not all rivers share the pronounced seasonality of the Alsea, many of them do (note the discharge peak associated with spring snowmelt on the Saco; Fig. 1C), and this seasonality has potentially important effects on the amount and composition of POC delivered during the year. Third, both the total annual discharge and the existence and number of large events varies inter-annually (Fig. 1C), and this variability can often be related to large-scale climatic forcing. For example, the Alsea's discharge during the 1997–1998 El Niño was considerably lower than during adjacent years (Fig. 1C). Lastly, simple time-series analyses, such as a plot of the cumulative residual of annual discharge (Wheatcroft and Sommerfield 2005), reveals sustained wet or dry periods that vary in length and timing. In some cases, the hydroclimatology is forced remotely, in the case of the Alsea by the PDO, which was in its cold phase from 1945 to 1975 (Fig. 1D); in other instances (Saco) the source of the variability is less clear.

In summary, precipitation at a point behaves as a random variable through time and is subject to wide variation, including many zero values. This temporal variability is dampened as water propagates through the drainage basin due to storage effects and averaging over large spatial scale, but river discharge at the outlet of a basin still shows strong random variation (Pasternack 1999). Therefore, it is standard to take a probabilistic approach to describe temporal variations in discharge. Most commonly, it uses frequency analysis of daily flows, wherein the probability of a discharge is described by various distribution functions (e.g., 2- or 3-parameter log-normal, Pearson Type III).

Constituent load—Water flowing across the landscape carries with it both dissolved and solid (sediment, POC) constituents, most of which are eventually transported to the ocean. This simple statement encompasses a wide range of processes and variables that collectively make the prediction of constituent loads (kg yr^{-1}) exceptionally challenging (Cohn 1995; Syvitski et al. 2000). Nevertheless, the importance of this topic has motivated the development of a number of sophisticated process-response models (Coulthard 2001), as well as the creation of large observational programs (e.g., U.S. Geological Survey National Water-Quality Assessment Program).

The first set of processes that determine constituent load involves the development of soil and its mobilization from hill slopes to channels (Dietrich and Dunne 1978). Studies show that soil production depends on a wide variety of physical and biological processes, including wetting–drying and freezing–thawing cycles, tree-throw, and animal bioturbation (Heimsath et al. 2001; Gabet et al. 2003). Once produced, soil can be transported down slope by creep, mass movements (e.g., shallow land-sliding and debris flows), overland sheet wash, and channelized (i.e., gully) sediment transport. The existence and potential importance of these soil production and transport processes varies spatially and temporally and depends on both intra-basinal (lithology, vegetation) and extra-basinal (hydroclimate) effects. In the absence of soil, subaerial bedrock can be eroded by chemical attack and temperature fluctuations, thereby passing directly to streams.

Once delivered to channels, solids are moved downstream or exchanged with various bioreactive reservoirs (e.g., soils in the riparian zone or floodplain). Sediment within channels is mobilized by flowing water as either bed load (particles in intermittent contact with the bed) or suspended load (particles supported by fluid turbulence). Consequently, discharge exerts a first-order control on both types of sediment load, with a positive, monotonic relation. In many instances, bed load constitutes $< 1\%$ to 10% of a river's load; hence, focus is usually placed on measuring and estimating suspended load (Cohn et al. 1989; Syvitski et al. 2000). The relation between suspended sediment concentration and discharge, the so-called sediment-rating curve, is often modeled as a power law (Cohn 1995; Vogel et al. 2003). If sediment supply is limited during large discharge events, then the sediment-rating curve has downward curvature. Alternatively, processes such as landsliding may lead to threshold behavior, which results in upward curvature of the sediment-rating curve (Hicks et al. 2000; Hilton et al. 2008*a*). Similarly, over the course of a rainy season in semiarid environments, sediment concentrations at a given discharge usually decrease through the season as material is flushed out of the watershed.

