1-1-2013

Metals and Bacteria Partitioning to Various Size Particles in Ballona Creek Storm Water Runoff

J. S. Brown

E. D. Stein

D. Ackerman

John H. Dorsey
Loyola Marymount University

J. Lyon

See next page for additional authors

Authors
J. S. Brown, E. D. Stein, D. Ackerman, John H. Dorsey, J. Lyon, and P. M. Carter

SETAC PRESS

Environmental Toxicology and Chemistry, Vol. 32, No. 2, pp. 320–328, 2013

Printed in the USA
DOI: 10.1002/etc.2065

METALS AND BACTERIA PARTITIONING TO VARIOUS SIZE PARTICLES IN BALLONA CREEK STORM WATER RUNOFF

JEFFREY S. BROWN,*† ERIC D. STEIN,† DREW ACKERMAN,†‡ JOHN H. DORSEY,§ JESSICA LYON,§ and PATRICK M. CARTER§‖

†Southern California Coastal Water Research Project, Costa Mesa, California, USA
‡Cardno ENTRIX, Raleigh, North Carolina, USA
§Department of Natural Sciences, Loyola Marymount University, Los Angeles, California, USA
‖WPS Environment and Energy, San Jose, California, USA

(*Submitted* 4 *June* 2012; *Returned for Revision* 29 *June* 2012; *Accepted* 14 *September* 2012)

Abstract—Many storm water best management practice (BMP) devices function primarily by capturing particulate matter to take advantage of the well-documented association between storm water particles and pollutants. The hydrodynamic separation or settling methods used by most BMP devices are most effective at capturing medium to large particles; however, these may not be the most predominant particles associated with urban runoff. The present study examined particle size distribution in storm water runoff from an urban watershed in southern California and investigated the pollutant–particle associations of metals (Cu, Pb, Ni, and Zn) and bacteria (enterococci and *Escherichia coli*). During small storm events (≤0.7 cm rain), the highest concentration of pollutants were associated with a <6-μm filter fraction, which accounted for 70% of the per storm contaminant mass but made up more than 20% of the total particle mass. The pollutant–particle association changed with storm size. Most pollutant mass was associated with >35 μm size particles during a 5-cm rain event. These results suggest that much of the contaminant load in storm water runoff will not be captured by the most commonly used BMP devices, because most of these devices (e.g., hydrodynamic separators) are unable to capture particles smaller than 75 μm. Environ. Toxicol. Chem. 2013;32:320–328. © 2012 SETAC

Keywords—Particle size distribution Storm water Pollutant partitioning Laser in situ scattering and transmissometry BMPs

INTRODUCTION

Pollutants in storm water are associated mainly with suspended particles, which act as the transport vector to downstream areas [1-4]. Previous studies of runoff from parking lot and road surfaces demonstrated that the majority of pollutants are associated with fine particles, typically smaller than 50 μm [5,6]. These fine particles have a propensity to settle downstream and accumulate in bays and estuaries, where they may contribute to sediment contamination [7,8].

In many urban watersheds, such as the Ballona Creek watershed, pollutants in storm water runoff and in downstream bays and estuaries have resulted in water bodies being listed as impaired under Section 303(d) of the Clean Water Act. These water bodies are then subject to total maximum daily load requirements to reduce loading of urban-associated contaminants such as metals, bacteria, and organic contaminants. The most common approaches to meeting total maximum daily load requirements for urban storm water are through installation of best management practices (BMPs) designed to capture or treat pollutants before they are discharged to streams or receiving waters [9]. The mechanism used by most BMPs is settling or filtering of storm water particles as a means of reducing loading of the attached pollutants [10]. Consequently, BMP effectiveness is a function of the efficiency of particle capture relative to the concentration of bound pollutants in the storm water runoff.

The effectiveness of BMPs at pollutant removal is complicated by the fact that the timing of runoff of pollutants, including metals and bacteria during storms, is not static. Pollutant concentrations and loads are typically higher during the early portion of storms and during the earlier storms of the season [11-13]. Although most pollutants remain particle bound throughout most storms [11], more recent research has shown that the ratio of particulate to dissolved concentration varies over the course of storms as a function of storm size, antecedent conditions, and surrounding land use [14]. These factors can further affect BMP performance and concentration of pollutants delivered to downstream water bodies.

Management of storm water runoff through BMPs can be improved by an increased understanding of the dynamic relationship between pollutants and particles. Because fine particles predominate in storm water runoff, it is important to move beyond pollutant characterization as either particle-bound or dissolved. Knowing the relationship between pollutants and specific particle sizes over the course of storms, and between different storms within a season, will allow managers to more effectively target BMP design and implementation. Although these relationships have been described well in runoff from developed surfaces [2,3], less is known about how the partitioning between pollutants and various size particles changes over the course of storms and seasons sampled from urban flood control channels that integrate runoff from a variety of land surfaces.

The goal of the present study was to improve the understanding of pollutant–particle relationships in urban storm water runoff. The study focused on answering the following three questions, based on data collected from the Ballona Creek watershed: (1) What is the pollutant–particle association in urban

* To whom correspondence may be addressed (jeffb@sccwrp.org).
Published online 12 November 2012 in Wiley Online Library (wileyonlinelibrary.com).

storm water? (2) Does the association change over the course of a storm? (3) Does the association change among storms?

METHODS

Study area

Sampling occurred in the Ballona Creek watershed, located in western Los Angeles County, California, USA (Fig. 1). The Ballona Creek watershed above the sampling point drains 230 km^2 and is approximately 85% developed, representing a typical urbanized watershed for southern California [15]. Runoff from the upper half of the watershed is conveyed through a series of underground storm drains, discharging to a concrete-lined channel that ultimately flows to Santa Monica Bay, Santa Monica, California, USA. Sampling occurred from the Sepulveda Boulevard Bridge, located 7.2 km downstream from where Ballona Creek becomes an open channel, 6.8 km upstream from the mouth, and 2.0 km upstream above the zone of tidal influence. Average annual rainfall in the watershed ranges from 340 to 530 mm, with the majority of storms occurring from January to March.

