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Temporal patterns and controls on runoff magnitude and solution chemistry of urban catchments in the semiarid southwestern United States

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Abstract:

Urban expansion and the scarcity of water supplies in arid and semiarid regions have increased the importance of urban runoff to localized water resources. However, urban catchment responses to precipitation are poorly understood in semiarid regions where intense rainfall often results in large runoff events during the short summer monsoon season. To evaluate how urban runoff quantity and quality respond to rainfall magnitude and timing, we collected stream stage data and runoff samples throughout the 2007 and 2008 summer monsoons from four ephemeral drainages in Tucson, Arizona. Antecedent rainfall explained 20% to 30% of discharge (mm) and runoff ratio in the least impervious (22%) catchment but was not statistically related to hydrologic responses at more impervious sites. Regression models indicated that rainfall depth, imperviousness and their combined effect control discharge and runoff ratios ($p < 0.01$, $r^2 = 0.91$ and 0.75, respectively). In contrast, runoff quality did not vary with imperviousness or catchment size. Rainfall depth and duration, time since antecedent rainfall and event and cumulative discharge controlled runoff hydrochemistry and resulted in five specific solute response patterns: (i) strong event and seasonal solute mobilization (solute flush), (ii) event chemostasis and strong seasonal flush, (iii) event chemostasis and weak seasonal flush, (iv) event and seasonal chemostasis and (v) late seasonal flush. Our results indicate that hydrologic responses of semiarid catchments are controlled by rainfall partitioning at the event scale, whereas wetting magnitude, frequency and timing alter solute stores readily available for transport and control temporal runoff quality. Copyright © 2012 John Wiley & Sons, Ltd.

KEY WORDS urban; runoff; semiarid; water quality; runoff ratio

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INTRODUCTION

Programs such as the Nationwide Urban Runoff Program (Athayde *et al*., 1983), the National Stormwater Quality Database (Pitt *et al*., 2008) and an extensive body of research (e.g. Brabec *et al*., 2002; Maestre and Pitt, 2006; Wenger *et al*., 2009) have advanced our understanding of how urbanization alters runoff quantity and quality. Despite these advances nationally, little attention has been paid to how urbanization affects storm runoff quantity and quality in arid and semiarid catchments. Efforts in these regions largely have focused on describing runoff characteristics across urban land cover types (e.g. Maestre and Pitt, 2006; Tiefenthaler *et al*., 2008), and few studies have addressed the seasonal variability of runoff quantity and quality (e.g. Lee *et al*., 2004), which is of particular importance in arid and semiarid regions where water resources are limited, streamflows are episodic and urban runoff is increasingly viewed as a renewable water resource. Given that arid and semiarid regions are experiencing some of the fastest urban growth (Berling-Wolff and Wu, 2004; Norman *et al*., 2009) and may be facing increased aridity and increased variability in rainfall (Seager *et al*., 2007; Serrat-Capdevila *et al*., 2007), understanding how the seasonal variability of rainfall affects runoff and water quality will be critical for managing future water resources.

The importance of ‘focused urban runoff recharge’ as a renewable water resource has increased in recent years in arid and semiarid regions (Decook and Foster, 1984; Chralowicz *et al*., 2001; City of Santa Clara, 2011). It is well established that urbanization increases runoff magnitude and duration, decreases time to concentration and increases water yields (Paul and Meyer, 2001; Walsh *et al*., 2005; Maestre and Pitt, 2006; Kennedy, 2007; Shaver *et al*., 2007). It is also established that ephemeral waterways, in addition to mountain front and mountain block recharge, are areas of focused runoff infiltration, making stream channel losses an important groundwater recharge pathway in arid and semiarid regions (Eastoe *et al*., 2004; Goodrich *et al*., 2004; Pool, 2005; Blasch *et al*., 2006; Scanlon *et al*., 2006; Coes and Pool, 2007). Therefore, by increasing the magnitude of runoff and streamflow, urbanization in arid and semiarid regions may enhance ephemeral channel losses and groundwater recharge and subsequently augment renewable

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groundwater resources. However, increasing the magnitude of runoff and streamflow from urban areas may also increase the delivery of contaminants to areas of focused recharge (Fischer *et al*., 2003; Carlson *et al*., 2011).

A substantial number of studies indicate that stream water quality decreases as urbanization increases (e.g. Walsh *et al*., 2005; Rose, 2007). Early stormwater studies and monitoring efforts focused on the role of land use as the primary control of runoff quality (Klein, 1979; Heaney and Huber, 1984). However, findings from extensive national stormwater monitoring programs, such as the Nationwide Urban Runoff Program and the National Stormwater Quality Database, suggest that the characteristics of the regional rainfall regime impart a stronger effect on stormwater quality than land use alone (Athayde *et al*., 1983; Pitt *et al*., 2008). The effects of rainfall characteristics in controlling urban runoff quality, solute sourcing and transport have received little attention in arid and semiarid regions where rainfall is episodic. Several studies indicate that solute flushing from semiarid uplands and hill slopes in response to summertime rainfall result in elevated streamflow solute concentrations (Parks and Baker, 1997; Brooks *et al*., 2007; Harms and Grimm, 2010). In addition, positive correlations between solute concentrations in runoff, antecedent dry days and rainfall characteristics have been identified in both, semiarid urban and nonurban systems (Ishaq and Alassar, 1999; Westerhoff and Anning, 2000; Welter *et al*., 2005; Lewis and Grimm, 2007), suggesting that solute sourcing, retention and transport are controlled by the frequency and magnitude of wetting (Welter *et al*., 2005; Harms and Grimm, 2010).

Given that the temporal distribution of rainfall may control catchment hydrologic and hydrochemical responses in semiarid regions, in this study, we ask: How do urban runoff quantity and quality vary throughout the summer monsoon and what are the controlling mechanisms? Here we examine monsoonal urban runoff quantity and quality of four urbanized catchments in Tucson, Arizona. We expected that runoff quantity would increase with impervious cover, rainfall magnitude and cumulative rainfall, whereas solute concentrations in runoff would vary inversely with rainfall and discharge magnitude and decrease as the summer monsoon progressed.

STUDY REGION OVERVIEW AND STUDY PERIOD

The study sites are located within an alluvium-filled valley in the Basin and Range region of southern Arizona and form part of the Tucson Metropolitan area, which is bounded by the Santa Catalina Mountains to the north, the Rincon Mountains to the east and the Tucson Mountains to the west. The study sites drain to Rillito Creek (Figure 1), which along with the Santa Cruz River and its major tributaries, Canada del Oro, Pantano Wash and Tanque Verde Creek, flow intermittently towards the northwest (Wilson *et al*., 1998). Because these major ephemeral waterways have been identified as areas of focused groundwater recharge, they are particularly important for localized water resources conservation and management. Intense groundwater mining to support agriculture and urban growth has lowered the water table up to 61 m in areas of the basin's central well field, shifting the streamflow regime of the basin waterways from perennial to ephemeral (Wilson *et al*., 1998; Gelt *et al*., 1999).

The mean annual temperature and precipitation in the Tucson Basin are 20.2 °C and 310 mm, respectively. The climate is semiarid with an annual potential evaporation of 1960 mm, six times more than the mean annual precipitation (Wilson *et al*., 1998; Gelt *et al*., 1999), whereas annual evapotranspiration can exceed 250 mm (Unland *et al*., 1996). Precipitation is distributed bimodally with approximately 48% of rainfall occurring during the summer months and 52% occurring in the winter (Gelt *et al*., 1999). Summer monsoonal rainfall events are short in duration, high in intensity, spatially heterogeneous and follow an extended period of hot and dry conditions and are driven by atmospheric convection (Gelt *et al*., 1999; Hoffmann *et al*., 2007; Renard *et al*., 2008; Stone *et al*., 2008). Summertime storms generate a larger fraction of annual runoff than winter precipitation events (Goodrich *et al*., 2008; Stone *et al*., 2008), which are colder, of lower intensity and longer duration. This study was conducted during the 2007 and 2008 summer monsoons, which officially span the period between 15 June and 30 September (Guido, 2008). The Tucson Basin received approximately 172.2 and 242.8 mm of rainfall during the 2007 and 2008 monsoon, respectively.

