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**U.S. Department of the Interior**
**U.S. Geological Survey**

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# Suspended Sediment and Organic Contaminants in the San Lorenzo River, California, Water Years 2009–2010

By Amy E. Draut[1] , Christopher H. Conaway[1, 2], Kathy R. Echols[3], Curt D. Storlazzi[1], and Andrew Ritchie[1,4]

## Abstract

This report presents analyses of suspended sediment and organic contaminants measured during a two-year study of the San Lorenzo River, central California, which discharges into the Pacific Ocean within the Monterey Bay National Marine Sanctuary. Most suspended-sediment transport occurred during flooding caused by winter storms; 55 percent of the sediment load was transported by the river during a three-day flood in January 2010. Concentrations of polyaromatic hydrocarbons can exceed regulatory criteria during high-flow events in the San Lorenzo River. These results highlight the importance of episodic sediment and contaminant transport in steep, mountainous, coastal watersheds and emphasize the importance of understanding physical processes and quantifying chemical constituents in discharge from coastal watersheds on event-scale terms.

## Introduction

The San Lorenzo River drains a 350 km$^2$ watershed in the mountains of coastal California, debouching into Monterey Bay at the city of Santa Cruz (fig. 1). The San Lorenzo Basin primarily consists of uplifted and faulted marine sedimentary rocks that reach elevations of more than 760 m, and

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have steep, unstable slopes and erodible soils (Griggs and Paris, 1982). It is, therefore, an example of the class of streams with typically high sediment yield (small, steep, mountainous watersheds in tectonically active areas) known to contribute substantial quantities of sediment to the world's oceans (Milliman and Syvitski, 1992). The San Lorenzo ecosystem includes terrestrial aquatic habitat used by endangered and threatened species, such as steelhead (*Oncorhynchus mykiss*), tidewater goby (*Eucyclogobius newberryi*), western pond turtle (*Actinemys marmorata*), and red-legged frog (*Rana draytonii*), and the river discharges into sensitive marine habitats of the Monterey Bay National Marine Sanctuary. Many parts of the river corridor and the coastal region around its mouth are used extensively for human habitation and recreation, and the beaches near its mouth are economically important to the Santa Cruz area.

The U.S. Geological Survey (USGS) completed an event-based sampling program of the San Lorenzo River in Santa Cruz during water years 2009 and 2010 (October 1, 2008, through September 30, 2010) to analyze the amount and composition of suspended sediment and to assess quantities of some persistent organic pollutants transported by the river and entering Monterey Bay during high-flow events. Because high sediment loads and organic contaminants can negatively affect coastal ecosystems, data from this study support ongoing and future assessments of ecosystem health in the San Lorenzo watershed and Monterey Bay.

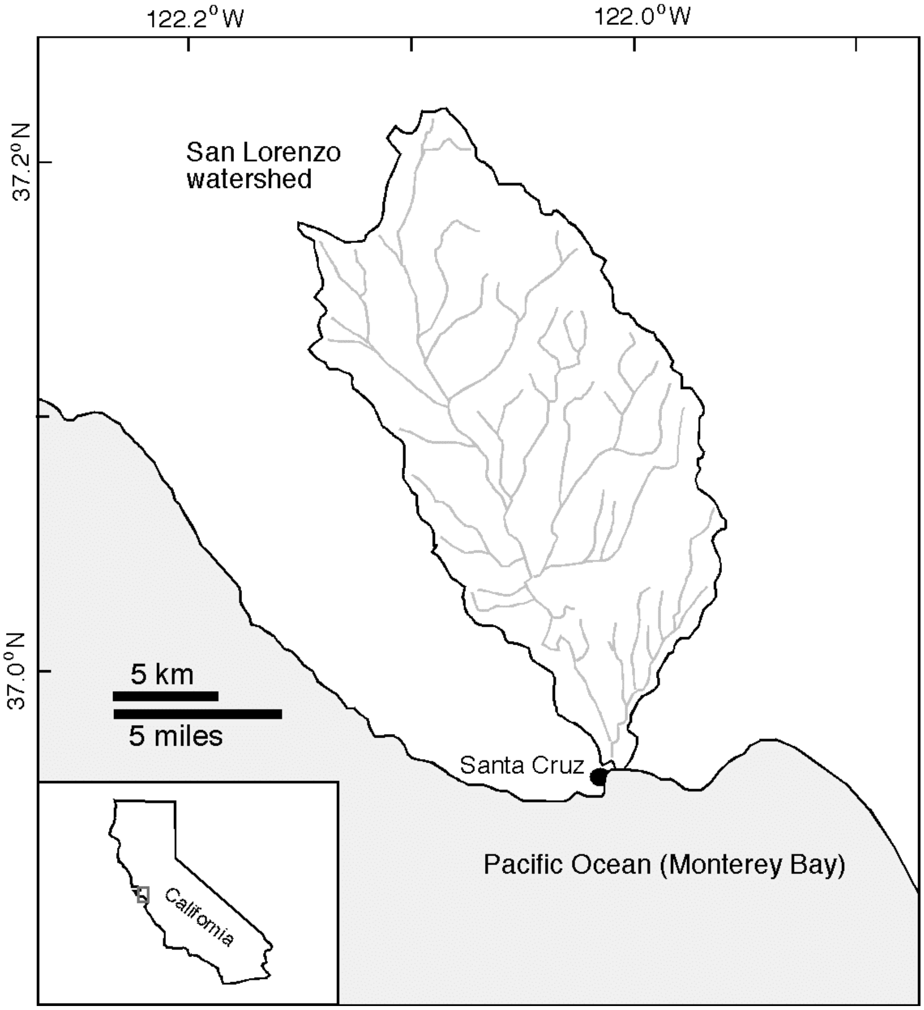


**Figure 1.** Location map showing the San Lorenzo watershed, central California.

## Project Objectives

The objectives of this study were twofold: (1) to quantify suspended-sediment concentration and grain size delivered by the San Lorenzo River into Monterey Bay, and (2) to measure concentrations of polycyclic aromatic hydrocarbons (PAHs) in the San Lorenzo River during high-flow events. Measuring suspended-sediment concentration and grain size supported complementary USGS investigations of sediment transport in shallow coastal waters offshore of Santa Cruz (Buscombe and others, 2010; Lacy and others, 2010; Rubin and others, 2010). Measurements of persistent organic pollutants in the river discharge are relevant to all recent and ongoing environmental and ecological studies of the San Lorenzo and nearshore Monterey Bay ecosystems (Copeland, 1986; Best and Griggs, 1991; Cahill, 2006; Central Coast Long-term Environmental Assessment Network, 2007; National Marine Fisheries Service, 2010).