Sample collection

Three types of measurements were made during a series of storm events over four storm seasons. Particle size distribution was measured over the course of six storms, trace metals were measured in four storms, bound to various particle size fractions, and bacteria were measured in the particle-bound phases during eight storms.

Samples for metals and bacteria were taken directly from the creek, using a United States Geological Survey depth-integrated sampler or by collecting water pumped from the creek. For the pumped samples, storm water from Ballona Creek was pumped vertically 10 m from the concrete channel bed to the top of the bridge over the channel. Water was pumped through Teflon or silicon tubing (9.5 mm inside diameter) attached to a 25.4-mm angle iron bolted to the concrete channel bottom. Samples were pumped using a Masterflex I/P 77410-10 peristaltic pump with two heads in parallel and Masterflex Norprene I/P 73 tubing. Creek water was transported to the bridge and through a filter with 480-μm mesh sump filter (Cole-Parmer Low-cost In-line Strainer System). The bowl and mesh of the sump filter were manually switched out approximately every 15 minutes or when

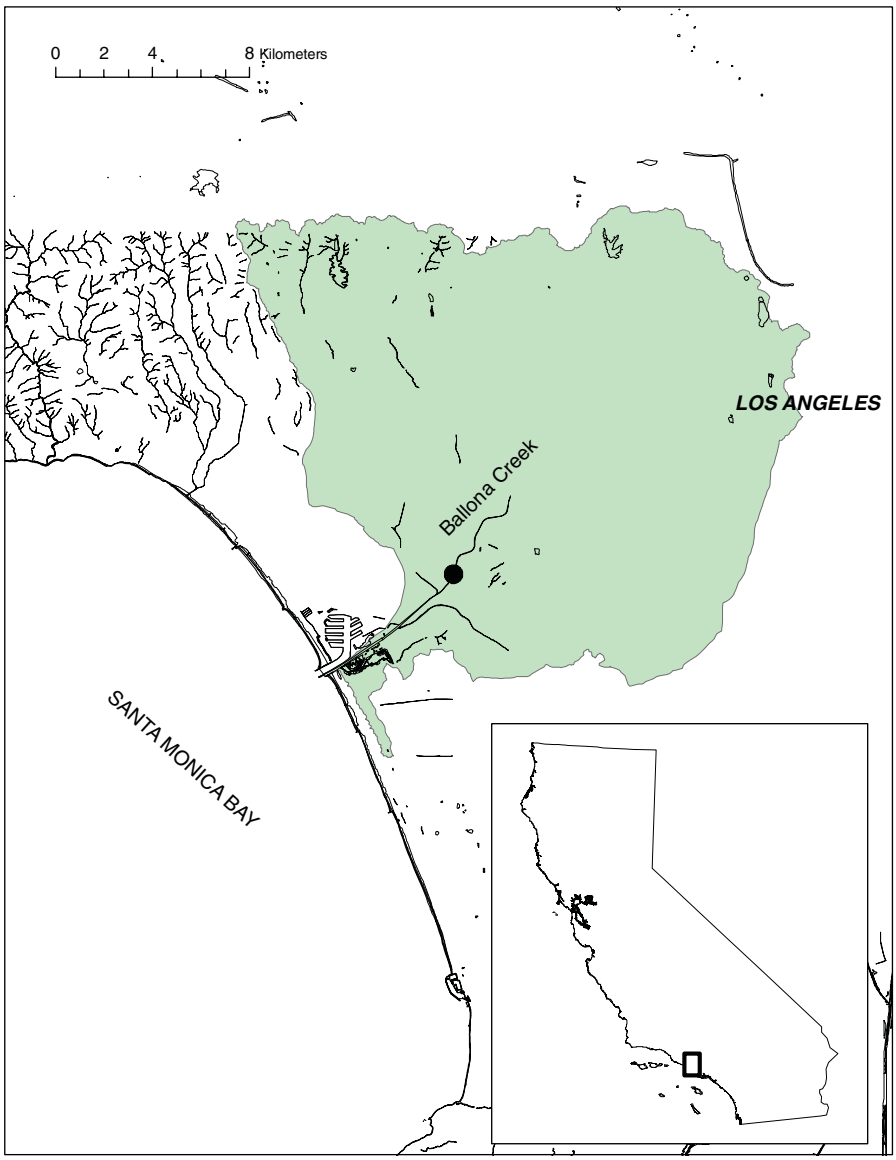

Fig. 1. Sampling location within the Ballona Creek watershed in southern California, USA. The shaded area represents the extent of the watershed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

they became clogged with leaves, small sticks, trash, or other debris. Pumping rates were maintained at > 3 L/min (0.8 m/s) to ensure no particle settling in the tubing, based on validation studies conducted by Brown et al. [16]. Between 3 and 10 samples were collected for each storm, with a greater number of samples collected during the earlier storms in the present study. Samples were collected throughout each storm, often with a higher sampling frequency at the beginning of each event to characterize any first-flush response in metal or bacteria concentrations. Samples were held on ice and transported to the laboratory for filtration within 1 h of collection to minimize flocculation and settling.

Particle size distribution was continuously monitored throughout most storms using the laser in situ scattering and transmissometry device (Sequoia Scientific) as described by Brown et al. [16]. Laser refractometry produces particle density estimates by shining a laser through a parcel of water to calculate particle size distribution based on the amount of scatter induced by the particles. The method relies on assumptions about particle shape and density, and requires that water samples have sufficient transmissivity for penetration by the laser beam [17]. Although this technique has not been widely used to measure particle size distribution in storm water, Brown et al. [16] demonstrated that with appropriate field procedures, in situ laser refractometry produces particle density estimates and size distribution estimates that are comparable to laboratory methods.

Water was pumped from the creek, as described, and run through the laser in situ scattering and transmissometry to continually sample storm water at 1-min intervals. Technical difficulties with the pump setup prevented us from characterizing particle distribution for at least a portion of each storm. As such, we were able to characterize the particle size distribution during the peak flow for only six of the eight storm events sampled. Nevertheless, we characterized the distribution of particle sizes during the initial portion (i.e., rising limb of the hydrograph) of all storms, thereby allowing us to assess the portion of the hydrograph associated with first flush responses.