Points used to calibrate sediment-rating curves often exhibit significant scatter around the discharge-based predictive function. There are two primary factors that explain this variability independent of discharge: runoff source and scaling. First, for any given discharge, the source and concentration of sediment varies as a function of runoff type. Groundwater does not carry sediment into rivers, whereas overland flow does. Overland flow that occurs because infiltration capacity is exceeded moves over a longer path and, thus, has greater duration of contact with loose soil particles that may be entrained and transported to channels. Overland flow that occurs due to soil saturation preferentially occurs first in convergent hollows closer to channel heads and, thus, has a shorter overland path along which to pick up particles. This phenomenon is expressed in observational data of discharge and suspended sediment concentration during a single event as a so-called 'hysteresis loop,' whereby the sediment concentration on the rising limb of a hydrograph is different (usually higher) from that at a given discharge on the falling limb (Whitfield and Schreier 1981; Gao and Pasternack 2007). Second, for any given discharge, the range of sediment concentration is a predictable function of spatial and temporal scales. Small basins exhibit a sensitive response to short-duration, intense local storms and the effects of land use and vegetation. However, such local effects rarely occur over a whole large basin simultaneously. For example, landslides can only occur on relatively steep slopes, so large basins with large areas of mid- and lowlands cannot ever experience simultaneous landslide production of sediment over their whole areas (Benda and Dunne 1997). Overall, the differential timing of precipitation, land use and land-cover effects in different sub-basins causes a smoothing effect that keeps the range of sediment concentration in large streams smaller than that exhibited in smaller upstream tributaries.

In addition to sediment, rivers transport a heterogeneous mixture of organic matter (OM) that ranges from reactive freshwater phytoplankton and discrete vascular plant debris to more resistant organic matter bound to inorganic particles from soils and bedrock (Hedges et al. 1986; Masiello and Druffel 2001; Raymond et al. 2004). The same mechanisms and factors that control the concentration and composition of the inorganic sediment load, also mobilize distinct pools of OM. Hence, discharge also exerts first-order control on concentration and composition of POC in most SMRS. For example, Gomez et al. (2003) showed that the composition of POC (expressed as OC content, C:N ratios, δ^{13}C values) in New Zealand's Waipaoa River changes with discharge, reflecting the differential mobilization of distinct pools of OM. At low flows, most of the POC is plant detritus entrained from topsoils of riparian origin. In contrast, at moderate discharges the composition of POC suggests a significant fraction is derived from deeper soil horizons mobilized by gully erosion. Finally, during extreme discharge events, the POC composition reflects regolith and bedrock sources mobilized by landslides. It is important to note that the absolute concentrations of all of these OM pools increase with increasing discharge, but that they do so at different rates. Similar processes have been invoked to explain the variable compositions of POC in other rivers (Kao and Liu 1996; Masiello and Druffel 2001; Goñi et al. 2005). Based on these observations, we expect that the rating curve for bulk POC would be different from that of inorganic sediments and that different pools of OM likely have distinct rating curves, which reflect the compositional differences of the POC observed at different flows.

Analytical estimates of effective discharge

Effective discharge of suspended matter is the product of flow frequency and transport magnitude (Wolman and Miller 1960) and, as the preceding section has shown, these variables depend on a host of other processes and parameters. Nevertheless, by considering explicitly the functional form of transport magnitude and frequency the idea of effective discharge can be further developed (Wolman and Miller 1960; Nash 1994; Vogel et al. 2003). We start by considering that a river's discharge is often log-normally distributed (Fig. 2); hence, the frequency distribution of the logarithm of daily discharge (ln Q) is

$$f(\ln Q) = \frac{1}{\sigma_q\sqrt{2\pi}} \exp\left\{-\left[(\ln Q - \langle Q\rangle)^2 \Big/ 2\sigma_q^2\right]\right\} \quad (1)$$

where $\langle Q\rangle$ and σ_q are the mean and standard deviation of ln Q, respectively. Further, if the suspended load of constituent i, L_i, is a power-law function of discharge (Fig. 2), that is

$$L_i = a_i Q^{b_i} \quad (2)$$

where a_i and b_i are the empirically determined rating coefficient and exponent, respectively (Cohn 1995; Syvitski et al. 2000), then the transport effectiveness (E; Fig. 2) is the product of $f(\ln Q)$ and L_i.

The maximum of the transport effectiveness curve (Fig. 2), the effective discharge, Q_e, can be determined by setting $\partial E/\partial Q = 0$ and solving for Q, which for the examples used herein yields (Nash 1994; Goodwin 2004)

$$Q_e = \exp\left[b\sigma_q^2 + \langle Q\rangle\right] \quad (3)$$

A very important point to note is that the idea of an effective discharge is not specific to either the functional form of the discharge distribution (Eq. 1) or the relationship between discharge and load (Eq. 2), and many analytical versions of Eq. 3 exist (Vogel et al. 2003; Goodwin 2004). The overall conclusions made below will not change with other functional forms; however, for the purposes of further discussion we will assume log-normality and a power law as adequate representations of the discharge probability distribution function and constituent load, respectively.