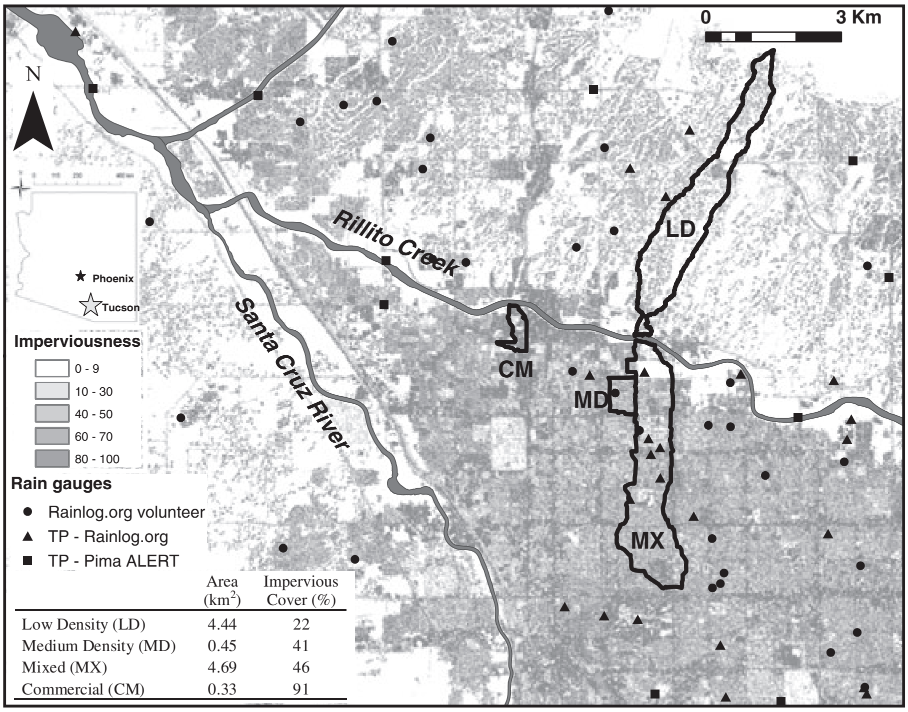
METHODS

Catchment characterization

We used surface topography and stormwater drainage system data provided by the City of Tucson's Office of Conservation and Sustainable Development to select study sites that are hydrologically contiguous and isolated from adjacent catchments. The selected catchments captured a range of urban catchment sizes, slopes, orientations and land uses typical of the Tucson Basin (Gallo *et al*., in revision). In brief, percent impervious cover (IC; imperviousness henceforth) was 22%, 41%, 46% and 91% in the low-density (LD), medium-density (MD), mixed (MX) and commercial (CM) catchment, respectively, and was calculated as

$$\mathrm{IC} = \frac{100}{a_\mathrm{c}} \cdot \sum_{x=i}^{n} a_{\mathrm{LC}x} \cdot f\mathrm{IC}_{\mathrm{LC}x} \qquad (1)$$

where a_c is the catchment size or area in square kilometers and $a_{\mathrm{LC}x}$ is the area in square kilometers of land cover x, which were calculated in ArcMap 9.0 using the default 'Area Calculation by Gauss' method, and $f\mathrm{IC}_{\mathrm{LC}x}$ is the fraction of the imperviousness of land cover x obtained from the City of Tucson's Office of Conservation and Sustainable Development. Here we do not use the 2001 National Land Cover Database imperviousness product because large parcels that were not urbanized in 2002 had been developed by 2005. Other catchment descriptions such



	Area (km^2)	Impervious Cover (%)
Low Density (LD)	4.44	22
Medium Density (MD)	0.45	41
Mixed (MX)	4.69	46
Commercial (CM)	0.33	91

Figure 1. Location and major characteristics of our five study sites in the Tucson Basin and of rain gauges used to quantify precipitation in the study. All catchments drain untreated storm runoff to Rillito Creek, a major ephemeral wash. The catchments span a range of sizes (0.32–4.69 km^2) and impervious covers (22%–91%). Black circles denote locations of manual rain gauges, triangles and squares denote location of tipping bucket rain gauges

as channel substrate characteristics and land use can be found in the work of *Gallo et al.* (in revision).

Monsoonal rainfall

The spatial distribution of monsoonal precipitation in the Southwest is highly variable (Comrie and Broyles, 2002; Goodrich *et al*., 2008; Renard *et al*., 2008), and most summertime rain days receive only one precipitation pulse. Although radar rainfall products exist, they tend to underestimate convective rainfall depth and overestimate rainfall duration (Xie *et al*., 2006). Therefore, to calculate rainfall depth in millimeters (P_{depth}) for any given rainfall event at each site during the study period, we used an inverse distance weighted method as outlined by Garcia *et al*. (2008) to interpolate spatially distributed precipitation point data obtained from Rainlog.org (http://rainlog.org) and the Pima County Regional Flood Control District Automated Local Evaluation in Real Time (ALERT) System (http://www.rfcd.pima.gov/wrd/alertsys/index.htm; Figure 1). Several rainfall monitoring sites within our study catchments were also equipped with Rainlog.org tipping bucket rain gauges or were located near the ALERT System tipping buckets. Therefore, we used Rainlog.org and ALERT System tipping bucket rain gauge data (tipping resolutions of 2.54 and 1 mm, respectively) to calculate (i) rainfall duration (P_{duration}) in hours, (ii) time since antecedent rainfall or time since last rain in days and (iii) the fraction of rainfall that precipitated during each rainfall pulse on the few days when more than one rainfall event was observed. Some studies indicate that under very high and very low rainfall intensity tipping, buckets may underestimate P_{depth} (e.g. Ciach, 2003). To generate a spatially weighted catchment wide rainfall intensity ($P_{\text{intensity}}$) estimates, we calculated $P_{\text{intensity}}$ by dividing P_{depth} by P_{duration}. Antecedent rainfall depth, duration and intensity refer to the P_{depth}, P_{duration} and $P_{\text{intensity}}$ of the prior rainfall event. Cumulative rainfall over the duration of the monsoon was calculated by adding the depths of all monsoonal rainfall events.

Discharge and runoff ratio

We installed pressure transducers (Submerged Flow Module 720, Teledyne Technologies, Lincoln, Nebraska, stage accuracy ± 0.3 cm) along stable cross sections at the outlet of each catchment to record stage data every minute. We calculated instantaneous discharge (Q_t) in liters per second using Manning's equation (ASCE, 1996):

$$Q_t = A\frac{1000}{n}R_h^{2/3}s^{1/2} \tag{2}$$

where A is the cross-sectional area of flow within the channel in m^2, n is the channel roughness coefficient, R_h is the hydraulic radius in meters and s is the energy slope. The energy slope was assumed to be approximately equal to the bed slope. We chose a Manning's approach because of the lack of pre-existing discharge data at these sites and because generating rating curves presented itself as a physical hazard because of the flash flood conditions that accompany monsoonal stream flow. On the basis of the channel substrate, we used n values of 0.025 for earthen channels at LD and MX, 0.013 for a concrete lined channel at CM and 0.024 for a corrugated metal pipe at MD (ASCE, 1996). Owing to data losses during download, we present discharge data for three of our four sites for 2007.

Event discharge depth in millimeters (Q, discharge henceforth) was calculated as

$$Q = \frac{6 \times 10^{-5}}{a_c} \cdot \sum_{t=0}^{i} Q_t \tag{3}$$

where 6.0×10^{-5} is a conversion factor with units of seconds per cubic millimeter. The event runoff ratio has units of percentage of P_{depth}, calculated by dividing discharge by P_{depth} and multiplying by 100. Monsoonal discharge accumulated up to and including runoff event i (CQ, cumulative discharge henceforth) was calculated as

$$CQ = \sum_{i=1}^{i} Q_i \tag{4}$$

Total cumulative monsoonal discharge ($\mathrm{CQ_{tot}}$) at each site per year was calculated by adding the discharge depth of all monsoonal runoff events. Normalized cumulative monsoonal discharge for each event (NCQ) was calculated as the ratio of CQ to $\mathrm{CQ_{tot}}$.

Runoff sample collection

Runoff samples were collected every 20 min for up to 4 h in clean acid washed, combusted (500 °C for 3 h) 1-l glass bottles using automatic samplers (Teledyne ISCO 6712, Lincoln, NE) with Teflon® tubing installed at the outlet of each catchment. An additional uncapped bottle was added as a control blank, which was filled with deionized water and processed in the same way as the runoff samples. The samples were capped with Teflon caps, placed in dark chilled (~4 °C) coolers and immediately transported to the University of Arizona for processing.