Flow data were obtained from the U.S. Army Corps of Engineers for the Ballona Creek flow gauge (http://www.spl.usace.army.mil/cgi-bin/cgiwrap/zinger/slLatestBasin.cgi?lacda + stage), located near the sample collection site.

Laboratory analysis

Fecal indicator bacteria and metals associated with various size fractions were measured by filtering storm water through a series of progressively smaller Nitex filters manufactured by Sefar (Table 1). Filter sizes ranged from 0.45 to 200 μm for the first storm, but because the measured distribution of metals and bacteria from early storms was mostly in the smaller fractions, the range was reduced to 6 and 35 μm for the last five storm events. Because of the difficulty in extracting bound particles from the filters, metals and bacteria were measured in the filtrate that passed through each filter. The constituent fraction associated with each size fraction was estimated as the difference in concentration between filtrate from successively smaller filters. Before filtering, concentrations were measured in each sample of raw runoff. The sample then was passed through the first filter in the series using a sterile 47-mm filtering funnel vacuum system. The filtrate was sampled using three serial dilutions, beginning by placing 1 ml filtrate in 99 ml sterile dilution water to produce a 0.01 dilution, then repeating the same steps to yield 0.001 and 0.0001 dilutions. The remaining filtrate then was passed through the next filter in the series.

Filtrate aliquots were tested for *Escherichia coli,* using Colilert-18 and for enterococci using Enterolert (IDEXX) [18]. The filtrate samples for total metals were acidified with nitric acid and analyzed by inductively coupled plasma mass spectrometry, using U.S. Environmental Protection Agency (U.S. EPA) method 200.8 m. The metals analyzed included Cu, Pb, Ni, and Zn (reporting levels = 0.8, 0.1, 0.5, and 0.5 μg/L, respectively).

Event flow-weighted mean concentrations (EMCs) were calculated for the metals and bacteria data. Using only those samples for a single storm, the EMC was calculated according to the following equation:

$$EMC = \frac{\sum_{i=1}^{n} C_i \times F_i}{\sum_{i=1}^{n} F_i}$$

where *EMC* was event flow-weighted mean concentration for a particular storm, C_i was individual runoff sample concentration of *i*th sample, F_i was instantaneous flow at the time of *i*th sample, and n was number of samples per event.

Data analysis

To more readily compare data among the various filtration size classes used during different storms in the present study, the metals and bacteria data were consolidated to three size ranges: <6 μm, 6 to 35 μm, and >35 μm.

Differences in the proportions of total particle mass represented by the different filter fractions were assessed using the Kruskal-Wallis analysis of variance on ranks, followed by the Student-Newman-Keuls multiple comparison procedure to identify which fractions were significantly different. Significance was determined at $\alpha = 0.05$.

RESULTS

Particle size distribution

The dominant particle size varied over the course of each storm, with fine particles often dominating during the early part of the storm and the proportion of coarser particles increasing later in the storm. For most events, there was an increase in the silt/clay fraction (<63 μm, Wentworth scale [19]) as storm water began to flow in the channel, with a peak in concentration that occurred before the peak in storm flow. The peak concentrations of the silt/clay fraction varied among storms by a factor

Table 1. Filter sizes (μm) used during the storms monitored for bacteria and metals bound to particulates[a]

Storm date	Bacteria filter sizes (μm)								Metals filter sizes (μm)							
	0.45	1	5	6	35	125	200	Raw	0.45	1	5	6	35	125	200	Total
1/14/2006	x	x	x		x	x	x	x								
3/3/2006		x	x		x	x		x								
3/28/2006		x	x		x	x		x								
2/3/2008				x	x			x								
12/15/2008				x	x			x	x	x	x		x	x	x	x
2/5/2009				x	x			x		x	x		x	x	x	x
1/17/2010				x	x			x				x	x			x
2/19/2010				x	x			x				x	x			x

[a] Because of the measured distribution of bacteria in the early storms and the difficulty of passing storm water through the smallest filter sizes, the range was reduced to 6 and 35 μm for the last storm events. "Raw" indicates samples that were not filtered before analysis.

of 23, ranging from 60 to 1,356 μl/L (measured as particle volume/volume solution by the particle size analyzer). No significant relationship was found between the silt/clay peak concentration and preceding volume of storm water ($p = 1.00$, Spearman rank correlation), flow velocity ($p = 1.00$), volume of storm water before the peak in storm flow ($p = 0.95$), or number of dry antecedent days ($p = 0.35$). Because the silt/clay fraction was the predominant particle size class for the first 50 to 75% of the storm volumes, we focused on this size class for the subsequent analysis of pollutant partitioning.

Distribution of contaminants among particle sizes

Most trace metals, with the exception of Pb, were associated with fine particles. Copper, Ni, and Zn were most strongly associated with the <6-μm fraction (Fig. 2). For example, 51% of the mean Cu EMC was associated with the <6-μm fraction, 33% associated with the >35-μm fraction, and 16% associated with the 6- to 35-μm fraction. In contrast, concentrations of Pb were slightly greater in the >35-μm filter size fraction, with 44% associated with the >35-μm fraction, compared with 33% associated with the <6-μm fraction and 23% associated with the 6- to 35-μm fraction.

Likewise, bacteria tended to be associated with the <6-μm fraction. Approximately 50% of the *Enterococcus* concentration and 63% of the *E. coli* concentration were associated with this smallest filter fraction (Fig. 2). The EMCs varied; the proportion of enterococci associated with the <6-μm fraction ranged from 26 to 78% of the EMCs among the eight storm events, whereas the proportion of *E. coli* associated with this fraction ranged from 45 to 82%.