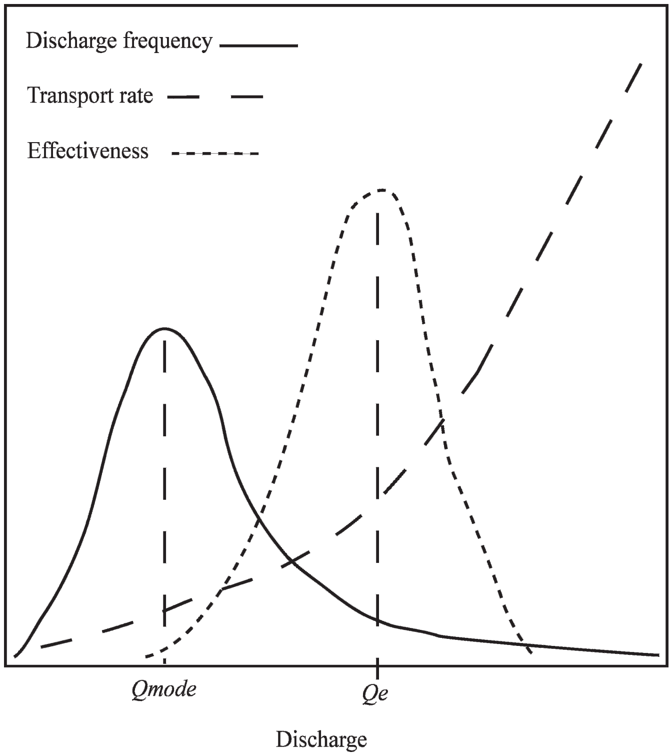

Fig. 2. Graphical representation of the probability distribution function of discharge (solid line), transport rate or load (dashed line), and the resultant effectiveness curve (dotted line). Also shown are the discharge mode and the effective discharge, Q_e (after Wolman and Miller [1960]).

Two key implications arise from the preceding. First, because rivers differ in the magnitude ($\langle Q \rangle$) and variability (σ_q) of their discharge, the effective discharge of a given constituent will also vary between rivers even if the rating curve was the same. Moreover, as discharge variability increases, the magnitude of the effective discharge also increases (Nolan et al. 1987; Vogel et al. 2003). Thus, all other issues being equivalent, one would expect that rivers in arid environments, which are characterized by extreme variability, to have much larger effective discharges relative to their mean discharge than rivers in more temperate environments. Second, for any given river, the effective discharge of different constituents (sediment, POC, dissolved organic carbon [DOC]) will vary because the discharge-specific concentration (load) of that constituent varies. As the rating exponent (b_i) for constituent i increases, the effective discharge of that constituent will also increase. Moreover, the larger the separation between rating exponents of different constituents, the larger the difference in effective discharges, even though the probability distribution function of the discharge has not changed. This potential separation of the effective discharge of various suspended constituents means that they may be delivered to the coastal ocean under varying conditions that will favor either dispersal or burial (discussed below).

Case studies

Although the idea that there are different effective discharges of delivery for various river constituents is a potentially powerful one, the data required to test this hypothesis rigorously are lacking. Therefore, in the following we examine several SMRS where some of the necessary parameters have been collected. Our purpose is to explore the potential of the Q_e concept and highlight important knowledge gaps.

One of the best-studied SMRS is the Waipaoa River of the North Island of New Zealand (Gomez et al. 2003, 2004; Hicks et al. 2004). Although the basin area is < 1600 km^2 and average discharge is ~ 35 m^3 s^{-1}, intense rainfall and severe deforestation by European settlers have resulted in an estimated suspended-sediment load of 14×10^9 kg yr^{-1} (Hicks et al. 2004). A 13-yr record of daily discharge data was found to be approximately log-normal (Fig. 3A) and yielded estimates of $\langle Q \rangle$ and σ_q that were 2.75 and 1.10, respectively (Table 1). Next, suspended sediment and POC data collected from June 1999 to April 2000 at the Kanakanaia gauging station (Gomez et al. 2003), the location of the discharge measurements, were used to estimate rating curves for each constituent (Fig. 3B). Applying Eq. 3 to the derived values results in Q_e estimates for sediment and POC of 292 m^3 s^{-1} and 197 m^3 s^{-1}, respectively, which represent $Q : Q_{mean}$ of 8 and 6 (Table 1). Hence, as one might expect from considering how different constituents are mobilized in response to erosive events (Gomez et al. 2003; Hilton et al. 2008*a*, *b*), POC delivery likely occurs at a lower effective discharge that occurs more frequently relative to effective discharge for sediment delivery.