Laboratory analysis and solute load calculations

Sample aliquots for bacterial analyses were immediately poured off into sterile 250-ml HDPE bottles and shipped overnight on ice to the USDA-ARS in Maricopa, Arizona. All other aliquots were filtered within 24 h of sample collection and stored at 4 °C with the exception of aliquots for metal analysis, which were stored at room temperature. Sample aliquots for nutrient analysis, including ammonium-nitrogen (NH_4-N), orthophosphate-phosphorous (PO_4-P), dissolved organic carbon (DOC) and total dissolved nitrogen (TDN), were filtered through precombusted 0.7-µm glass fiber filters (Whatman GF/F) and stored in clean precombusted amber glass bottles with Teflon-lined caps. Aliquots for anion, cation and metal analyses were filtered through 0.45-µm membrane filters (Millipore MF). Analysis of NH_4-N and PO_4-P were performed on a SmartChem Discrete Analyzer (Westco Scientific, Brookfield, CT) with detection limit (DL) of 0.002 and 0.001 $\mathrm{mg\,l^{-1}}$ for NH_4-N and PO_4-P, respectively. Dissolved organic carbon and TDN analyses were performed on a Shimatzu TOC/TN Analyzer (Shimadzu, Columbia, MD) with a method DL of 0.05 $\mathrm{mg\,l^{-1}}$ for DOC and 0.05 $\mathrm{mg\,l^{-1}}$ for TDN. Anions (Cl, nitrate-N (NO_3-N), nitrite-N (NO_2-N) and sulfate-S (SO_4-S)) were analyzed in a Dionex Ion Chromatograph (ICS-3000, DIONEX, San Jose, CA) with an AS23 column (DL = 0.05 $\mathrm{mg\,l^{-1}}$). Dissolved organic nitrogen (DON) was calculated by subtracting NO_3-N, NO_2-N and NH_4-N from TDN. Base cations (calcium (Ca), sodium (Na), magnesium (Mg), potassium (K)) and metals (lead (Pb), zinc (Zn), iron (Fe), copper (Cu), cobalt (Co), nickel (Ni), aluminium (Al), manganese (Mn), vanadium (V), cadmium (Cd), arsenic (As) and mercury (Hg)) were analyzed on an inductively coupled plasma mass spectrometer (Elan DRC-II ICP-MS, DL = 0.001 $\mu\mathrm{g\ l^{-1}}$) using sample aliquots stored in precleaned glass bottles with Teflon caps and preserved with nitric acid (HNO_3) to approximately 1% and pH 2 to 3. *Escherichia coli* analyses followed US Environmental Protection Agency method 1604 (EPA, 2002). Duplicates of two sample dilutions (1.0 and 0.1 ml) were passed through a 0.45-µm sterile filter to retain bacteria, plated in BBL™ MI agar (Becton, Dickinson and Co.), supplemented with 5 $\mu\mathrm{g\,ml^{-1}}$ of cefsulodin to inhibit Gram-positive bacterial growth and incubated at 35 °C for 24 h. Blue or indigo colonies were counted as presumptive for *E. coli.*

Solute loads for each runoff event (L_e) were calculated as

$$L_e = 60 \sum_{t=1}^{n} c_t \cdot Q_t \tag{5}$$

where 60 has units of seconds and c_t is the solute concentration in mass per liter. Linear interpolation was used to calculate c_t between two measured data points. Monsoonal loads accumulated up to and including runoff event L_e ($\mathrm{CL_e}$) were calculated as

$$\mathrm{CL_e} = \sum_{i=1}^{i} L_{ei} \tag{6}$$

The $\mathrm{CL_e}$ for each solute at each site for each year were summed to calculate the total cumulative monsoonal load ($\mathrm{CL_{tot}}$). The normalized cumulative monsoonal load (NCL) for each event refers to the ratio of $\mathrm{CL_e}$ to $\mathrm{CL_{tot}}$.

Statistical analysis of rainfall–runoff

Statistical analyses of rainfall–runoff and runoff quality were performed using JMP 8.0.2 (JMP®, Version 8.0.2. SAS Institute Inc., Cary, NC, 1989-2009). Data were log transformed before analysis to normalize the distribution of the variance in our data set (Driver and Troutman, 1989). To determine whether rainfall characteristics were significantly different between water years and among sites, we performed mean *t*-tests across water years and Tukey–Kramer comparison of means across sites on the total number of rainfall events, cumulative rainfall, P_{depth}, P_{duration}, $P_{\mathrm{intensity}}$, time since antecedent rainfall and antecedent rainfall depth, duration and intensity. To identify whether discharge and runoff ratios varied over the monsoon, we regressed discharge and runoff ratios versus day of year and cumulative rainfall. We also used linear regression to determine if discharge and runoff ratios varied with imperviousness, catchment size or any other rainfall characteristic across sites. To determine how discharge and runoff ratios relate to rainfall characteristics at each site, we regressed discharge and runoff ratios against day of year, cumulative rainfall, P_{depth}, $P_{\text{intensity}}$, P_{duration}, time since antecedent rainfall and antecedent rainfall conditions. On the basis of the correlation analysis, we generated a two-component regression model for discharge and runoff ratios that included the multiplicative effects of rainfall characteristics with imperviousness and catchment size.

Statistical analysis of runoff quality

To identify how solute concentrations changed over the season, we regressed mean event concentrations (solute concentrations henceforth) versus day of year and cumulative rainfall. For further statistical analyses, solute concentrations, discharge, cumulative discharge and all rainfall characteristics were log-transformed to linearize power relationships and to normalize the distribution of our data (Edwards, 1973; Godsey *et al.*, 2009). We assessed the effect of rainfall and runoff characteristics and timing on runoff solute hydrochemistry by calculating the coefficient of correlation (r) of solute concentrations against discharge, cumulative discharge, runoff ratios, P_{depth}, P_{duration}, $P_{\text{intensity}}$, time since antecedent rainfall, antecedent rainfall conditions, imperviousness and catchment size. Solute concentration–discharge relationships (c_e–Q) with significant negative slopes were interpreted as solute dilution, whereas nonsignificant regressions (slope = 0) were indicative of solute chemostasis (Godsey *et al.*, 2009). Solute chemostatic conditions indicate that solute concentrations are stable and non-variant with respect to stream discharge suggesting that discharge is not a primary control of solute dynamics (Godsey *et al.*, 2009). We calculated the slope (m) and performed t-tests (H_o: $m = 1$) of the NCL to normalized cumulative discharge regression (NCL-NCQ) to distinguish early seasonal flushing ($m < 1$) from late seasonal flushing ($m > 1$) and seasonal chemostasis ($m = 1$). Although this technique has been mainly used to describe event scale solute flushing patterns in urbanized catchments (Deletic, 1998; Lee *et al.*, 2003; Obermann *et al.*, 2009), here we have modified it similar to Lee *et al.* (2004) to identify seasonal solute responses.

We used a standardized Wards clustering analysis (Sall *et al.*, 2007) on the r values of each solute to rainfall, runoff and land cover variables to identify groups of solutes with similar seasonal responses. Only independent variables with more than four significant solute correlations were included in the clustering analysis. For further analysis and interpretation, we retained solute response clusters with a standardized Euclidian distance between them greater than 2.0. Finally, we use a Tukey–Kramer method to compare mean coefficients of correlation ($\bar{r}$) of the previously selected rainfall and runoff characteristics across solute clusters and test for between grouping response differences.

RESULTS

Sampling period and monsoonal rainfall

Rainfall–runoff monitoring and water quality collections spanned a large range of P_{depth} and time since the onset of the monsoon over the 2 years of study (Figure 2). The 2007 monsoon had significantly ($p < 0.05$) less seasonal rainfall than the 2008 monsoon (average seasonal rainfall of 193 and 247 mm, respectively), which can be attributed to a significantly lower number of rainfall events in 2007 than in 2008 (23.0 and 28.3 average rainfall events, respectively; Table I). Although seasonal rainfall was greater in 2008, there were no significant differences in P_{depth}, $P_{\text{intensity}}$ and P_{duration} or time since antecedent rainfall between monsoon seasons, and rainfall characteristics did not vary significantly with day of year and were similar to those reported in other studies in the region (e.g. Mendez *et al.*, 2003).