Although the majority of the metals and bacteria concentrations were associated with the <6-μm fraction, this particle size fraction represented a significantly lower proportion of the total mass of storm water particles ($H = 50.39$, $p < 0.01$). Less

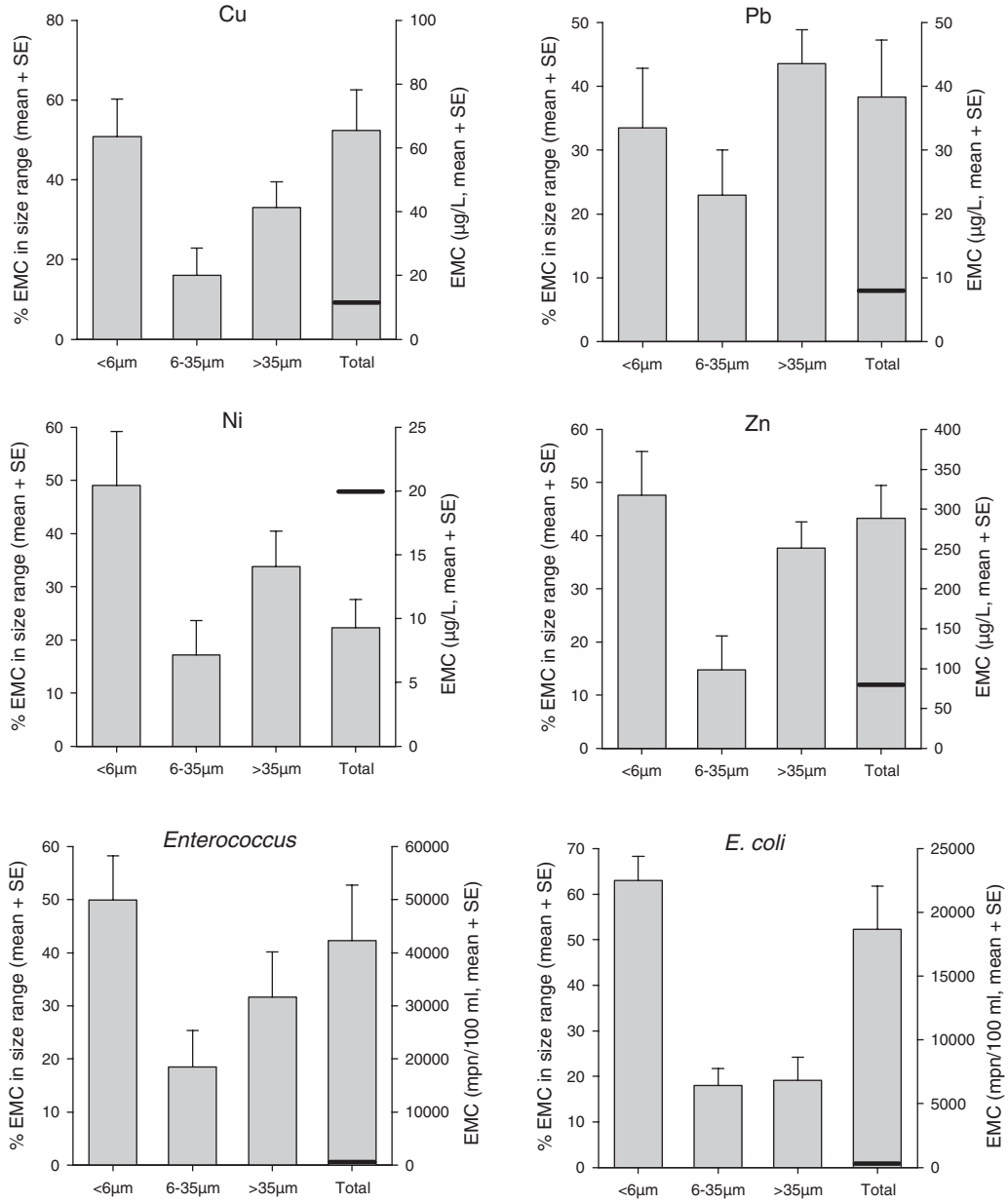

Fig. 2. Proportion of flow-weighted event mean concentration (EMC) associated with the various filter fractions (first three bars in each graph), and the overall EMC (fourth bar). The data represent the mean of the EMCs from the four (metals) or eight (bacteria) storm events. The vertical line above each bar represents the standard error (SE). The horizontal slash on the fourth bar indicates the water quality standard used for comparison.