## Study Site

Rainfall events, which are concentrated in late fall, winter, and early spring in the area's Mediterranean-type climate, commonly increase the San Lorenzo River flow by three to four orders of magnitude. Because of this hydrologic response to rain, and the opportunity for high flows to access potential sediment- and pollutant-source areas more readily than would low flows, water-sampling efforts were focused on high-flow events. Streamflow on the San Lorenzo River is monitored continuously by the USGS Water Resources Discipline at USGS gaging station 11161000 (San Lorenzo River near Santa Cruz; *http://waterdata.usgs.gov/ca/nwis/uv/?site_no=11161000*, last accessed February 20, 2011). The gaging station is approximately 4 km upstream of the river mouth (fig. 2). The 3.5-km reach of the San Lorenzo River between U.S. Highway 1 and the river mouth is confined entirely by man-made levees (Griggs and Paris, 1982).

Water samples were collected from a bridge-box sampling platform installed on a pedestrian bridge that spans the San Lorenzo River 2 km upstream of the river mouth (figs. 2 and 3). This sampling location was chosen as the downstream-most site where the sediment and contaminant content of the river could be assessed while involving minimal tidal influence and allowing safe personnel access. The sampling bridge is 200 m upstream of the confluence of ungaged Branciforte Creek and the San Lorenzo River (fig. 2), therefore, samples discussed in this report do not include any sediment or contaminants introduced by Branciforte Creek. For safety reasons, samples were collected only during daylight hours.


**Figure 2.** Aerial photograph showing the lowermost 6 km of the San Lorenzo River, Santa Cruz, California, the locations of U.S. Geological Survey gaging station 11161000, and the sampling bridge from which water samples were collected for this study. The river discharges into the Pacific Ocean within the Monterey Bay National Marine Sanctuary. Image from Google Earth, 2009.

# Methods

## Suspended-Sediment Concentration and Grain Size

Following standard methods, water samples for suspended-sediment analysis were collected using a US D-95 sampler (Edwards and Glysson, 1999; Federal Interagency Sedimentation Project, 2000) mounted on a bridge-box platform at a fixed location above the thalweg of the San Lorenzo River (fig. 3). The sampler was deployed using a hand-operated reel winch to maintain a constant transit rate during sampling. Depth-integrated samples were collected in 1-liter bottles using a 0.25-inch-diameter nozzle.

Suspended-sediment samples were analyzed at the USGS Water Resources Discipline laboratory in Marina, California. To analyze the concentration and the proportion of sand-sized material the samples were decanted after 7–10 days of settling time; excess water and organic matter were removed using wet suction from a vacuum pump, and the sand fraction was separated from silt and clay by filtering through a 0.063-mm sieve. Both fractions (sand and silt-plus-clay) of each sample were dried in crucibles in an oven at 103$^{o}$C and then weighed. On selected samples, grain size of the sand fraction was analyzed in further detail. The sand fraction of each sample was separated by wet-sieving with deionized water into 0.125-, 0.25-, 0.5-, and 1.0-mm fractions, oven-dried, and weighed. For several samples collected during a large flood in January 2010, the grain size distribution of the silt-and-clay fraction (divisions at 0.002, 0.004, 0.008, 0.016, and 0.031 mm between clay, very fine silt, fine silt, medium silt, and coarse silt, respectively) was analyzed by pipette separation.

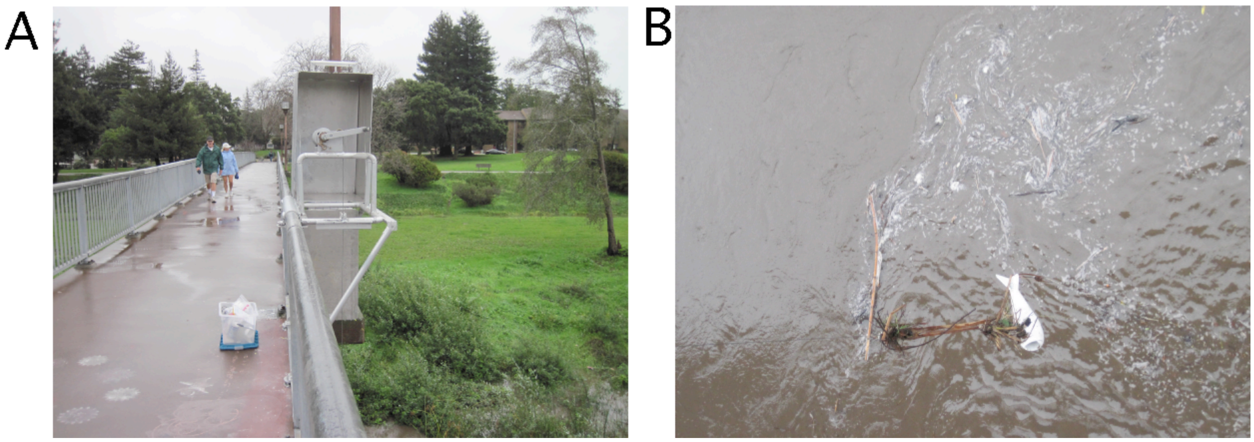


**Figure 3.** Field photographs of *A,* the bridge-box sampling platform; and *B,* the US D-95 sampler lowered from the pedestrian bridge into the San Lorenzo River, Santa Cruz, California.