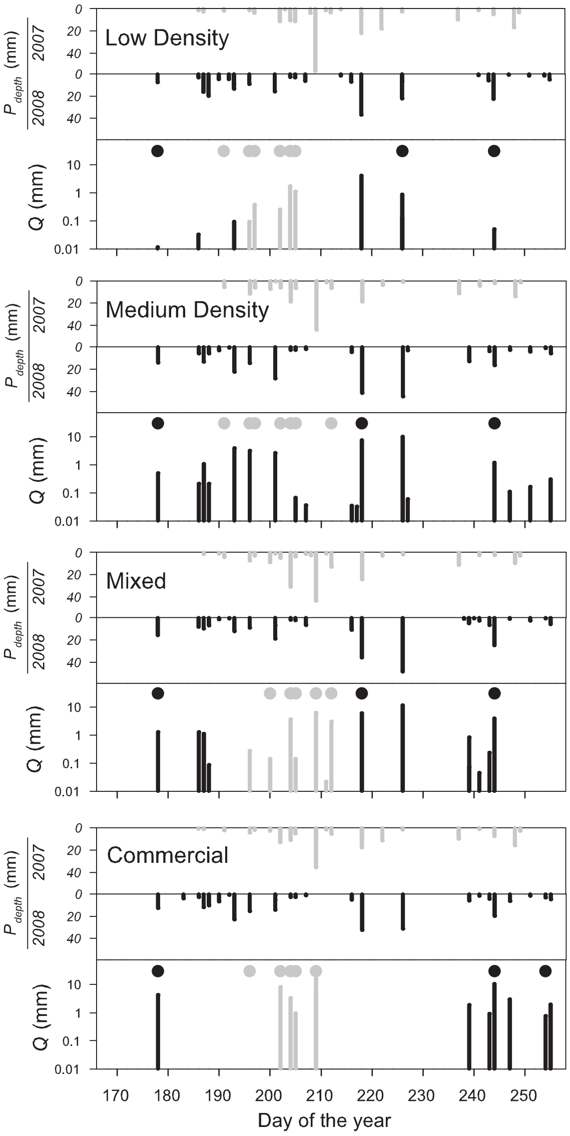


Figure 2. Rainfall hyetographs and discharge for the 2007 (gray) and 2008 (black) summer monsoons at each of our study sites. Circles indicate discharge events sampled for runoff quality. Discharge records for the Medium Density site during 2007 are not available

Table I. Mean characteristics of rainfall, discharge and runoff ratio (min–max) at the study sites during the 2007 and 2008 summer monsoons

	Seasonal rainfall (mm)^{a}		Rainfall events		P_{depth} (mm)^{b}	P_{duration} (h)^{b}	$P_{\text{intensity}}$ (mm h^{-1})$^{b\,c}$	Time since last rain (days)^{b}	Discharge (mm)^{b}	Runoff ratio (%)^{b}
	2007	2008	2007	2008						
LD (20^{d})	197	239	23	28	8.3 (<1–55.8)^{A}	1.0 (<0.1–3.9)^{A}	15.0 (0.3–87.3)^{A}	3.2 (<0.1–13.5)^{A}	0.5 (<0.1–1.7)^{B}	3.1 (<0.1–15.6)^{B}
MD (17^{d})	184	251	22	29	9.2 (<1–44.5)^{A}	1.3 (<0.1–5.7)^{A}	11.4 (0.7–58.0)^{A}	3.0 (<0.1–10.6)^{A}	1.8 (<0.1–9.9)^{B}	8.2 (0.8–22.3)^{B}
MX (18^{d})	198	253	24	30	8.5 (<1–43.4)^{A}	1.1 (<0.1–4.0)^{A}	12.1 (0.5–58.7)^{A}	2.7 (<0.1–10.6)^{A}	2.2 (<0.1–11.3)^{AB}	9.8 (1.2–23.6)^{B}
CM (12^{d})	176	227	22	28	8.3 (<1–35.4)^{A}	1.1 (<0.1–4.0)^{A}	17.0 (0.3–77.4)^{A}	3.0 (<0.1–12.4)^{A}	4.8 (0.8–16.0)^{A}	38.3 (18.5–61.8)^{A}

Rainfall depth (P_{depth}), duration (P_{duration}), intensity ($P_{\text{intensity}}$) and time since last rain are not significantly different among years or study sites and are, on average, 8.6 mm, 1.1 h, 13.7 mm h^{-1}, and 2.9 days, respectively.

[a] Interpolated from rainfall gauges located at a distance no greater than 4 km from each catchment centroid.

[b] Mean values sharing the same superscript letter are not significantly ($p > 0.05$) different from each other.

[c] The highest $P_{\text{intensity}}$ values observed for short duration events.

[d] Total number of runoff events monitored.

Discharge and runoff ratio

Across sites, discharge and runoff ratios did not vary significantly or predictably with day of year or cumulative rainfall. However, discharge and runoff ratios increased significantly with P_{depth} ($r^2 = 0.52$ and 0.08, respectively), imperviousness ($r^2 = 0.20$ and 0.65, respectively) and antecedent rainfall duration ($r^2 = 0.13$ and 0.12, respectively) and decreased significantly with catchment size ($r^2 = 0.15$ and 0.20, respectively). Not surprisingly, discharge and runoff ratios were significantly larger at the commercial site (CM), which has the highest imperviousness, than at all other sites (Table I). At each site, discharge and runoff ratios were most significantly correlated with P_{depth} (Table II). The strongest discharge–P_{depth} correlation was at CM ($r = 0.95$) and the weakest at the low density (LD) site ($r = 0.47$) (Table II). Correlations of discharge and runoff ratios to P_{duration} and $P_{\text{intensity}}$ were weaker than correlations with P_{depth}. Interestingly, discharge and runoff ratios correlated significantly with antecedent rainfall depth and duration at LD only, whereas discharge or runoff ratios did not correlate with day of year, cumulative rainfall or antecedent rainfall characteristics at any of the sites.

On the basis of the results of the discharge and runoff ratio regression analyses, we constructed multiple regression models with discharge and runoff ratio as response variables and land cover (imperviousness or catchment size), rainfall characteristics (P_{depth}, P_{duration}, $P_{\text{intensity}}$ or antecedent rainfall duration) and interactive terms (e.g. imperviousness × P_{depth}) as independent variables. No significant correlations between imperviousness, catchment size and rainfall characteristics were observed. Statistical models including catchment size explained a smaller fraction of the discharge and runoff ratio variance than models that included imperviousness. Of the models generated, the most robust included P_{depth}, imperviousness (IC) and their interaction ($P_{\text{depth}} \times IC$) and predicted 91% of the variance in discharge and 75% of the variance in runoff ratio ($p < 0.01$; Figure 3). Removing large P_{depth} values from the model returned r^2 values of 0.87 and 0.73 for discharge (Q) and runoff ratio (RR), respectively, demonstrating that large P_{depth} did not weigh disproportionately into the model. The regression equations are as follows:

$$Q = -4.91 + \left(0.23P_{\text{depth}}\right) + (0.09\text{IC}) + \left[0.01\left(P_{\text{depth}} - 13.13\right)(\text{IC} - 45.37)\right] \tag{7}$$

$$\text{RR} = -18.65 + \left(0.39P_{\text{depth}}\right) + (0.58IC) + \left[0.02\left(P_{\text{depth}} - 13.13\right)(\text{IC} - 45.37)\right] \tag{8}$$

The next best performing statistical model included antecedent rainfall duration, imperviousness and antecedent rainfall duration × imperviousness predicted 25% and 65% of the variance in discharge and runoff ratio, respectively. Models that included more than two independent variables (e.g. imperviousness, P_{depth} and antecedent rainfall duration) did not improve the fraction of the variance explained by the statistical model.

Table II. Coefficient of correlation and significance of fit (r and p) of discharge and runoff ratio to rainfall characteristics

					Antecedent rainfall	
	Catchment (n)	P_{depth}	$P_{\mathrm{intensity}}$	P_{duration}	intensity	duration
Discharge	LD (20)	0.42 (0.04)	ns	ns	−0.47 (0.04)	0.55 (0.02)
	MD (17)	0.92 (<0.01)	0.58 (0.01)	0.54 (0.02)	ns	ns
	MX (18)	0.92 (<0.01)	0.69 (<0.01)	0.65 (0.01)	ns	ns
	CM (12)	0.95 (<0.01)	0.77 (0.01)	ns	ns	ns
Runoff ratio	LD (20)	ns	ns	ns	−0.46 (0.05)	0.57 (0.01)
	MD (17)	0.58 (0.01)	ns	0.48 (0.04)	ns	ns
	MX (18)	0.70 (<0.01)	0.56 (0.02)	ns	ns	ns
	CM (12)	0.64 (<0.01)	ns	ns	ns	ns

Nonsignificant correlations ($p > 0.05$) are reported as 'ns'.