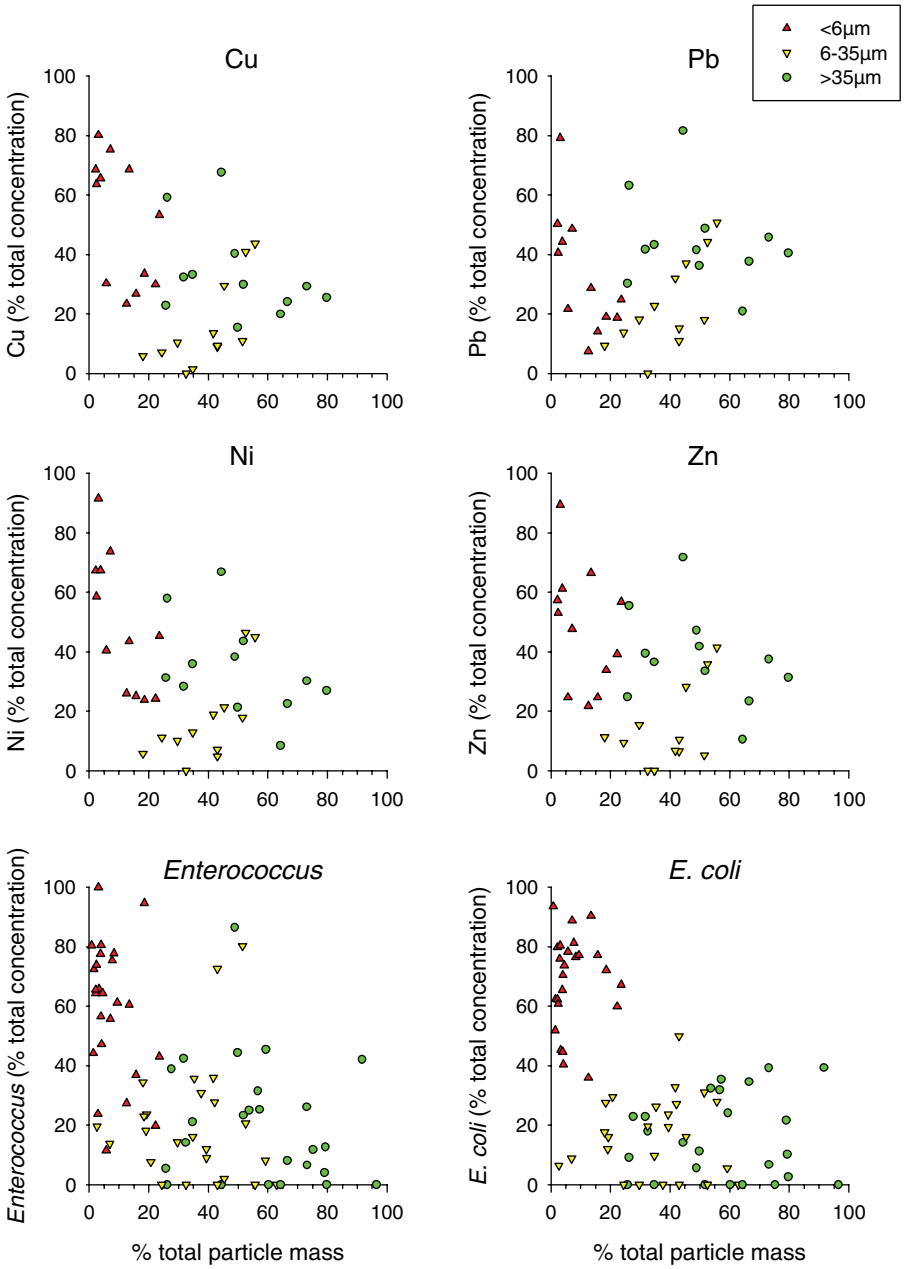

Fig. 3. Association of metals and bacteria with the relative amounts of particles in storm water samples. Data were pooled over four storm events for metals and eight events for bacteria. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

than 25% of the total particle concentration was represented by the <6 µm particles (Fig. 3). In contrast, the 6- to 35-µm fraction made up approximately 39% of the total particle mass (on average), whereas the >35-µm fraction made up approximately 50%.

Within-storm variability

Metal concentrations were generally highest during the early portion of storms across all particle size classes. The highest concentrations typically occurred in samples collected before the peak in storm flow and decreased toward the recessional end of the hydrograph. The average ratio in concentrations of total metals between the first and last samples was 2.9 for Cu, 2.3 for Ni, and 1.8 for Zn. For Pb, however, no difference was found in concentrations between the first and last samples collected. Whereas concentrations of Cu, Ni, and Zn tended to be highest at the beginning portions of storms, the peak in metal mass discharge coincided with the peak in flow rate for all particle size categories (Fig. 4). This trend was consistent for each of the metals, including Pb.

Unlike metals, no consistent trend was found in bacteria concentrations over the course of the storms. Concentrations of enterococci and *E. coli* did not exhibit a first flush-like response, and bacteria concentrations appeared to be independent of storm water flow volume at the time of sampling.

Like metals, the peak in bacteria (most probable number) discharge coincided with the peak in storm water flow rate (Fig. 4). This pattern was consistent for both enterococci and *E. coli*. The bacterial discharge associated with the individual fractions generally exhibited this same pattern.

The pollutant–particle association was not always consistent within each storm. Cu mass discharge was consistently associated with the <6-µm fraction throughout storms with peak

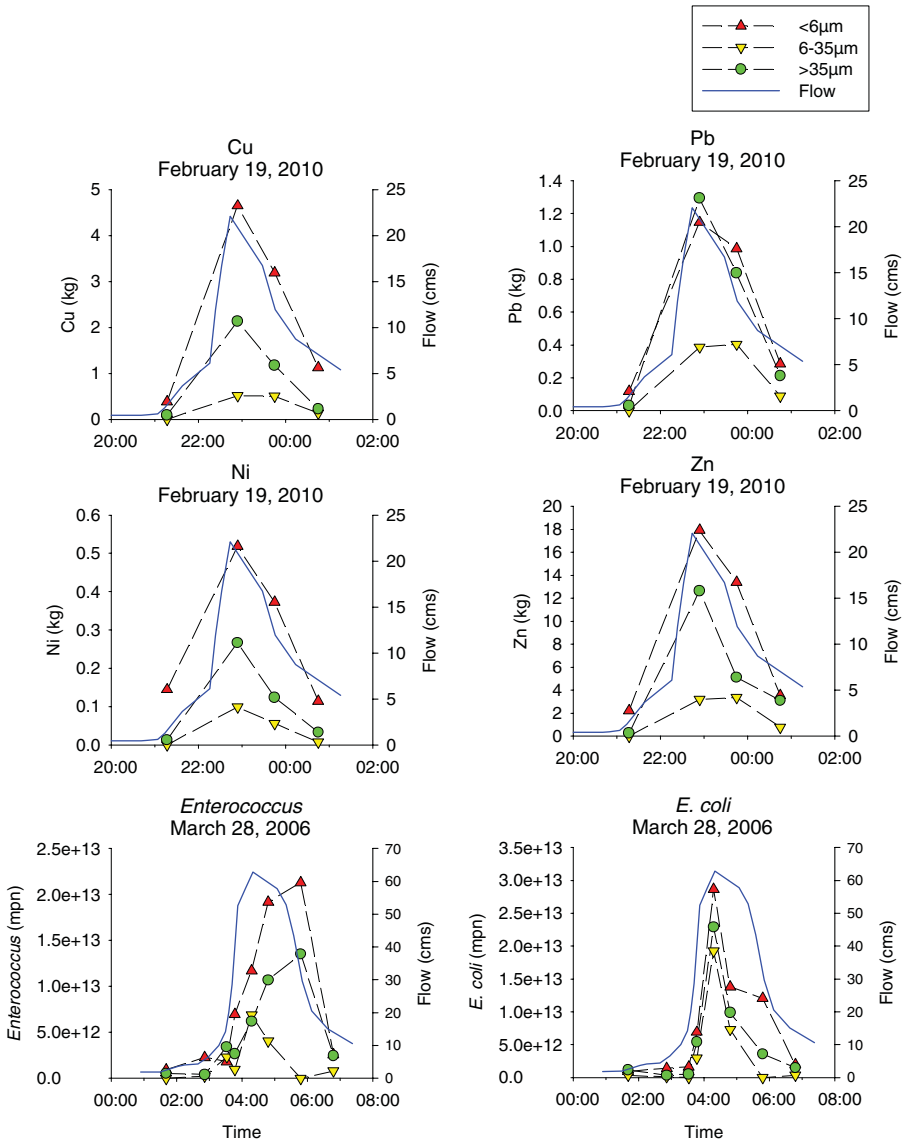

Fig. 4. Metal and bacteria mass discharge distributed among the three filter fractions, relative to storm flow rate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