The generality of the Waipaoa results may be extended by considering the aforementioned Alsea River of western Oregon. The Alsea basin is roughly half the size of the Waipaoa, but has a slightly higher average discharge (~ 42 m^3 s^{-1}). Daily discharge measurements over the full period of record (1939 to present) yielded estimates of $\langle Q \rangle$ and σ_q that were 2.84 and 1.38, respectively. A suspended sediment and POC sampling effort during water year 2008 (J. A. Hatten unpubl.) collected samples over a broad range of discharges ($\sim$ 50-fold), which has yielded results comparable to an earlier sampling effort by the U.S. Geological Survey (Fig. 4). Similar to the Waipaoa River, the rating exponent (b_i) for POC was considerably less than that obtained for sediment, thereby resulting in Q_e values of 1925 m^3 s^{-1} and 970 m^3 s^{-1} for sediment and POC, respectively. These flows are quite large and correspond to $Q : Q_{mean}$ of roughly 46 and 15, with return periods of many decades. These large effective discharges are consistent with prior estimates made for Pacific Northwest rivers based on both empirical measurements (Nolan et al. 1987) and the analytical approach (Nash 1994) described herein.

The idea that different riverine constituents (e.g., POC vs. sediment) have distinct effective discharges can be applied to different components of the POC load (e.g., fossil or petrogenic carbon vs. modern carbon). Research conducted by Kao and Liu (1996, 1997, 2002) in the 980-km^2 Langyang-Hsi River basin, an SMRS draining the

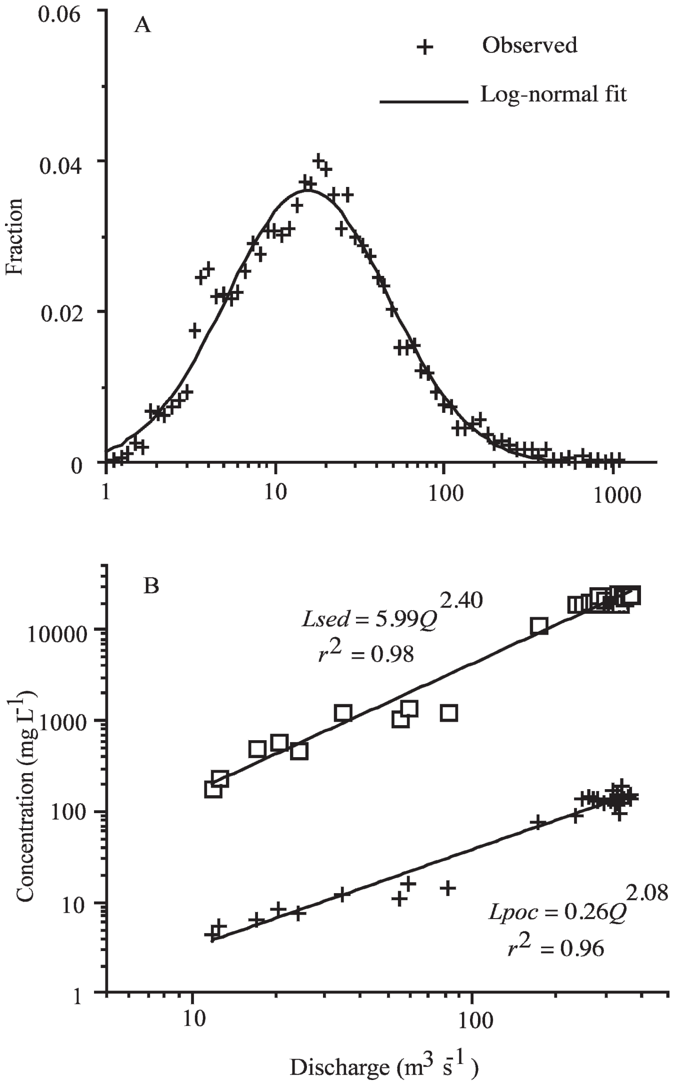

Fig. 3. (A) The observed (pluses) frequency distribution of discharge measured at the Kanakanaia gauging station on the main stem of the Waipaoa River (Hicks et al. 2000) and a log-normal fit (solid line). (B) Suspended sediment (open squares) and POC concentration (pluses) in mg L^{-1} as a function of discharge (m^3 s^{-1}) at the Kanakanaia gauging station (data from Gomez et al. 2003). The resultant power laws are for fits between Q and the constituent-specific load (L_i).