### Sediment-Load Calculation

A suspended-sediment rating curve was formulated by using all measurements made during water years 2009 and 2010. On the basis of the same measurements, the total San Lorenzo River sediment load was calculated using a sum of values derived from rating curves and interpolation between discrete sample values and 15-minute-resolution “instantaneous” discharge data from USGS gaging station 11161000. For the purposes of estimating sediment load, a separate suspended-sediment rating curve (not shown) was developed using only discharge values below 100 $m^3/s$. Sediment load for discharge less than 100 $m^3/s$ was then calculated using 15-minute discharge data and the linear-regression equation for that specialized rating curve, or, when samples were available, by interpolating between suspended-sediment concentration (SSC) in samples collected during these low-flow periods. Sediment loads for events with discharge greater than 100 $m^3/s$ were calculated using instantaneous discharge data (assuming a 5-minute lag time between discharge at the gaging station and at the sampling station) and values interpolated between SSC samples collected during these high-flow periods. For those load calculations and for SSC values in table 1, we assumed a 15-minute lag time to account for the transit time for flows less than 28 $m^3/s$ to travel from the gaging station downstream to the sampling station, and we assumed a 5-minute lag time for flows above 28 $m^3/s$. Interpolation of discharge to assume a 5-minute lag time between the stream gage and the sampling station during high flow was calculated by assuming that discharge changed in a linear fashion between 15-minute measurements at the gaging station. Interpolation of sediment load was done by calculating the ratio of SSC to discharge for samples and assuming that any change in that ratio between discrete samples occurred in a linear fashion with time. The product of this estimated ratio paired with the instantaneous discharge data was then used to estimate sediment load for discrete 15-minute intervals and summed into annual values.

## Polycyclic Aromatic Hydrocarbon Analysis from Whole Water Samples

Fifteen samples were collected at the same location as noted above, with the same US D-95 sampler for analysis of 27 polycyclic aromatic hydrocarbons (PAHs); however, specialized sampling and handling protocols were observed. The depth-integrated samples were collected using acid-cleaned, methanol-rinsed Teflon bottles and nozzles. Samples from the Teflon US D-95 bottles were transferred carefully to 2.3 or 4.0 L amber glass bottles that were pre-cleaned for trace organic and trace element sampling (I-CHEM). Samples were transported immediately to a laboratory where 30 mL of pesticide-grade dichloromethane (DCM) was added to the amber glass containers and then stored at $4^{o}C$ until the samples were shipped to the USGS Columbia Environmental Research Center (CERC) in Columbia, Missouri, for PAH extraction and instrumental analysis.

Samples received at CERC were spiked with 100 ng of deuterated PAH surrogates (see table 3 for list of compounds in the mix), predominately priority-pollutant PAHs. Water samples were then liquid-liquid extracted with three 50-mL portions of dichloromethane for approximately 1 L of sample;

samples larger than 1 L had 2–3 extractions. The DCM extracts were combined for samples of more than 1 L and evaporated to 1 mL using a Caliper Turbovap. Following evaporation the samples went through a two stage cleanup: (1) flash gel permeation chromatography, followed by (2) a flash basic alumina column fractionation. PAHs are eluted in the second fraction off of alumina. The resulting fraction is evaporated under nitrogen gas and transferred to vials for full-scan gas chromatography mass spectrometry (GC/MS) analysis of PAHs. The final volume was 200 µL with 100 ng d14 p-terphenyl added as an internal standard. Three µL was injected as a cool-on column technique. The GC/MS was a bench-top Thermo Voyager GC Trace system. The column was a 30 mm by 0.15 mm by 0.1 µm film BPX-5 (SGE, Austin, Texas). The temperature program started at 100°C held for 1 minute and was increased by 3 degrees per minute to 338°C. Full-scan MS was done spanning 50–820 amu. Method blanks (*n*=3) showed little or no PAH background, and the process matrix blank had only a slight background of naphthalene and 2-methyl naphthalene.

## Results

Water year 2009 (WY09) was a dry year for the San Lorenzo River, with discharge substantially below average throughout most of the year (fig. 4) and an annual runoff of 0.05 $km^3$ compared to an average annual value of 0.11 $km^3$ (table 2). Water year 2010 (WY10) was substantially wetter than WY09. A tropical storm (named Melor) caused the first flood on October 13, 2009, followed by larger flood peaks in January 2010; thereafter, daily streamflow followed the average 1953–2008 daily discharge trend line for the remainder of WY10 (fig. 4B). The peak flow during the study interval was 359 $m^3/s$ on January 20, 2010, during a winter storm that lasted from January 19 to 21. A flood peak of that magnitude has an estimated return interval of 4–5 years in the San Lorenzo watershed. The annual runoff for WY10 was 0.12 $km^3$, slightly greater than the average annual value (table 2). Suspended-sediment concentration and discharge for water years 2009 and 2010 (fig. 5) show a significant, positive linear relationship ($p$<0.05, $R^2$=0.884 from linear regression). A reverse hysteresis relationship in the data is apparent at the high-flow portion of the rating curve (fig. 5), representing the rising and falling limb of the WY 2010 peak flood event (fig. 6).

The results for annual and major storm-event suspended-sediment loads are shown in table 2. The WY09 annual load was 7,236 metric tons of suspended sediment, and the annual load in WY10 was 41,237 metric tons. Approximately 63 percent of the WY09 annual load was transported during a storm from February 15 to 17, 2009, that had a peak discharge of 126 $m^3$/s. In WY10, approximately 65 percent of the annual load was transported during the three-day storm in January 2010 mentioned above, which also accounted for 55 percent of the sediment load for years WY09 and WY10 combined.