flow rates of less than 50 cm/s but alternated between the <6-µm, 6- to 35-µm, and >35-µm fractions for storms with peak flow rates of more than 200 cm/s (Fig. 4). Enterococci usually had a greater association with the <6-µm fraction throughout storms that had flow rates of less than 60 cm/s, but this trend was not consistent (Fig. 4); enterococci alternated between the <6-µm and >35-µm fractions over the course of the storm that had the lowest peak in flow rate (15 cm/s). *Escherichia coli* discharge tended to have a consistently high association with the <6-µm fraction throughout the course of most events (Fig. 4).

Among-storm variability

The association of metals with particle size appeared to be influenced by storm size. Storms with lower total flow volumes ($\leq 4.7 \times 10^5$ m^3, $\leq$0.7 cm rain event) had relatively lower masses of metals discharged, and these metals had a greater association with the <6-µm filter fractions (Fig. 5). At a storm volume of 1.7×10^6 m^3, the distribution of metals among the filter fractions was approximately equal. The largest storm in the present study (4.0×10^6 m^3, 4.8 cm rain event) had the greatest metal mass discharge, and the metals tended to have a higher association with the >35-µm filter fraction.

Changes in the bacteria–particle association with storm size appeared to be indicator dependent (Fig. 5). Similar to metals, enterococci had a greater association with larger particle fractions as storm size increased. For storms smaller than 1×10^6 m^3, a greater proportion of the bacteria discharge was associated with the <6-µm fraction, but the association changed to the larger-sized particles as storm size increased. In contrast, *E. coli* was associated with the <6-µm fraction throughout the range of storm sizes sampled.

DISCUSSION

In the Ballona Creek watershed, most storm water metals and bacteria were associated with the <6-µm filter fraction at lower storm volumes, but the association shifted to larger particles with larger storms. Storm water volumes in Ballona Creek between 1987 and 1998 indicate that 63% of the storms were small ($\leq$700,000 m^3 daily flow volume), with only 6% of

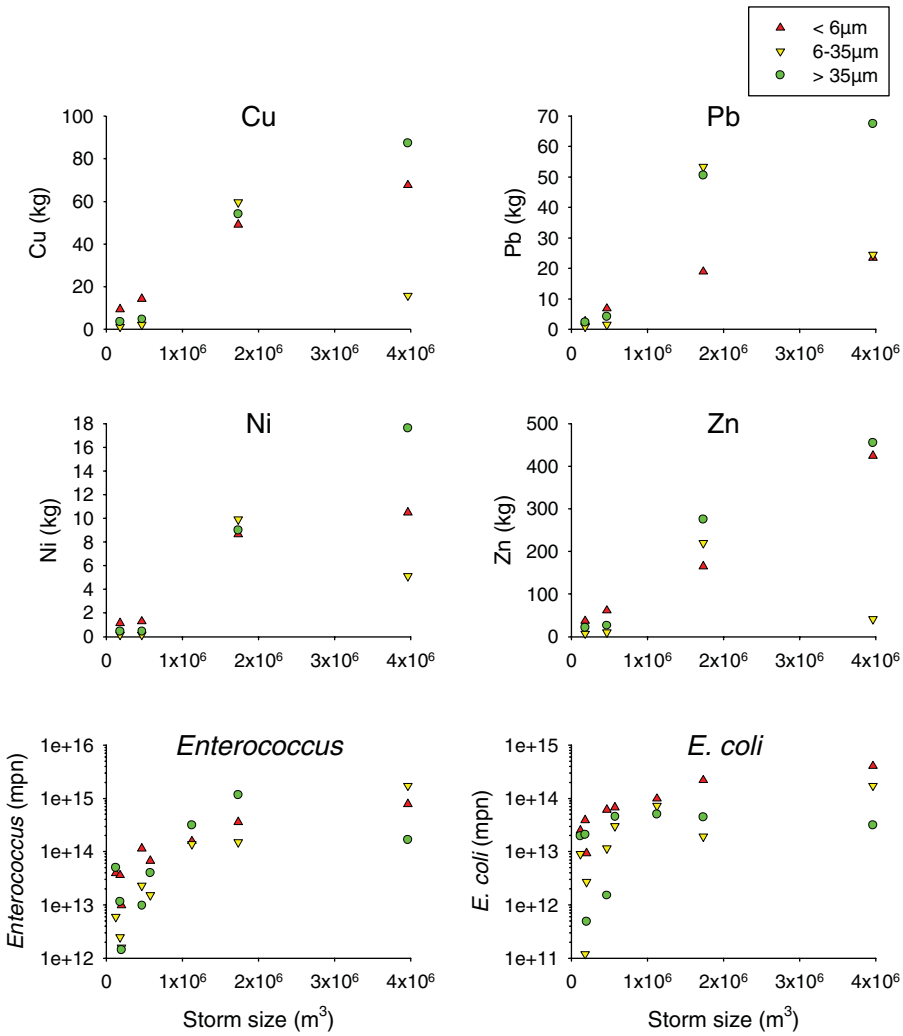

Fig. 5. Association of metals and bacteria with particle size relative to storm size. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the events having flow volumes equal to or greater than the largest storms measured in the present study (>4,000,000 m^3 daily flow volume). Therefore, most pollutants are expected to be associated with the <6-µm fraction for most events. However, because larger storms discharge greater amounts of contaminants, the distribution of metals and enterococci is expected to be much more comparable among the particle size ranges on an annual mass discharge basis. Using the distribution of metals identified in the present study with the storm volumes measured between 1987 and 1998, the mass of Cu discharged would have been very similar between the <6-µm (36% of the mass) and >35-µm size fractions (also 36% of the mass) over this 12-year period. Likewise, the distribution was similar for Ni (34% of the mass associated with the <6-µm fraction, 37% associated with the >35-µm fraction), but it is estimated that a greater mass discharge would have been associated with the >35-µm fraction for Pb and Zn. For Pb, 19% of the mass was estimated to be associated with the <6-µm fraction, compared with 44% associated with the >35-µm fraction. For Zn, the mass distribution was estimated to be 34% associated with the <6-µm fraction and 42% associated with the >35-µm particles over a 12-year time scale.