mountains of NE Taiwan, supplies the necessary data. Starting with tabulated data collected by Taiwan's Water Resources Agency, a 20-yr record of daily discharge from the Lang-Yang Bridge gauging station (No. 2560H006; http://gweb.wra.gov.tw/wrwebeng/) was used to estimate $\langle Q \rangle$ and σ_q, resulting in 3.96 and 0.91, respectively (Table 1). Suspended-sediment samples were collected over an 11-month period, and analyzed for total suspended matter and POC content (Kao and Liu 1996). In addition, the $\Delta^{14}C$ composition of a small number of samples was determined and these data used to estimate the fraction of fossil (i.e., ^{14}C-free) and modern (i.e., ^{14}C-replete) POC (POC_{fossil} and POC_{modern}, respectively). Although this approach oversimplistically assumes that $\Delta^{14}C$ composi-

Table 1. Literature-derived parameters for several small, mountainous river systems.

River and constituent	Q_{mean} (m^3 s^{-1})	$\langle Q \rangle$	σ_q	b_i	Q_e (m^3 s^{-1})
Waipaoa	35	2.75	1.10	—	—
sediment	—	—	—	2.40	285
POC (total)	—	—	—	2.08	194
Alsea	42	2.84	1.38	—	—
sediment	—	—	—	2.48	1,925
POC (total)	—	—	—	2.12	970
Langyang-Hsi	61	3.96	0.91	—	—
sediment	—	—	—	2.13	306
POC_{fossil}	—	—	—	2.12	304
POC_{modern}	—	—	—	1.78	229
Nivelle	5	NK*	NK*	—	—
POC-summer	—	—	—	2.46	155
POC-winter	—	—	—	1.87	66

* NK = not known.

tions only reflect variable mixtures of fossil and modern end members, rather than the presence of aged carbon with different residence times in the watershed, it allows us to assess whether different pools of POC (fossil vs. modern) have distinct rating curves. Indeed, the resultant rating exponents are 2.13, 2.12, and 1.78 for sediment, POC_{fossil} and POC_{modern}. Not surprisingly, the exponents of sediment and POC_{fossil} are nearly identical and much greater than that of POC_{modern}. Such differences are consistent with the discharge-dependent mechanisms responsible for the mobilization and export of different types of particles discussed previously (e.g., topsoil and gully erosion, landslides [Leithold and Blair 2001; Gomez et al.

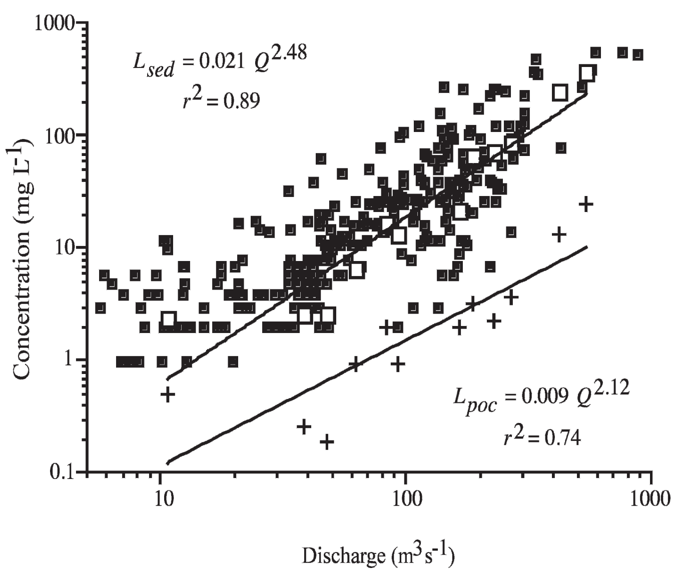

Fig. 4. Suspended sediment (open squares) and POC (pluses) as a function of discharge measured on the Alsea River during water year 2008 (J. A. Hatten unpubl.). In addition, sediment data (solid squares) collected by the U.S. Geological Survey during water years 1973 and 1974 are shown for comparison. The resultant power laws are for fits between Q and L_i.