The concentration of PAH compounds in San Lorenzo River water is shown in table 4 and summarized in table 5. The sum concentrations of low- and high-molecular-weight PAH compounds show a linear increase with stream discharge between zero and about 50 $m^3$/s (figs. 7 and 8). The sum concentration of PAHs is relatively constant between 50 and 100 $m^3$/s (figs. 7 and 8), although this is somewhat obscured by large variations in naphthalene in the low molecular weight PAH data (table 4 and fig. 7). Above a discharge of 100 $m^3$/s, there is high variation in the sum of PAH concentrations (figs. 7 and 8), including during the January 2010 major storm event.

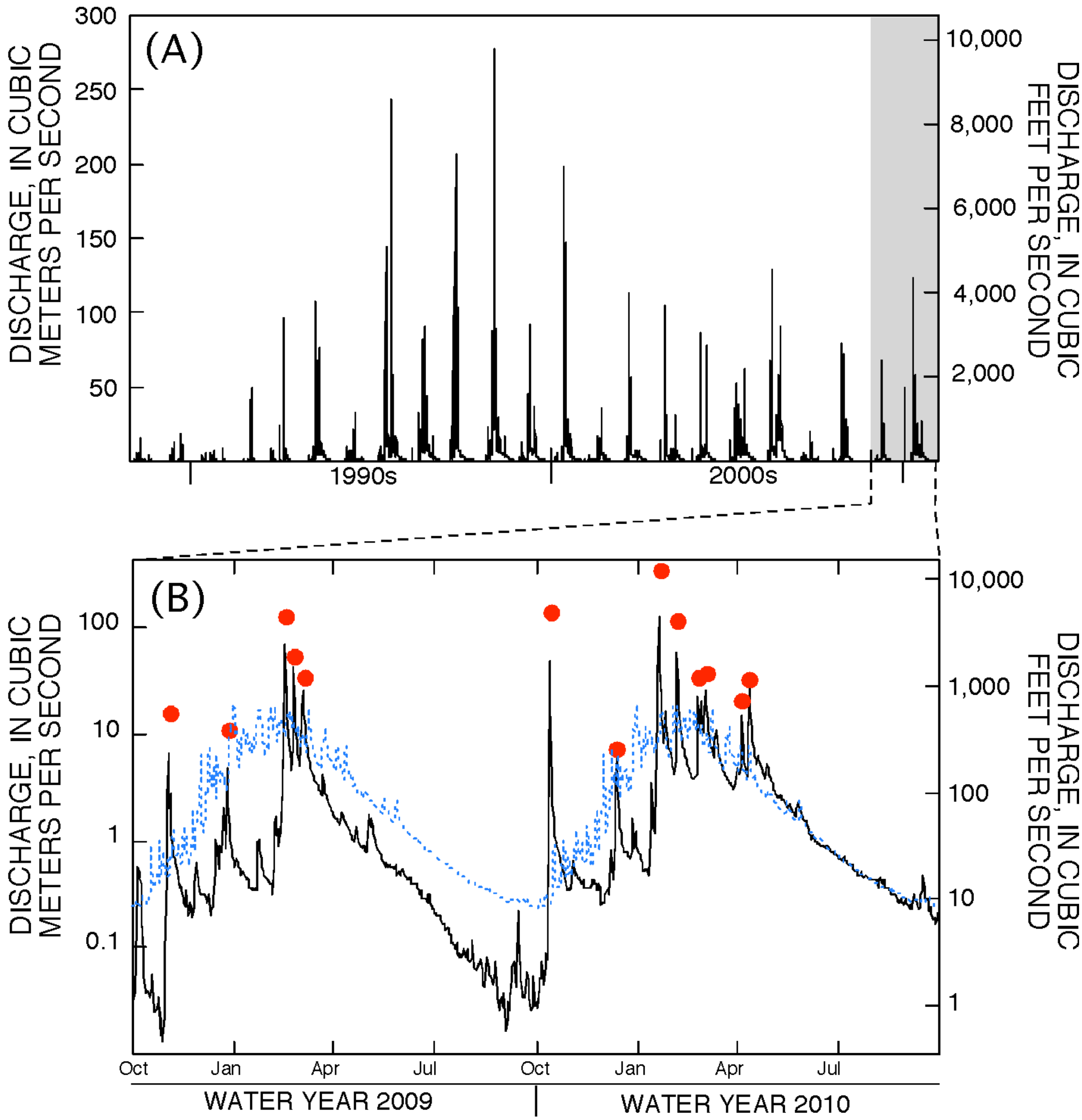


**Figure 4.** Hydrographs of the San Lorenzo River, Santa Cruz, California, showing discharge measured at USGS gaging station 11161000 (location on fig. 2). *A,* Daily average discharge for water years 1987 through 2010, the interval from which a continuous record is available for this station. Water years 2009 and 2010 are shaded gray. *B,* Daily average discharge (black line) measured during WY09 and WY10. Red dots indicate instantaneous

peak discharge of the largest floods during those years. The blue dashed line shows the mean value of daily average discharge for each day for water years 1988 through 2009. Note the logarithmic scale on the vertical axis in (B).

To generate a first-order approximation of PAH loading to Monterey Bay from the San Lorenzo River, we assumed a linear relationship between stream discharge and PAH concentration. The total concentration of low molecular weight PAHs in whole water samples shows a weak but significant positive correlation with discharge ($p$=0.04, $R^2$=0.15 from linear regression). Variation in naphthalene concentrations are the most confounding factor in the degree of correlation ($R^2$). Using this simple linear-regression analysis, the WY10 annual load of low molecular weight PAHs can be estimated at 7 kg per year. On average, 75 percent of the sum concentration of low molecular weight PAHs was made up of naphthalene and phenanthrene (table 4). The sum concentration of high molecular weight PAHs in whole water samples shows a stronger, significant positive correlation with discharge ($p$=0.001, $R^2$=0.55 from linear regression). Using this simple linear-regression analysis, the WY10 annual load of high molecular weight PAHs is estimated at 20 kg. The contribution of individual compounds to the high molecular weight PAH sum is more evenly weighted than in the low molecular weight PAH sum, with individual compounds contributing about 6±4 percent of the total (average value with standard deviation).