Although the sampling location for the present study was near the bottom of the watershed, and therefore included storm water runoff from a mixture of land uses (residential, commercial, and transportation), the results in the present study were similar to those from studies that focused solely on highway runoff, collected at the source of the runoff. For example, Li et al. [20] observed that particles <10 µm make up less than 20% of the total particle mass in storm water runoff from highways in southern California, which was similar to our observations. Li et al. [20] also observed that the highest particle concentrations occurred within the first hour of runoff and decreased rapidly thereafter, which is similar to the pattern measured in the runoff at Ballona Creek in the present study. Sansalone et al. [21] similarly observed that metal partitioning between particle and dissolved phase was related to rainfall and storm flow intensity in runoff from urban roadways. In the present study of the runoff from an entire watershed, we observed that contaminant distribution among particle size was related to storm size, with greater association with larger particles during larger storms.

Whether most metals were associated with particles, or whether they were freely dissolved (conventionally defined as <0.45 µm), is unclear. Sansalone et al. [21] determined that for metals in highway runoff, the majority of Cu, Ni, and Zn were dissolved, but Pb was equally split between the dissolved and particle-bound fractions. We found a similar trend, with Cu, Ni, and Zn associated with the <6-µm filter fraction and Pb concentrations divided between the <6-µm and >35-µm filter

sizes in storm water from Ballona Creek. Data from the one storm event in which we measured both total and dissolved metals indicate that approximately 18% of the Cu, Ni, and Zn and 3% of the Pb were in the dissolved form. However, these data are from the largest storm event sampled. Because we observed a greater association of metals with larger particles as storm size increased, the proportion of metals in the dissolved phase during a smaller storm event may have been different. The distribution of metals between the particle-bound and unbound fractions can be influenced by a variety of mechanisms, which were not investigated in the present study. Hydrous Fe oxide has been shown to be a factor controlling metal partitioning in urban runoff [22] and could have sequestered the metals in the <6-μm fraction. Previous studies have also shown that metal partitioning can be influenced by the organic carbon content of the dissolved phase [11,23], which would be useful to measure in future investigations. Adsorption to bacteria is another possible fate of the metals. Fein et al. [24] determined that carboxyl and phosphate functional groups within bacteria cell walls adsorb trace metals under the pH conditions of most natural and contaminated aqueous systems.

Most bacteria were associated with the <6-μm filter fraction, but it is unclear whether the bacteria were bound to the smallest particle sizes or were free floating. Krometis et al. [25] determined that approximately 60% of enterococci and *E. coli* were associated with the suspended fraction of runoff from low-density residential and institutional (university) drainage areas. Jeng et al. [8] determined that 91% of enterococci and 78% of *E. coli* were not associated with particles in storm water. Of those organisms that were attached to particles in that study, most of the enterococci were associated with particles between 10 and 30 μm, whereas *E. coli* tended to attach to particles over a wider range in size (0.45–30 μm). Therefore, bacteria in the <6-μm fraction in Ballona Creek may have been freely suspended, rather than particle bound, and may have been associated with dislodged biofilms coating wetted areas of storm drain pipes, as suggested by Skinner et al. [26].

To evaluate the potential for toxicity in the receiving water, the total metal EMC values were compared with California Ocean Plan thresholds [27]. Marine receiving water standards were used for the evaluations instead of the freshwater standards, because Ballona Creek is not expected to have much water contact recreation compared with the nearby coastal environment, especially during storm events. Daily maximum thresholds were used for comparison: Cu = 12 μg/L, Pb = 8 μg/L, Ni = 20 μg/L, Zn = 80 μg/L. Each of the storms had metal concentrations that exceeded toxicity threshold values. All of the Cu, Pb, and Zn EMCs exceeded the daily maximum limits. Copper and Pb EMC values exceeded these thresholds by up to a factor of 8, whereas Zn EMCs exceeded by up to a factor of 5. Nickel EMC values did not exceed the threshold in any of the storms sampled.

The bacteria values were compared with water quality standards established to protect water contact recreation in coastal waters [27]. The EMCs for total enterococci were compared with the enterococci 30-d mean standard (35 most probable number/100 ml), whereas total *E. coli* was compared with the fecal coliform 30-d mean standard (200 most probable number/100 ml). Objectives do not currently exist for *E. coli* in the marine environment; however, because *E. coli* makes up a proportion of the total fecal coliforms, the fecal coliform objective would be a conservative threshold for comparison. Bacteria concentrations exceeded the water quality objectives during each of the storm events sampled. Enterococci EMCs exceeded water contact objectives by up to a factor of 2,750. For *E. coli*, EMCs exceeded the water contact objective by up to a factor of 179.

Increasing desire has been expressed to remove contaminants in runoff, using BMPs before the storm water reaches its receiving water. Structural BMPs (including hydrodynamic settling chambers) have been installed at inlets to Ballona Creek to capture particulates, trash, and debris [28]. However, most of these devices are able to capture only the larger sand particles (≥250 μm), without removing contaminants that are either dissolved or bound to small particulates [29]. In the present study, more than 50% of the Cu, Ni, Zn, *Enterococcus*, and *E. coli* were associated with filter size fractions that would not have been captured by these devices. Studies of metals accumulation in urban soils have shown that trace metals primarily accumulate in clay, fine silt, and very fine sand fractions before washoff or resuspension as dust [2,30]. Alternative structural BMPs, including media filters, have been developed to capture dissolved contaminants. Using these devices during the initial portions of storms would maximize contaminant removal efficiency, because the highest concentrations of metals in the present study were found in the early part of the hydrograph. Storm size should also be considered because metals and bacteria tended to be associated with larger particle sizes during the larger storm events.