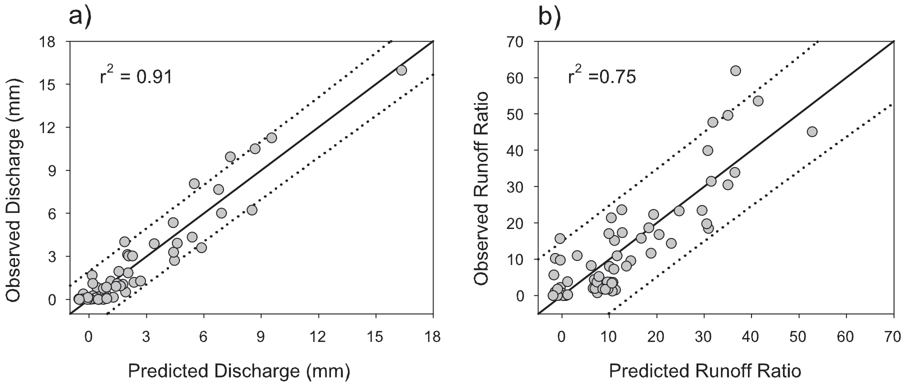


Figure 3. (a) Observed discharge versus predicted discharge and (b) observed runoff ratio versus predicted runoff ratio from a two-component least squares statistical model that includes P_{depth}, imperviousness and $P_{\mathrm{depth}} \times$ imperviousness. Both models are highly significant ($p < 0.01$). Dashed lines denote the 95% prediction interval

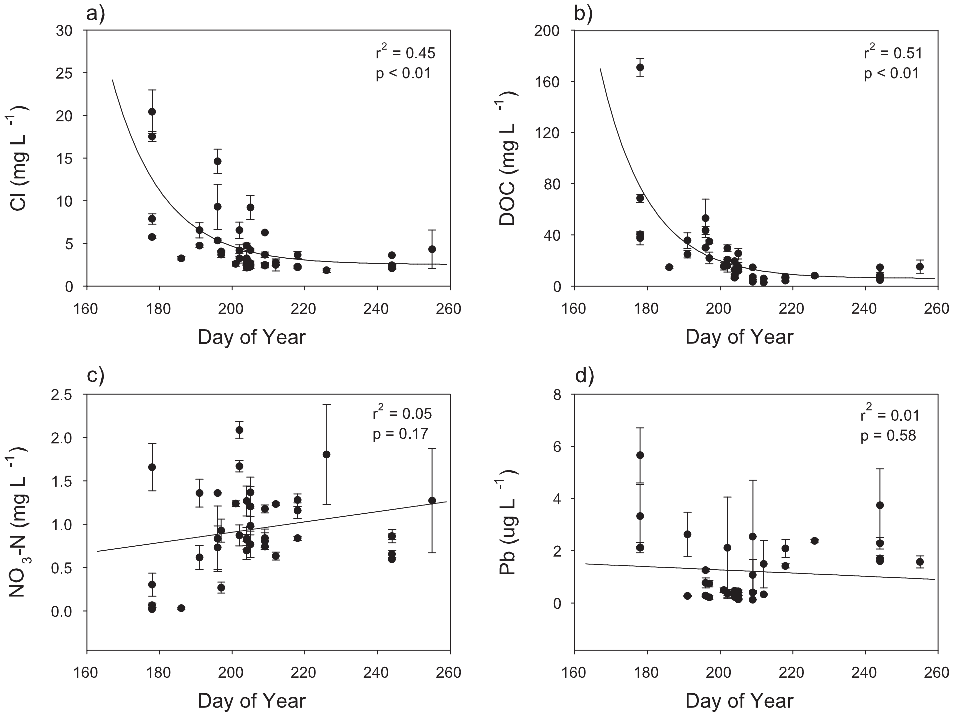


Figure 4. Mean seasonal solute concentrations of (a) Cl, (b) DOC, (c) NO_3-N and (d) Pb against day of the year during both the 2007 and 2008 monsoon. We observe a significant exponential decrease in Cl and DOC concentration as the monsoon progresses. In contrast, concentrations of NO_3-N and Pb do not vary significantly over the monsoon

Solute hydrochemistry

Most solute concentrations exhibited seasonal responses like those illustrated by Cl and DOC, where concentrations decreased significantly and exponentially with increasing day of year (Figures 4a and 4b) and cumulative rainfall. However, NO_2-N, *E. coli* and PO_4-P concentrations exhibited seasonal responses similar to those illustrated by NO_3-N and Pb, which remained invariant with respect to day of year (Figures 4c and 4d) and cumulative rainfall.

Solute concentration responses to P_{depth}, $P_{duration}$, time since antecedent rainfall, discharge and cumulative discharge varied in their strength and direction (Table III). For example, as illustrated in Figures 5a and 5b, DOC significantly decreased as discharge increased, NO_3-N weakly increased ($0.1 > p > 0.05$) with discharge and Cl and Pb varied independently of discharge and behaved chemostatically ($m = 0$). Similarly, the log–log regressions of solute concentration versus cumulative discharge indicate that Cl and DOC significantly decreased as cumulative discharge increased, NO_3-N significantly increased with cumulative discharge and Pb behaved chemostatically (Figures 5c and 5d). Most solute concentrations ($n > 19$) significantly decreased as cumulative discharge and $P_{duration}$ increased and significantly increased as time since antecedent rainfall increased. About half the solutes significantly decreased as discharge and P_{depth} increased, and most solutes did not correlate with imperviousness, catchment size (Table III), $P_{intensity}$ or antecedent rainfall depth, intensity and duration. Interestingly, *E. coli* did not correlate significantly with any rainfall or runoff characteristics. The NCL-NCQ analyses indicate that about half of the solutes ($n = 12$) exhibited an early season solute flush ($m < 1$; Table III), for example, Cl and DOC (Figures 6a and 6b), whereas approximately half ($n = 12$) exhibited seasonal solute chemostasis ($m = 1$), for example, NO_3-N and Pb (Figures 6c and 6d). Interestingly, PO_4-P was the only solute to exhibit a late seasonal flush ($m > 1$).

Five distinct seasonal solute response patterns, clusters C1–C5, were identified with the clustering analyses (cluster distance > 2.0; Figure 7). The mean correlation ($\bar{r}$) and maximum significance values of solute concentrations versus P_{depth}, $P_{duration}$, time since antecedent rainfall, discharge and cumulative discharge and the mean NCL-NCQ regression slope ($\bar{m}$) for each cluster (Table IV) highlight differences in seasonal solute cluster responses to rainfall and runoff. Specifically, cluster C1 was the only cluster that was significantly and negatively

Table III. Correlations (r) of mean storm solute concentrations to select rainfall and runoff characteristics, imperviousness and catchment size; and slope of normalized cumulative load to normalized cumulative discharge regression ($m_{NCL\text{-}NCQ}$)

Solute	P_{depth}[a]	$P_{duration}$[a]	Time since last rain[b]	Discharge depth[c]	Cumulative discharge[c]	Impervious cover[a]	Catchment area[a]	$m_{NCL\text{-}NCQ}$[c]
Cl	−**0.35** *	−**0.57** *	**0.61** *	−0.24	−**0.48** *	0.31 **	−0.18	**0.90***
NO_2-N	−0.27	0.06	**0.34** *	−0.01	−0.13	0.09	−0.03	0.90**
NO_3-N	−0.04	**0.37** *	−**0.41** *	0.36 **	**0.49** *	−0.06	0.02	1.01
NH_4-N	−**0.37** *	−**0.43** *	0.31 **	−**0.41** *	−**0.55** *	−0.01	−0.20	0.88 **
DON	−**0.52** *	−**0.45** *	**0.43** *	−0.19	−**0.44** *	−0.02	−0.04	**0.50***
SO_4-S	−**0.57** *	−**0.54** *	**0.62** *	−**0.43** *	−**0.6** *	0.10	−0.03	**0.87***
PO_4-P	−0.04	0.24	−**0.38** *	**0.45** *	**0.40** *	**0.34** *	−0.14	**1.06***
DOC	−**0.51** *	−**0.57** *	**0.66** *	−**0.51** *	−**0.71** *	−0.11	0.01	**0.80***
Escherichia coli[d]	−0.09	0.09	0.44	−0.04	−0.24	0.38	0.31	n.a.
Ca	−0.09	−**0.49** *	**0.56** *	−0.26	−**0.35** *	0.12	−0.1	0.97
K	−0.25	−**0.48** *	**0.71** *	−0.33	−**0.68** *	−0.12	−0.03	0.96
Mg	−**0.43** *	−**0.55** *	**0.66** *	−**0.45** *	−**0.66** *	−0.06	−0.13	0.95
Na	−0.28	−**0.48** *	**0.64** *	−0.27	−**0.37** *	0.26	−0.13	0.93
As	−0.16	−**0.52** *	**0.64** *	−0.23	−**0.45** *	0.01	0.02	**0.96***
Al	−0.04	−0.24	**0.41** *	−0.25	−**0.41** *	−0.22	0.02	0.98
Cd	−0.29 **	−**0.43** *	**0.47** *	−0.35 **	−**0.44** *	0.22	−**0.35** *	0.93
Co	−**0.48** *	−**0.52** *	**0.46** *	−**0.40** *	−**0.69** *	−0.05	−0.19	**0.87***
Cu	−**0.57** *	−**0.58** *	**0.70** *	−0.35 **	−**0.6** *	0.15	−0.12	**0.88***
Fe	−0.25	−**0.35** *	**0.41** *	−**0.45** *	−**0.67** *	−0.20	0.07	0.99
Hg	−**0.64** *	−**0.56** *	**0.63** *	−**0.84** *	−**0.70** *	0.11	−0.16	0.90
Mn	−**0.49** *	−**0.49** *	**0.53** *	−**0.53** *	−**0.68** *	−0.25	−0.03	0.95
Ni	0.03	−**0.34** *	**0.53** *	−0.11	−0.24	0.06	−0.19	0.93
Pb	0.27	0.01	**0.33** *	0.01	0.05	0.03	−0.27	0.97
V	−**0.41** *	−**0.61** *	**0.73** *	−**0.40** *	−**0.65** *	0.12	−0.18	**0.93***
Zn	−**0.46** *	−**0.46** *	**0.65** *	−0.28	−**0.45** *	0.27	−0.27	**0.81***