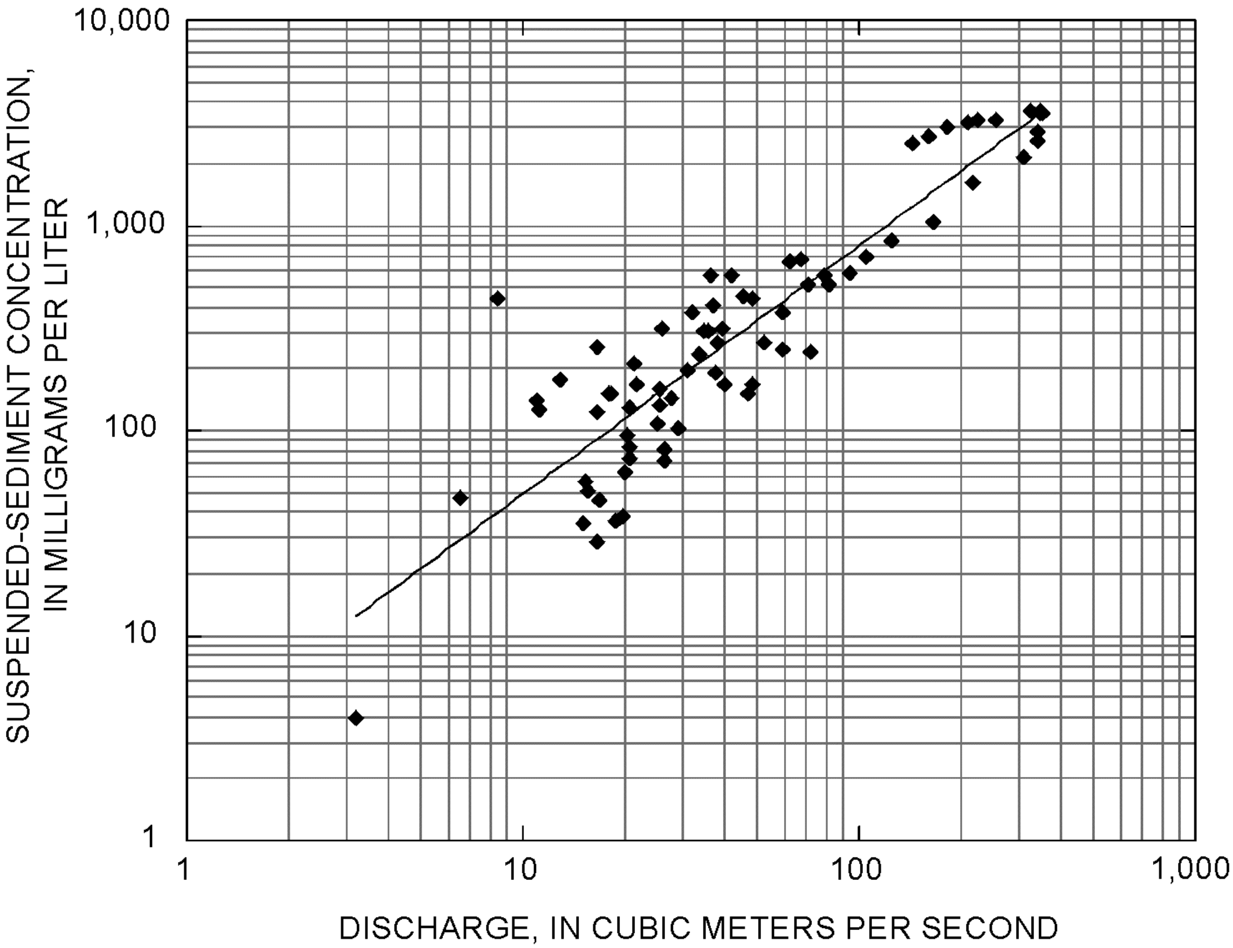


**Figure 5.** Suspended-sediment concentration during high flow in the San Lorenzo River, Santa Cruz, California, during water years 2009 and 2010. The rating curve best-fit line, y=10.117x, and correlation coefficient, $R^2$=0.8845, were calculated using all data from water years 2009 and 2010.

The concentration of some PAH compounds in the San Lorenzo River water samples presented here exceeded U.S. Government water-quality criteria (table 5), specifically the California Toxics Rule (CTR), which applies to total recoverable PAH in water samples. The CTR is a U.S. Environmental Protection Agency published water-quality objective to limit concentrations of toxic substances in California inland waters (including enclosed bays and estuaries), including some PAHs that are known to be human health risks (U.S. Environmental Protection Agency, 2000). Median values for the concentration of benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, and benzo[a]pyrene exceeded the CTR criteria by factors of 2 to 5, and maximum concentrations of these compounds exceeded the CTR by factors of 10 to 50. The California Ocean Plan is water-quality control plan developed by the State of California for marine waters (outside of enclosed bays, estuaries, and coastal lagoons) that provides 30-day average concentration criteria for some PAHs known to affect human health adversely. The PAHs listed in the California Ocean Plan are: acenaphthylene, fluorene, phenanthrene, anthracene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenz[a,h]anthracene, and benzo[g,h,i]perylene (California Environmental Protection Agency, 2005). The California Ocean Plan requires that the sum of the 30-day average concentrations of these PAHs shall not exceed 8.8 ng/L. Although PAH measurements in this study represent instantaneous values in river water, and they were compared in this report to a 30-day average criteria for ocean water, it is notable that the sum of California Ocean Plan-listed PAHs (table 5) can exceed the numeric value of the water-quality criteria by an order of magnitude or more in individual samples. The sum concentration of California Ocean Plan-listed PAHs shows a significant positive correlation with discharge ($p$=0.0000002, $R^2$=0.86 from linear regression). Using this simple linear regression analysis, the WY10 annual load of California Ocean Plan listed PAHs can be estimated to be 10 kg.