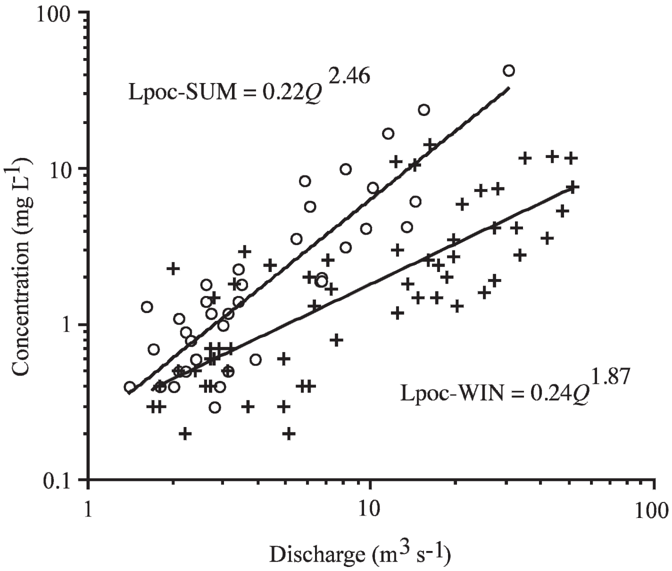

Fig. 5. Summer (open circles) and winter (pluses) POC concentration (mg L^{-1}) as a function of discharge (m^3 s^{-1}) for the Nivelle River at St. Pee-sur-Nivelle (from Coynel et al. 2005). The resultant power laws are for fits between Q and L_i.

2003]). Combining the rating exponents with the discharge parameters results in effective discharge estimates for sediment and POC_{fossil} and for POC_{modern} of 306 m^3 s^{-1}, 304 m^3 s^{-1}, and 229 m^3 s^{-1}, respectively (Table 1), which correspond to $Q : Q_{mean}$ ratios of $\sim$ 5 and 3.5.

The last case study centers on the Nivelle River, a very small river (238 km^2, Q_{mean} = 5.2 m^3 s^{-1}) that drains a portion of the Pyrenean mountains of SW France (Coynel et al. 2005). There, intensive (sometimes hourly) sampling of suspended sediment and POC over a 1-yr period (1996) revealed pronounced seasonality in the relationship between discharge and the concentration of sediment and POC. For both constituents, concentrations are higher for a given discharge during the summer months (Apr–Oct) compared to winter (Nov–Mar; Fig. 5), with rating exponents of 2.46 and 1.87 for the POC rating curves, respectively. Because the available discharge record is short (Coynel et al. 2005), it is not possible to provide accurate estimates of $\langle Q \rangle$ or σ_q (this issue is discussed in more detail below). Therefore, for illustrative purposes we have assumed σ_q = 1.2 and $\langle Q \rangle$ = 1.5, which together with the rating exponents listed above, yields effective discharges of 66 m^3 s^{-1} and 155 m^3 s^{-1} for winter and summer POC delivery, respectively. If, as is true in many temperate environments, wave energy is higher during the wintertime, then both the delivery *and* ocean dispersal of POC in the Nivelle River system will likely vary seasonally.

Implications

Previous sections have identified two key variables that determine effective discharge of different riverine constituents: discharge variability, σ_q, and constituent-specific rating exponent, b_i. In the following, we explore briefly the implications that variability in these two terms has for POC delivery, and then close by discussing how constituent-specific effective discharges might influence oceanic fate.

Discharge variability—For rivers with a two-parameter log-normal discharge distribution, σ_q provides the most succinct summary of discharge variability, and because this term is squared in the effective discharge relationship (e.g., Eq. 3), it is of primary concern. A useful step in predicting general patterns of effective discharge in unstudied SMRS would be to determine how σ_q varies as a function of basin area and climatic region. Based on data compiled by Nash (1994; his table 1) for 55 free-flowing rivers in the contiguous United States, there is a very weak negative relationship between basin area and σ_q, with much scatter (0.5–2.5) for small basins (10^2–10^4 km^2), but $\sigma_q \leq 1$ for larger basins. The reason for the latter is that larger basins have a wider diversity of water sources (snowmelt, groundwater), partial watershed coverage of rainfall, and greater transmission losses; hence, flows are steadier (Lane et al. 1997). The reason that smaller basins have such large variability in σ_q is likely related to hydroclimatic effects, whereby rivers in more arid environments have higher σ_q compared to those in wetter climates. In partial support for this statement is the fact that σ_q exhibits an inverse relationship with latitude along the well-known wet-to-dry climatic gradient of the U.S. West Coast, as shown by the Umpqua (northern, wetter), Eel and Salinas (southern, drier) Rivers, which have σ_q of 1.08, 1.98, and 2.65, respectively (analysis based on 50 yr of daily data for each river).