Only rainfall variables that yielded significant solute regressions are shown. Correlations with a significance level less than 0.1 are in bold.

[a] $n = 35$ for all solutes except for *E. coli*, where $n = 9$, and Hg, where $n = 13$.

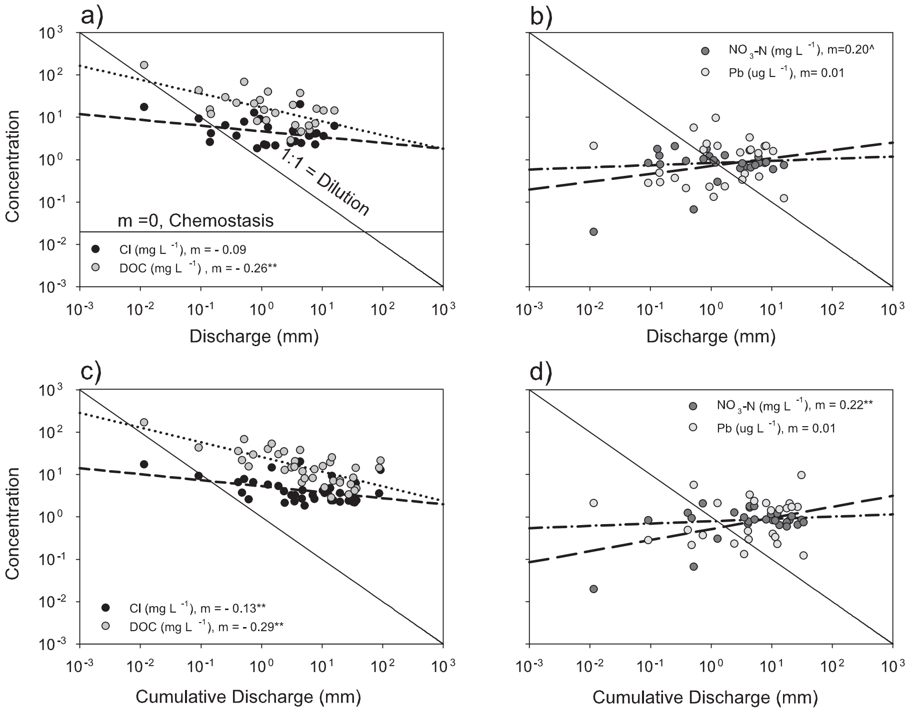
[b] $n = 31$ for all solutes except for *E. coli*, where $n = 9$, and Hg, where $n = 13$.

[c] $n = 26$ for all solutes except for *E. coli*, where $n = 6$ and Hg, where $n = 9$.

[d] Because *E. coli* was only measured for two to three storm events for each site, we have not calculated NCL.

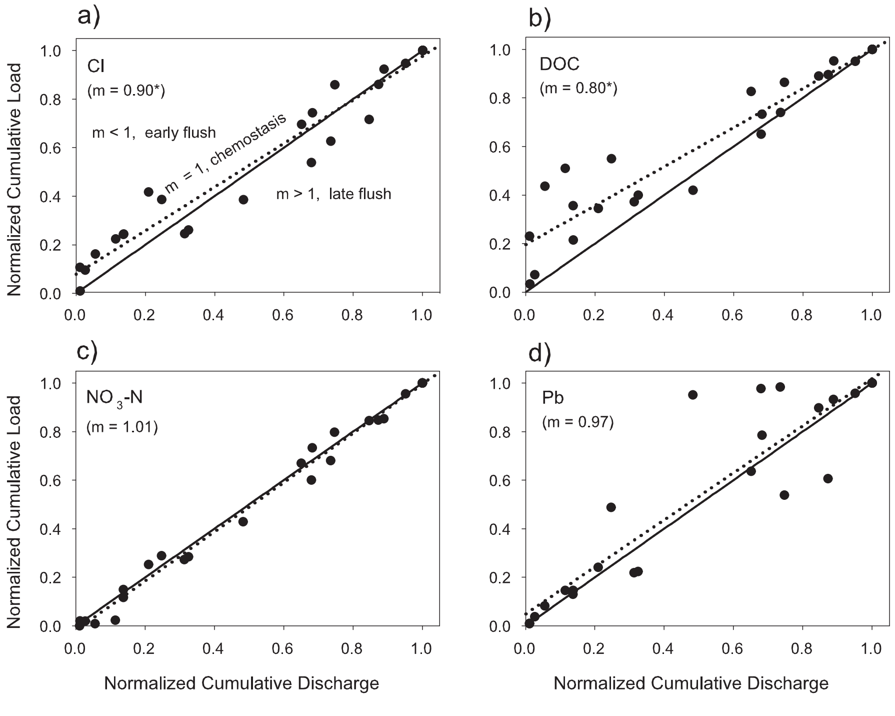
*Solute correlations and $m_{NCL\text{-}NCQ}$ with $p < 0.05$.

**Solute correlations and $m_{NCL\text{-}NCQ}$ with $0.05 < p < 0.1$.



** denotes significant regressions at $p < 0.05$.
^ denotes regression at 0.05 ? $p < 0.10$.

Figure 5. Mean event concentrations of Cl, DOC, NO_3-N and Pb against (a and b) discharge and (c and d) cumulative discharge. Data that plot along a 0 slope line denote solute chemostasis, whereas points plotting along a −1:1 line exhibit solute dilution



* denotes slopes significantly different from 1.

Figure 6. NCL versus NCQ for Cl, DOC, NO_3-N and Pb. Solid lines denote slope $(m) = 1$; dotted lines are regressions for NCL-NCQ. Slopes $(m) < 1$ denote early seasonal solute flushing, $m > 1$ indicate late season flush and $m = 1$ indicate seasonal solute chemostasis

correlated with P_{depth} ($\bar{r} = -0.51$). Clusters C1 and C2 were significantly and negatively correlated with P_{duration} (−0.56 and −0.46, respectively). Clusters C1, C2 and C3 were positively correlated with time since antecedent rainfall, with C1 having the strongest significant positive correlation ($\bar{r} = 0.62$, 0.53 and 0.53 for C1, C2 and C3, respectively), whereas C5 exhibited a significant negative correlation to time since antecedent rainfall (−0.39). Only

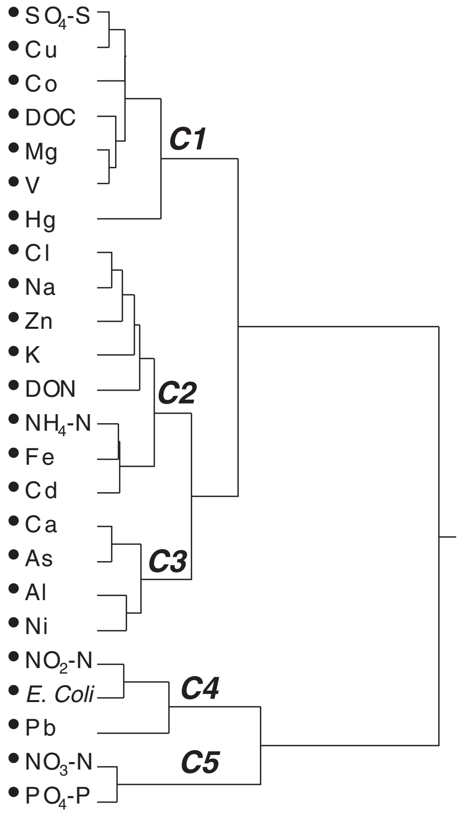


Figure 7. Clustering analysis dendrogram The clusters are indicative of 5 major patterns of seasonal solute responses

clusters C1 and C5 were significantly correlated with discharge; C1 was negatively correlated (−0.48), whereas C5 was positively correlated (0.41). A similar pattern was observed for cumulative discharge where C1 had a stronger significant negative correlation (−0.67) than C2 (−0.51) and C5 had a significant positive correlation (0.47). Curiously, C4 was not significantly or strongly correlated to any of the aforementioned variables, although the strongest correlation was with time since antecedent rainfall.