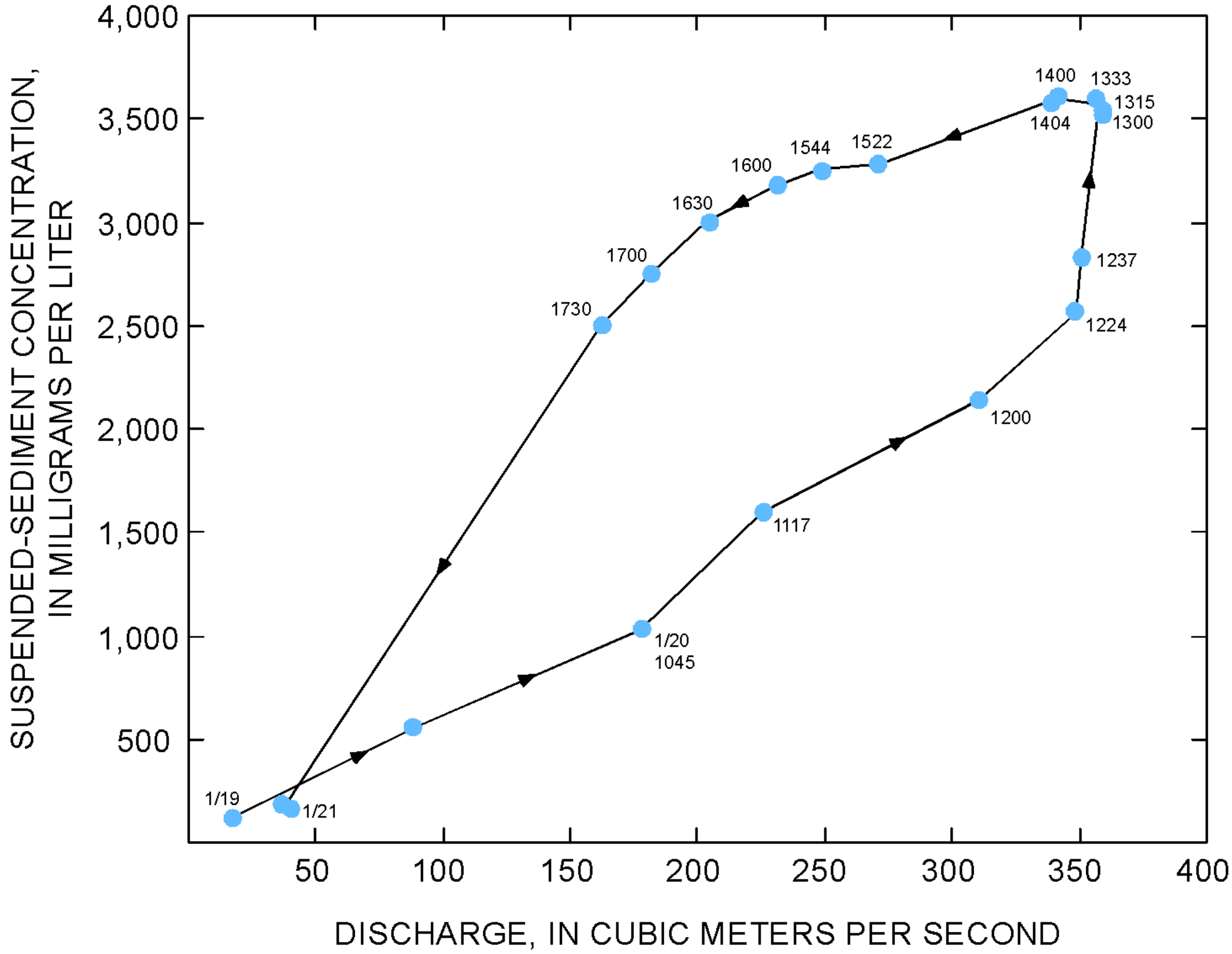


**Figure 6.** Suspended-sediment concentration measured during a three-day flood from January 19 to 21, 2010, San Lorenzo River, Santa Cruz, California, showing reverse hysteresis—sediment concentrations were substantially higher on the falling limb of the hydrograph than on the rising limb. Sampling times are marked between January 20, 2010, at 1045 and 1730 PST. The flood peak of 359 $m^3/s$ occurred at approximately 1330 PST on that day.