Two additional factors must be considered in determining patterns of σ_q: only a small fraction of SMRS are gauged, and humans now affect discharge in complex and subtle ways. Hydrometeorological models hold great promise for solving the first challenge. By taking a water-balance approach and considering basin relief effects, as well as temperature effects (rain vs. snow), models have demonstrated considerable skill in simulating individual event discharges (Miller and Kim 1996; Westrick and Mass 2001), as well as global runoff patterns (Fekete et al. 2002). An important next step is to run these models for a sufficiently wide range of SMRS over sufficiently long time periods (Kettner et al. 2007) to construct regional patterns in daily discharge variability and identify 'end-member' rivers (e.g., low vs. high σ_q) where constituent loads may be more rigorously quantified. Human effects on runoff and river hydrographs pose an even more difficult challenge because they often involve multiple, counterbalancing effects that are strongly dependent on basin scale. For example, deforestation typically leads to increased runoff and, hence, greater discharge peaks (Bowling et al. 2000), whereas reservoirs lead to increased evaporation or irrigation diversions. Despite this complexity, the acute societal need to determine water budgets has led to a growing body of empirical data (Vörösmarty et al. 2003), which may permit specific predictions of how σ_q has changed in recent decades.

Lastly, accurate determination of σ_q will be critical as highlighted by the marked differences in the magnitude and range of effective discharges derived for POC and sediment

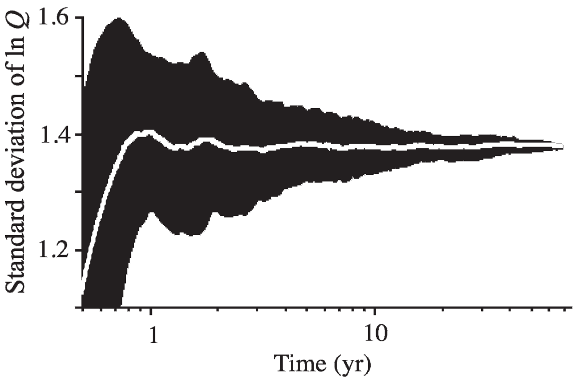

Fig. 6. The mean (white line) and standard deviation of σ_q as a function of the logarithm of record length in years. This figure was constructed using a re-sampling algorithm that randomly selected a starting point in the Alsea River daily discharge record ($n = 25{,}075$) and calculated the cumulative standard deviation of ln Q (σ_q) from 2 d to 25,075 d. This process was repeated 50 times and the mean and standard deviation computed from these realizations. Data are from the U.S. Geological Survey.

for the Alsea vs. Waipaoa Rivers despite similarities in their rating exponents (Table 1). To explore how much discharge data are needed to accurately describe a river's flow regime, we used an ~ 69-yr record of daily discharge ($n = 25{,}075$) for the Alsea River to calculate σ_q with an increasingly large data set (i.e., 2–25,075 data points). The result indicates that roughly 20 yr of daily discharge data are needed to reach a reasonably stable σ_q (Fig. 6). Although the rate at which a river's discharge statistics stabilize will vary between rivers (e.g., less time for tropical or snowmelt-affected rivers and more time for arid rivers), it suggests that, perhaps, the Waipaoa data record used herein was not long enough to capture its true σ_q.

The constituent-specific rating exponent—This term (b_i) represents the rate of increase of a constituent's concentration (and hence load) as a function of increasing discharge (i.e., it is the slope of the rating curve in log–log plots of discharge vs. constituent concentration; Cohn 1995; Syvitski et al. 2000). An increase in b_i will result in a larger effective discharge (Table 1). As shown herein, but in a very preliminary manner, the relative magnitude of b_i varies between constituents in a predictable manner (i.e., $b_{sediment} > b_{POC\text{-}fossil} > b_{POC\text{-}modern}$). This important result is in need of further testing and the range of constituents that are placed within this framework should be expanded. For example, OM descriptors based on size (coarse- vs. fine-POC, colloidal OC, DOC), biochemical composition (PN, proteins, lignins, lipids), age (modern vs. fossil), and density (organic detritus vs. mineral-associated POC) should be measured to develop rating curves for these different OM constituents in end-member rivers. For example, systematic differences in the magnitude of the rating exponent of POC vs. PN may elucidate how the contribution of different reservoirs within a river basin (e.g., hill slope vs. riparian corridor) varies as discharge increases. Similarly, rating exponents < 1 for DOC indicate dilution at high discharges (Doyle et al. 2005), and could be useful in identifying basins with high infiltration rates. Overall we expect that by targeting specific combinations of constituents and quantifying b_i, future investigations will be able to better unravel the complex set of processes responsible for organic matter mobilization in SMRS.