DISCUSSION

Hydrology

Although a larger number of rainfall events led to greater cumulative seasonal rainfall for the 2008 monsoon, the consistency of rainfall characteristics across sites and years suggests that the differences observed in discharge and runoff ratios across catchments arise because of differences in rainfall partitioning at each site. Across sites, the runoff ratios that we report in this study agree with runoff ratios reported for other arid and semiarid urban catchments (Ishaq and Alassar, 1999; Goldshleger *et al.*, 2009) and are consistent with other studies where the smallest and largest discharge and runoff ratios occur at the lowest and highest imperviousness (Arnold and Gibbons, 1996; Rose and Peters, 2001; Lerner, 2002; Burns *et al.*, 2005; Endreny, 2005; Shuster *et al.*, 2005; Glick, 2009). The runoff ratios that we report are larger than those in nonurbanized catchments in the semiarid Walnut Gulch Experimental Watershed (e.g. mean runoff ratios of 2.4, 4.6 and 5.5 % at watersheds 11, 112, and 4, respectively; http://www.tucson.ars.ag.gov/dap/; Goodrich *et al.*, 2008), providing further evidence that urbanization increases runoff quantity in small semiarid catchments and suggesting that urbanization alters the localized water balance by reducing catchment water storage and enhancing runoff generation.

Hydrologic responses at the more impervious sites, MD, MX and CM, appear to be mainly controlled by the depth of each individual rainfall event and not by the temporal distribution of rainfall. The larger imperviousness and therefore smaller soil footprint at these sites may explain the lack of correlation of discharge and runoff ratio to antecedent conditions, cumulative rainfall and time since antecedent rainfall, which point to the absence of seasonal catchment wetting. It is plausible that by reducing pervious surfaces, imperviousness diminishes a catchment's capacity for soil-water storage, which when combined with the high daily evapotranspirative demand typical of arid and semiarid regions (Howell *et al.*, 1983; Grimmond and Oke, 1999), may decrease or eliminate the effect that antecedent conditions could affect rainfall–runoff responses.

In contrast, antecedent conditions explain a significant fraction of the variance in discharge and runoff ratio at LD (Table II), which is the least impervious (21%) site, suggesting that the degree of catchment wetting before a rainfall event is a more important control of hydrologic responses at low imperviousness than P_{depth} and $P_{\mathrm{intensity}}$. Several studies clearly demonstrate that antecedent conditions significantly affect rainfall–runoff processes in nonurbanized semiarid catchments (Osborn and Lane, 1969; Loik *et al.*, 2004); however, similar results have been reported in only a handful of urban studies and laboratory experiments (e. g. Shuster *et al.*, 2008; Smith *et al.*, 2005). It is plausible that a larger fraction of rainfall is partitioned into soil infiltration and ephemeral channel storage at this low imperviousness site, thus reducing the soil-water storage capacity and increasing the proportion of rainfall partitioned into runoff during subsequent precipitation events.

Our analyses indicate that independently, P_{depth}, imperviousness and all other rainfall variables are poor predictors of hydrologic responses. However, our two-component statistical model indicates that combined, P_{depth} and imperviousness impart a significant effect on discharge and runoff ratios (Figure 3; Equations 7 and 8). Specifically, our model suggests that the hydrologic responses resulting from any given rainfall input largely depend on the degree of imperviousness.

Although our study was not designed to test the effect of catchment size on hydrologic responses, our data indicate that discharge and runoff ratios decrease with increasing catchment size, which is consistent with observations made in other semiarid sites (Boughton and Stone, 1985; Stone *et al.*, 2008). Surprisingly, models

Table IV. Comparison of mean correlation values of solute concentrations to P_{depth}, P_{duration}, time since last rain, discharge and cumulative discharge among the five clusters identified with the clustering analysis (C1, C2, C3, C4 and C5), mean slope ($\bar{m}$) and SE of NCL-NCQ regressions for each cluster

Cluster	Solutes	P_{depth}	Rainfall duration	Time since last rain	Discharge depth	Cumulative discharge	NCL-NCQ ($\bar{m} \pm$ SD)	Solute behaviour
C1	SO_4-S, Cu Co, DOC, Mg, V, Hg	$-0.51^{C,*}$	$-0.56^{D,*}$	$0.62^{A,*}$	$-0.48^{D,**}$	$-0.67^{E,*}$	0.90 ± 0.02	Strong early seasonal flush; event solute flush, rapid increase in mobile solute reservoirs between storm events
C2	Cl, Na, Zn, K, DON, NH_4-N, Fe, Cd	-0.35^{B}	$-0.46^{CD,*}$	$0.53^{AB,**}$	-0.32^{CD}	$-0.50^{D,*}$	0.86 ± 0.05	Strong early seasonal flush, event chemostasis, rapid increase in mobile solute reservoirs between storm events
C3	Ca, As, Al, Ni	-0.07^{A}	-0.40^{C}	$0.53^{AB,*}$	-0.21^{BC}	-0.33^{C}	0.96 ± 0.01	Weak seasonal flush, event chemostasis, rapid increase in mobile solute reservoirs between storm events
C4	NO_2-N, *Escherichia coli*, Pb	-0.03^{A}	0.06^{B}	0.37^{B}	-0.01^{B}	-0.11^{B}	0.93 ± 0.04	Chemostasis, no increase in mobile solute stores after rainfall events
C5	PO_4-P, NO_3-N	-0.04^{A}	0.30^{A}	$-0.39^{C,*}$	$0.41^{A,*}$	$0.47^{A,*}$	1.04 ± 0.02	Late seasonal flush, concentrations decrease as time between rainfall events increases

Correlation values sharing the same superscript across clusters are not significantly different.
*Correlations with maximum $p < 0.05$.
**Correlations with $0.05 < \text{mean } p < 0.1$.

in our study including catchment size and P_{depth} did not yield significant statistical predictions of discharge and runoff ratio. We hypothesize that shifts in rainfall partitioning post-urbanization as well as the high spatial variability of summertime convective rainfall may obscure the effect of catchment size on discharge magnitude and timing. In summary, we show that urbanization alters rainfall partitioning in semiarid catchments resulting in decreased seasonal catchment wetting and enhanced delivery of event runoff to ephemeral waterways, suggesting that by delivering more runoff to areas of focused recharge, urbanization may enhance renewable groundwater supplies.

Water quality

In contrast with a large body of literature documenting urban runoff quality across a range of climates, we found that the overall quality of urban runoff does not vary in response to catchment size or imperviousness (Table III, e.g. Brabec *et al*., 2002; Glick, 2009; Schueler *et al*., 2009; Walsh *et al*., 2005; Wenger *et al*., 2009), suggesting that variable solute sourcing and pervious areas play an important role in solute transport during storm events and retention between storm events. Consistent with a large number of urban (e.g. Lee *et al*., 2002; Westerlund *et al*., 2003; Asaf *et al*., 2004; Soller *et al*., 2005) and nonurban studies (e.g. Kirchner *et al*., 2000; Welter *et al*., 2005; Godsey *et al*., 2009), we observed variable solute responses to rainfall and discharge (Figures 4 and 5; Table III). Specifically, several solutes exhibited event and seasonal solute dilution, whereas other solutes did not vary with discharge and cumulative discharge, indicating event and seasonal chemostasis. The NCL-NCQ regressions for half of the solutes addressed in this study are indicative of early seasonal solute flushing (Figure 6 and Table IV), which are consistent with observations made by Asaf *et al.* (2004) and Lee *et al.* (2004) and which are clearly highlighted by the exponential decay of Cl and DOC (Figure 4), among others, over time.