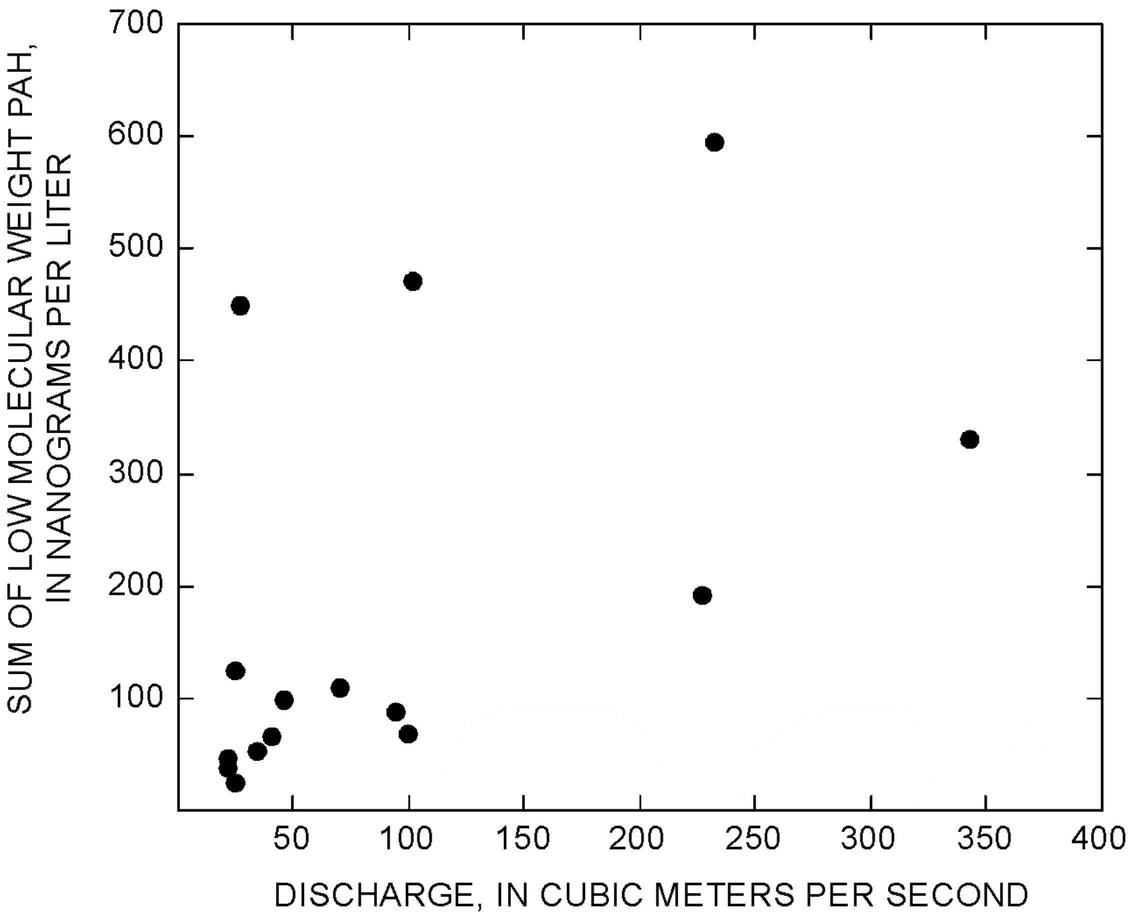


**Figure 7.** Sum concentration of low molecular weight polycyclic aromatic hydrocarbons measured in the San Lorenzo River, Santa Cruz, California, during water year 2010.

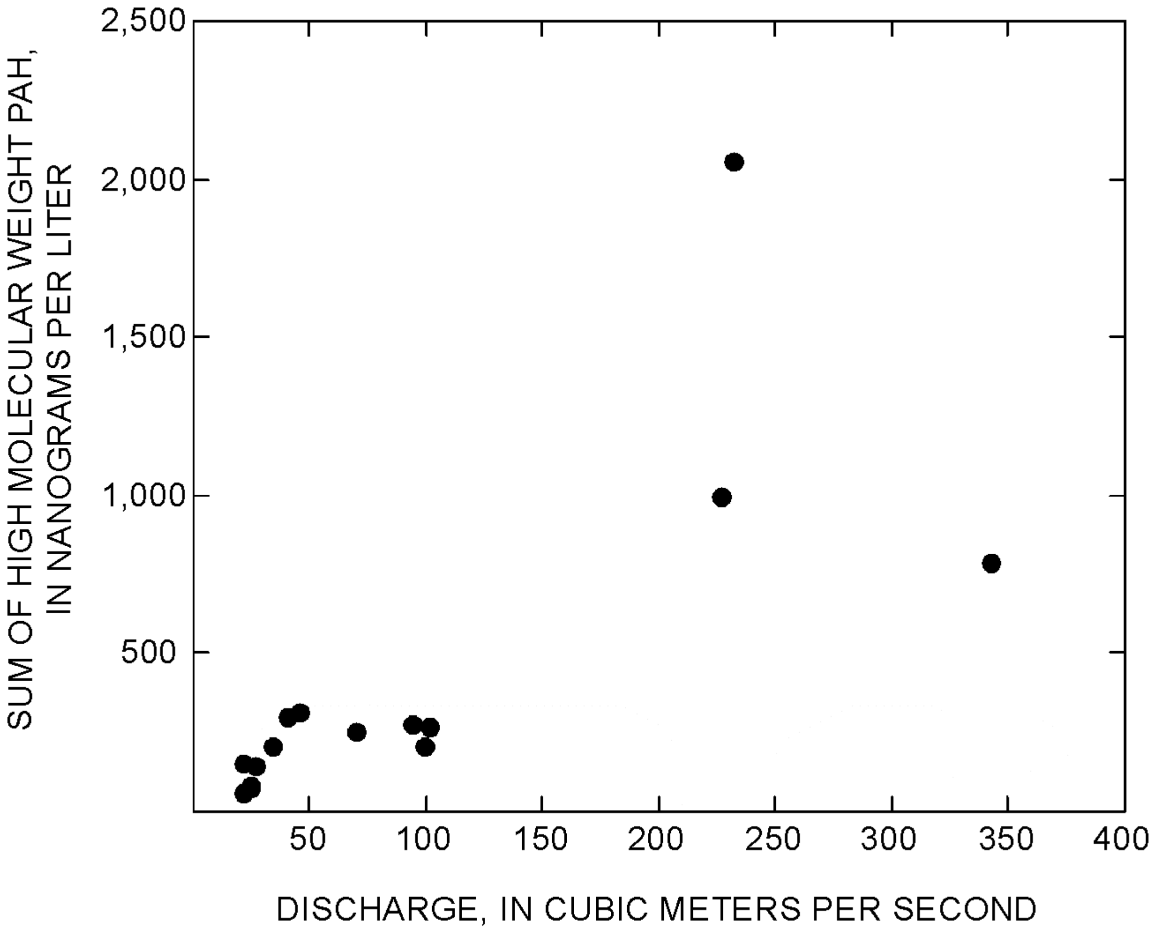


**Figure 8.** Sum concentration of high molecular weight polycyclic aromatic hydrocarbons measured in the San Lorenzo River, Santa Cruz, California, during water year 2010.