Ideally, rivers selected for future study should be representative of different hydroclimatic regions (wet tropical vs. temperate vs. Mediterranean), geology (friable vs. crystalline rocks), and varying levels of human perturbation (agriculture vs. timber harvest vs. road building). At a more detailed level, studies of riverine POC transport should at a minimum quantify constituent concentrations at a range of discharges. Although this statement may seem obvious, much prior research has been inadequate for the purposes used herein because one or both of these terms has not been well-characterized. Because a river's discharge continually varies, the mere act of sampling at different times results in data collection over a range of discharges. Unfortunately, as highlighted in multiple methods papers (Cohn et al. 1989; Cohn 1995; Horowitz 2003), such haphazard sampling will not likely capture the full range of the discharge distribution; hence, any attempts to determine a rating curve will fall short of the mark. In addition to capturing the widest possible range of discharges, it will be useful to spread sampling over different seasons to test whether there are predictable changes in POC composition or yield. Lastly, the possibility of event hysteresis between constituent concentration and discharge, as well as the short time scales of river discharge in SMRS calls for high-frequency sampling of floods to capture rising and falling limbs of the hydrograph.

River–ocean coherence—A key characteristic of SMRS, which distinguishes them from large-river systems, is that the movement of water and associated constituents from the hinterlands to the coastal ocean is event-dominated and occurs on time scales of hours to days (Fig. 1A; Wheatcroft et al. 1997). Therefore, discharge peaks often coincide with specific conditions in the coastal ocean, such as elevated wave energy or winds from a certain direction, forced by the weather systems that delivered the precipitation to the basins in the first place (Wheatcroft and Borgeld 2000; Harris et al. 2005). As a consequence, effective delivery of sediment and POC may occur under a relatively narrow range of oceanic conditions that favor or impede dispersal.

Coincidence of a particular discharge with a limited set of oceanic forcings has far-reaching implications for cross-margin transport and burial of solids. For example, on northern California's Eel River shelf, solids delivered during high discharges are rapidly removed from the surface plume in shallow water (Hill et al. 2000) where they cannot deposit because wave stresses are high (i.e., high discharges coincide with large waves). As material accumulates in the wave boundary layer, it eventually reaches concentrations that allow it to slide downhill, thereby providing efficient cross-shelf transfer (Traykovski et al. 2000; Scully et al. 2003). Deposition occurs where wave stresses are no longer high enough to maintain the solids in suspension (Harris et al. 2005). Because of the high accumulation rates in this region of the Eel shelf (Sommerfield and Nittrouer 1999), sediment and POC are rapidly moved through the surface-mixing layer of the seabed, resulting in efficient burial and preservation of sedimentary signals (Leithold and Hope 1999; Wheatcroft and Drake 2003). Conversely, under moderate discharge, concentrations of particles within the Eel River surface plume do not support rapid aggregation; hence, solids are 'stranded' in the plume (Hill et al. 2000; Geyer et al. 2004). Along-margin advection spreads material throughout the inner shelf, where it does eventually deposit under fair weather. This deposition is temporary, however, because subsequent storms re-suspend the material. In addition, because cross shelf transfer is minimal in typical Ekman bottom boundary layers, materials delivered during low-energy conditions are subject to repeated cycles of erosion and deposition that may lead to efficient degradation of POC.

It is important to recognize that river–ocean coherence does not mean that energetic waves always occur during discharge peaks. For example, flooding on the Hanalei River—a small, mountainous river on the island of Kaua'i—typically is caused by summertime convective storms that most often occur during quiescent ocean conditions (Draut et al. 2009). Therefore, sediment is deposited in relatively shallow water and is not remobilized until several months later under energetic winter conditions. Similarly, flooding on New Zealand's Waipaoa River occurs during offshore winds that result in relatively low wave energy (C. K. Harris unpubl.).

The possibility that different river constituents are delivered to the coastal ocean under specific oceanic forcings has interesting implications for understanding of the carbon cycle at the land–ocean interface. It may be that the timing of delivery (rather than the intrinsic chemical lability) of a given POC constituent controls its oceanic fate (i.e., mineralization vs. preservation). Temporal trends in the sedimentary records of coastal margins may, thus, reflect historical changes in river discharge characteristics (σ_q) and ocean conditions rather than putative changes in productivity or organic matter source. Variation in these latter factors has often been used to interpret down-core changes in the concentration and composition of terrestrial (and marine) POC in margin settings and link them to past climatic or anthropogenic changes. The possibility that historical changes in $\langle Q \rangle$ and σ_q, which reflect both climatic variability and human activity, may result in differences in the concentration and composition of terrestrial POC preserved in margin sediments should be tested in future studies of margin sedimentary records.

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