Acknowledgement—The authors thank G. Lyon, K. Smith, and J. Griffith (SCCWRP), J. Shrake, S. Porter, and the rest of the MACTEC sampling staff for their assistance in the setup and sampling efforts. The authors also thank the City of Los Angeles, California, USA, for providing financial support for the present study.

REFERENCES

1. Lau SL, Han Y, Kang JH, Kayhanian M, Stenstrom MK. 2009. Characteristics of highway stormwater runoff in Los Angeles: Metals and polycyclic aromatic hydrocarbons. *Water Environ Res* 81:308–318.
2. Lau SL, Stenstrom MK. 2005. Metals and PAHs adsorbed to street particles. *Water Res* 39:4083–4092.
3. Sansalone JJ, Buchberger SG. 1997. Characterization of solid and metal element distributions in urban highway stormwater. *Water Sci Technol* 36:155–160.
4. Surbeck CQ, Jiang SC, Ahn JH, Grant SB. 2006. Flow fingerprinting fecal pollution and suspended solids in stormwater runoff from an urban coastal watershed. *Environ Sci Technol* 40:4435–4441.
5. Furumai H, Balmer H, Boller M. 2002. Dynamic behavior of suspended pollutants and particle size distribution in highway runoff. *Water Sci Technol* 46:413–418.
6. Vaze J, Chiew FHS. 2004. Nutrient loads associated with different sediment sizes in urban stormwater and surface pollutants. *J Environ Eng* 130:391–396.
7. Bay S, Schiff K, Greenstein D, Tiefenthaler L. 1998. Stormwater runoff effects on Santa Monica Bay: Toxicity, sediment quality, and benthic community impacts. *Proceedings*, California and the World Ocean'97, San Diego, CA, USA, March 24–27 1997, pp 900–921.
8. Jeng HC, England AJ, Bradford HB. 2005. Indicator organisms associated with stormwater suspended particles and estuarine sediment. *J Environ Sci Health* 40:779–791.
9. Sample DJ, Heaney JP, Wright LT, Fan CY, Lai FH, Field R. 2003. Costs of best management practices and associated land for urban stormwater control. *J Water Resour Plann Manage* 129:59–68.
10. Ackerman D, Stein ED. 2008. Evaluating the effectiveness of best management practices using dynamic modeling. *J Environ Eng* 134: 628–639.
11. Characklis GW, Wiesner MR. 1997. Particles, metals, and water quality in runoff from large urban watershed. *J Environ Eng* 123:753–759.
12. Tiefenthaler LL, Stein ED, Schiff KC. 2008. Watershed and land use-based sources of trace metals in urban storm water. *Environ Toxicol Chem* 27:277–287.
13. Tiefenthaler LL, Stein ED, Schiff K. 2010. Levels and patterns of fecal indicator bacteria in stormwater runoff from homogenous land use sites and urban watersheds. *J Water Health* 9:279–290.

14. Yoon VK, Stein ED. 2008. Natural catchments as sources of background levels of storm-water metals, nutrients, and solids. *J Environ Eng* 134: 961–973.
15. Ackerman D, Schiff K, Weisberg S. 2005. Evaluating HSPF in an arid, urbanized watershed. *J Am Water Resour Assoc* 41:477–486.
16. Brown J, Ackerman D, Stein ED. 2012. Continuous *in situ* characterization of particulate sizes in urban stormwater: Methods testing and refinement. *J Environ Eng* 138:673–679.
17. Agrawal YC, Whitmire A, Mikkelsen OA, Pottsmith HC. 2008. Light scattering by random shaped particles and consequences on measuring suspended sediments by laser diffraction. *J Geophys Res (C: Oceans)* 113:C04023.
18. American Public Health Association American Water Works Association Water Environment Federation. 1998. *Standard Methods for the Examination of Water and Wastewater,* 20th ed. American Public Health Association, Washington DC.
19. Wentworth CK. 1922. A scale of grade and class terms for clastic sediments. *J Geol* 30:377–392.
20. Li YX, Lau SL, Kayhanian M, Stenstrom MK. 2005. Particle size distribution in highway runoff. *J Environ Eng Sci* 131:1267–1276.
21. Sansalone JJ, Buchberger SG, Al-Abed SR. 1996. Fractionation of heavy metals in pavement runoff. *Sci Total Environ* 189/190:371–378.
22. Bibby RL, Webster-Brown JG. 2006. Trace metal adsorption onto urban stream suspended particulate matter (Aukland region, New Zealand). *Appl Geochem* 21:1135–1151.
23. Grout H, Wiesner MR, Bottero JY. 1999. Analysis of colloidal phases in urban stormwater runoff. *Environ Sci Technol* 33:831–839.
24. Fein JB, Daughney CJ, Yee N, Davis TA. 1997. A chemical equilibrium model for metal adsorption onto bacterial surfaces. *Geochim Cosmochim Acta* 61:3319–3328.
25. Krometis LH, Characklis GW, Simmons OD, Dilts MJ, Likirdopulos CA, Sobsey MD. 2007. Intra-storm variability in microbial partitioning and microbial loading rates. *Water Res* 41:506–516.
26. Skinner JF, Guzman J, Kappeler J. 2010. Regrowth of enterococci and fecal coliform in biofilms. *Stormwater* July–August 2010.
27. State Water Resources Control Board (SWRCB)., 2009. *Water Quality Control Plan, Ocean Waters of California; California Ocean Plan.* SWRCB, Sacramento, California.
28. Brown J, Bay S. 2005. Assessment of best management practice (BMP) effectiveness. Technical report 461. Southern California Coastal Water Research Project, Westminster, California USA.
29. Smith KP. 2002. Effectiveness of three best management practices for highway-runoff quality along the Southeast Expressway, Boston, Massachusetts. U.S. Geological Survey Water Resources Investigations, Reston Virginia.
30. Luo X, Yu S, Li X. 2011. Distribution, availability, and sources of trace metals in different particle size fractions of urban soils in Hong Kong: Implications for assessing the risk to human health. *Environ Pollut* 59:1317–1326.