Most striking is that most solute concentrations, with the exception of NO_3-N and PO_4-P, varied positively with time since antecedent rainfall, suggesting that mobile solute reservoirs increase with increasing time between rainfall events. Our results are consistent with the 'pollutant washoff' concept and with literature where solute loads are, in part, reported to be a function of the length of time between rainfall events (e.g. Barbe *et al*., 1996; Lee *et al*., 2004; Soller *et al*., 2005; Maestre and Pitt, 2006; Lewis and Grimm, 2007; Soonthornnonda *et al*., 2008; Avellaneda *et al*., 2009). It is important to note that an increase in the magnitude of solute reservoirs does not exclusively refer to solute store replenishment via wet and aeolian deposition. Mechanisms that may increase the magnitude of easily mobilized solute reservoirs include physical and chemical weathering of geologic and urban materials (Norra *et al*., 2008), photo degradation of organic matter (Austin and Ballare, 2010), nonpoint solute sourcing (Lohse *et al*., 2008), variable contributing areas and solute transport (Bencala, 1984; Harms and Grimm, 2010) and processes such as decomposition and mineralization of organic matter in soils (Schlesinger, 1997) of pervious areas and within stream channels. Overall, our study supports the findings of Lee *et al.* (2004), who show that antecedent dry days have a larger effect on solute concentrations than rainfall characteristics.

The high variability of solute responses to rainfall and runoff presents a challenge in identifying the factors that control urban runoff quality. However, with the clustering analysis, we identified five solute response patterns that point to distinct solute sourcing and mobilization mechanisms (Table IV). Clusters C1 and C2 exhibit similar solute response patterns. The negative correlation of C1 solutes to P_{duration} and discharge, and the significant positive correlation to time since antecedent rainfall suggests that these solutes are readily flushed during runoff events and that solute reservoirs rapidly increase in magnitude between runoff events. The significant negative correlation of C1 and C2 to cumulative discharge and the NCL-NQL slopes point to an early seasonal solute flush and to potential solute retention and cycling later in the season of biogeochemically active solutes like DOC, SO_4-S, DON and NH_4-N. The major difference in the response between C1 and C2 responses is that C1 solutes appear to be more readily mobilized than C2 solutes as indicated by the stronger negative P_{depth}, discharge and cumulative discharge correlations. Interestingly, priority pollutants such as Zn, Co, Cd and Hg (Athayde *et al*., 1983) and biogeochemically active solutes DOC, SO_4-S, DON and NH_4-N clustered with C1 and C2, suggesting that in semiarid catchments, major factors controlling urban runoff quality are solute mobilization and potential retention and biogeochemical cycling as wetting event magnitude and duration increases.

Concentrations of C3 solutes, in contrast, do not vary significantly with P_{depth} or discharge, although mobile solute reservoirs appear to increase rapidly in magnitude between rainfall events and do exhibit a very weak early season solute flush. These complex responses may arise from variable solute sourcing and mobilization. Cluster C3 solutes, specifically Ca and Ni, are geologically abundant in the Tucson Basin (Robertson, 1989; Tadayon, 1995a; Tadayon, 1995b). It is plausible that early season mobilization of large solute stores accumulated over the dry months preceding the summer monsoon, coupled with widespread solute sourcing throughout the monsoon and weathering of geologic materials during and between rainfall events, results in solute chemostasis with respect to discharge and an overall weak seasonal flushing response.

Cluster C4 exhibits the strongest solute chemostasis, indicating that solute mobilization is invariant over time. Solute chemostasis may arise from variable solute sourcing and transport among our sites. For example, we expect *E. coli* stores to increase at different rates among our sites between rainfall events because known *E. coli* sources (e.g. wildlife, agricultural livestock and pets) are related to land use. The variability of solute sourcing across sites results in a chemostatic response pattern. Therefore, we suggest that the seasonal dynamics of C4 solutes are more tightly linked to the spatial characteristics of land cover than to the temporal characteristics of rainfall and runoff (Gallo *et al.*, in revision).

Finally, cluster C5 is the only cluster that exhibits a significant positive response to discharge and cumulative discharge, a late season flush and decreasing solute concentrations with increasing time since antecedent rainfall. Phosphorous (P) mobility in desert soils with abundant carbonates is driven by the preferential sorption of P to Ca and subsequent precipitation of Ca-P complexes (Lajtha and Schlesinger, 1988; Gonzalez-Pradas *et al.*, 1993; Cross and Schlesinger, 2001; Carreira *et al.*, 2006). Laboratory experiments show that a fraction of labile sorbed phosphorous can be released with salt and acidic solutions (Cross and Schlesinger, 2001; Carreira *et al.*, 2006) within hours of soil treatment (Shariatmadari *et al.*, 2006; Biabanaki and Hosseinpur, 2009). The rapid desorption and mobilization of phosphorous observed in laboratory experiments suggests that the PO_4-P we observed in runoff could be mobilized after soil wetting and may vary with the extent of wetting, resulting in increasing concentrations with increasing discharge and cumulative discharge. Interestingly, PO_4-P was the only solute to exhibit a significant positive correlation with imperviousness. Although a type I error could explain this relationship, it is plausible that in addition to sourcing form Ca-P complex dissolution, elevated PO_4-P deposition, as has been shown in the urban core of Phoenix, Arizona (Lohse *et al.*, 2008), in the months preceding the monsoon and enhanced mobility from impervious areas result in a positive correlation of solute concentrations with imperviousness.

With regard to NO_3-N, water limitations and the quick resetting of moisture conditions in the interstorm period (Table II) may limit biogeochemical processes such as nitrogen mineralization and fixation and subsequent NO_3-N production in soils. Physical sorption and precipitation of PO_4-P in soil solution and biological uptake of PO_4-P and NO_3-N are additional mechanisms that may decrease solute stores as time since antecedent rainfall increases. Although decreasing PO_4-P with increasing time since antecedent rainfall is reported in at least one other study (Passeport and Hunt, 2009), the arid land literature reports increasing rather than decreasing NO_3-N as time since antecedent rainfall increases because of elevated nitrification after a rainfall pulse and as flow path length increases (Welter *et al.*, 2005). It is plausible that the changes in flow paths and the quickly resetting moisture conditions alter physical and biogeochemical processes that control nitrogen, phosphorous and carbon fluxes and transformations in urban catchments. Further work is needed to assess how urbanization alters biogeochemical processes and nutrient cycling pathways given that the soil properties, the magnitude and frequency of wetting, the type of urban landscape and the length and characteristics of flow paths significantly affect nitrogen dynamics in semiarid regions (Loik *et al.*, 2004; Welter *et al.*, 2005; Hall *et al.*, 2009; McIntyre *et al.*, 2009).

CONCLUSIONS

The variability of hydrologic responses across the study sites was best explained by the combined effect of rainfall depth with imperviousness, indicating that the effect of rainfall on runoff responses varies with the extent of imperviousness. With the exception of the low imperviousness catchment, we found no evidence of seasonal catchment wetting resulting in increased water yields across our sites. Combined with increases in discharge and runoff ratio as imperviousness increases, our study suggests that urbanization enhances rainfall partitioning to runoff, decreases the potential for catchment water storage and enhances the resetting of moisture conditions between rainfall events. Solute concentrations in runoff did not vary with catchment size or imperviousness, and most mobile solute reservoirs increased with increasing time since antecedent rainfall. Using clustering analyses, we identified five general seasonal solute responses: (i) strong event and seasonal solute flush, (ii) event chemostasis and strong seasonal solute flush, (iii) event chemostasis and weak seasonal flush, (iv) event and seasonal chemostasis and (v) late seasonal flush.

Together, our results show that urbanization enhances the fraction of rainfall delivered to the major ephemeral waterways of the region, which, through focused recharge, may be beneficial for sustaining local water resources. However, rapid resetting of moisture conditions, particularly at higher imperviousness, may limit biogeochemical processing of solutes between wetting pulses, which combined with rapid buildup of solute reservoirs between rainfall events, enhances solute transport during runoff, pointing to a direct trade-off between the quantity of runoff available for recharge and its effect on groundwater supplies. Further research is needed to assess the extent to which urban runoff in semiarid regions alters biogeochemical processing between rainfall events and subsequent solute sourcing, transport and groundwater quality. However, we show that hydrologic responses of semiarid catchments are controlled by imperviousness and event scale hydrologic partitioning, whereas wetting magnitude, frequency and timing alter solute stores readily available for transport and control seasonal hydrochemical responses. We suggest that stormwater monitoring should be designed to capture a range of rainfall depths and antecedent dry days throughout the season to appropriately assess the effect of best management practices on stormwater quality.

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