## Discussion

### Sediment Load and Hysteresis

The transport of most (more than 60 percent) of the annual sediment loads during a few days in WY09 and WY10, and the fact that 55 percent of the total sediment load for the two-year study was accounted for in just three days of WY10, emphasizes the episodic nature of small mountain streams in general, and of the San Lorenzo River system in particular. A comparison of WY09 and WY10 sediment loads to average annual values (140,000 metric tons per year; Best and Griggs, 1991) is somewhat misleading because such values are biased by the largest, rare floods (50–100-year return interval) and rarely are attained. Taken together, these estimated sediment loads emphasize the importance of single events and “flashy” hydrology on a multiyear time scale.

Although it is common for flood events to have higher suspended-sediment concentrations on the rising limb of the flood compared to those on the falling limb, a result of decreasing sediment supply during the flood (for example, Topping and others, 2000), the opposite pattern (that is, reverse hysteresis) occurred during the largest San Lorenzo River flood of this study interval. As shown in figure 6, the SSC data presented here for the January 19–21, 2010, flood indicated reverse hysteresis, such that sediment concentrations on the flood’s falling limb were higher than those on the rising limb by a factor of 1.7. This may have been caused by some change in flow regime in the watershed, with potential causes being saturation-initiated mass wasting or increased overland flow; news reports at the time mentioned mudslides and flooding in the upper San Lorenzo watershed (Santa Cruz Sentinel, 2010). Another possible explanation for the reverse hysteresis is the suspended sediment peak lagging the discharge peak, as described by Dinehart (1998) and specifically illustrated in his figures 19 and 20. Although debris flows can produce episodic, large-volume sediment discharge from intense rain events in the Santa Cruz Mountains (Wiezorek, 1987), none is known to have happened in the San Lorenzo River during the January 19–21, 2010, storm.

## PAH Contaminants

The results of this study show that the concentrations of PAH compounds in San Lorenzo River water are elevated during rain events, consistent with these compounds entering the river in storm water runoff. The results also are consistent with the suggestion that higher concentrations of high molecular weight PAHs are caused by combustion products washing off roadways (CCLEAN, 2009). In addition, the PAH concentrations can exceed U.S. Federal and State water-quality criteria (table 5). These findings confirm that the San Lorenzo River can be a substantial source of PAH compounds to the Monterey Bay National Marine Sanctuary, as previously indicated by monitoring studies in the region (CCLEAN, 2007).

The relationship between PAH concentration and discharge (figs. 7 and 8) suggests a relatively predictable flux of PAH during low to moderate flows (less than 100 $m^3/s$), punctuated by highly variable concentrations and fluxes during larger discharges and storm events (greater than 100 $m^3/s$). The highest PAH concentrations are associated with high flow "washing" out contaminants that likely had accumulated in the watershed during several years; before the 359 $m^3/s$ flood peak in January 2010, a flow that high had not occurred since December 2005. Because PAHs are strongly sorbed to sediment particles, contaminant transport in the San Lorenzo River system, as in many Pacific coastal streams, is highly episodic and driven by intense rainstorms. Mixtures of PAH compounds have been shown to cause abnormalities in fish embryo development (Incardona and others, 2004). An exposure assessment for sensitive species (which is beyond the scope of this report) would require a more detailed consideration of the relationship among hydrologic conditions, contaminant sources, and contaminant concentrations; however, it is clear that timing and intensity of rainfall events are important variables in quantifying or modeling changes in PAH exposure to aquatic organisms.

Concentration of PAH in nearshore waters of northern Monterey Bay have been shown to exceed the California Ocean Plan water-quality objective for the protection of human health, such as in March 2006, which was one of the rainiest periods of 2000–2010 (CCLEAN, 2009); however, PAH concentrations usually are below this objective value. Nevertheless, the episodic nature of PAH delivery from the San Lorenzo River to Monterey Bay shown in this report, as well as the previous demonstration that PAH loads from the San Lorenzo River can exceed the contribution of other rivers to Monterey Bay (CCLEAN, 2007), suggests that the San Lorenzo River is a substantial source of PAHs to Monterey Bay. Delivery of contaminant pulses to the coastal ocean from river discharge could pose an even greater environmental concern under future scenarios of altered hydrologic connectivity among landscapes, groundwater, and streams owing to climate change and increased urbanization of this and other watersheds (for example, Intergovernmental Panel on Climate Change, 2007; Kaushal and others, 2008, 2010).

## Conclusions

The data presented in this report show the episodic transport of sediment transport in a steep, mountainous Pacific coastal watershed and demonstrate the importance of changing mass-transport conditions with increasing river discharge. Further, the contaminant data suggest that PAH concentrations can exceed regulatory criteria during high-flow events in the San Lorenzo River. Implications of these findings include the importance of maintaining USGS streamflow gaging on Pacific coastal streams to provide long-term records of potential sediment and contaminant transport. In addition, the results emphasize the importance of understanding physical processes and quantifying chemical constituents in loads from coastal streams on event-scale terms.

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Stricker, and Jonathan Warrick, and field equipment repairs were performed or assisted by Peter Dal Ferro, Peter Harkins, and Cordell Johnson. Allan Mlodnosky from the USGS California Water Science Center Sediment Laboratory supervised and performed suspended-sediment concentration and grain-size analyses. Kevin Feltz and Shannon Earhart from the USGS Columbia Environmental Research Center performed the PAH extraction and analysis. Reviewers Peter Swarzenski and Jonathan Warrick contributed numerous excellent suggestions and a timely review of our work. We thank the City of Santa Cruz for site access to the San Lorenzo River pedestrian bridge. Funding was provided by the USGS Mendenhall Posdoctoral Research Fellowship to C.H. Conaway.

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