DISSOLVED ORGANIC CARBON DYNAMICS IN URBAN AND DESERT STREAM ECOSYSTEMS

by

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ABSTRACT

Variation in stream chemistry is a function of the strength of terrestrial-aquatic linkages, the extent to which surface and groundwater exchanges, and the rate of in-stream biotic processes. The importance of these variables may fluctuate as a function of climate regime, catchment geomorphology, or level of human impact. A mechanistic understanding of the influence of each of these variables on ecosystem functioning will increase understanding of the role of streams in global nutrient and carbon cycles. Of particular interest is dissolved organic carbon (DOC), an important source of carbon and energy for microbial processes. Respiration by heterotrophic bacterial communities has recently been linked to the quality (ability of microbes to utilize C source) of the DOC pool in streams. DOC not only influences stream nutrient supply, but also the transport of contaminants and the attenuation of UV radiation. This dissertation focused on DOC delivery to two arid-land stream ecosystems, one native desert (Sycamore Creek, AZ), and one urban (Phoenix, AZ). The overall objectives of this work were to (1) document patterns in DOC quantity and chemical composition in response to flooding and groundwater exchange, (2) generate and test hypotheses explaining variation in DOC quantity and quality and (3) relate this variation to microbial activity. In the native desert stream ecosystem, the climate regime influenced seasonal variation in the quantity and quality of DOC inputs, with higher complexity and higher concentrations of DOC in summer monsoonal runoff. In contrast, human alteration of geomorphology and hydrologic flowpaths in the Phoenix metropolitan area significantly influenced stream-water chemistry in comparison to low-impact streams in the Sonoran Desert. In the city, mechanisms of nutrient retention and transformation were often shifted from dominance

by biotic to abiotic ones, severely dampening the influence of climate regime and substituting instead the maintenance of food production and waste management as the dominant large-scale controlling factors. Patterns of microbial respiration and extracellular enzyme production indicate that the community's ability to react to changes in DOM composition may create shifts in extracellular enzyme production while maintaining relatively consistent levels of community respiration.

This is dedicated to the memory of Dr. C. Lisa Dent, whose enthusiasm for life was enormous. Her contribution to the field of ecology provides inspiration for young scientist, and her friendship will never be forgotten.

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INTRODUCTION

Riparian-stream ecosystems are an important component of all biomes. They deliver nutrients and organic matter to lakes and estuaries, and thereby influence the productivity of these recipient ecosystems (Elder et al. 2000, Peterson et al. 2001, Boyer et al. 2002). Variation in stream-water chemistry is a function of terrestrial-aquatic linkages, mixing of surface and groundwater, and in-stream biological processes (Newbold et al. 1995, Dent et al. 2001). The importance of each of these variables may differ among streams with different climate regimes, geomorphologies, or levels of human impact (Jones 1997). An understanding of the interaction of each of these higher-order variables on ecosystem functioning will produce a better understanding of the role of streams in global nutrient and carbon cycles. Streams also provide a valuable laboratory for testing theory, as the unidirectional flow of water separates hot spots of biogeochemical cycling in space and time.

One constituent of interest in all aquatic ecosystems is dissolved organic carbon (DOC). DOC is particularly important as a source of carbon and energy for microbial communities living in pelagic and benthic environments. The heterogeneity of the DOC pool makes identifying controls on its size and structure difficult. Often a much larger pool of carbon than particulate organic matter, DOC was considered relatively invariant, almost non-reactive, in freshwater systems during much of the 20th century. The last 20 years has seen a change from that paradigm, as researchers have broadened the techniques they use to quantify the different compounds that make up the DOC pool.

Rates of respiration of heterotrophic bacterial communities have been linked to the quality of the DOC pool in streams. (Baker et al. 1999, Craft et al. 2002). For this

work the term quality is defined in relation to the ability of the microbial community to utilize a carbon source for carbon or energy. Previous research has suggested that quality of DOC is negatively correlated with the chemical complexity (arrangement of C, O, and H atoms) of DOC compounds; therefore, chemical complexity is often interchanged with quality. However, our measure of chemical complexity, SUVA, is not considered functionally interchangeable with the term quality in this research unless directly tested, although the connection most likely exists. DOC chemical composition is temporally and spatially variable in stream ecosystems, which could generate variability in microbial mineralization of organic matter and the release of inorganic nutrients. DOC chemical complexity may not only influence stream nutrient supply, but it also influences the transport of contaminants (Paul and Meyer 2001). Large DOC compounds form associations with heavy metals and pesticides, and these complexes remain dissolved, thereby facilitating transport downstream. And finally, DOC absorbs UV radiation, ameliorating the negative effects of UV on stream biota while being transformed at the same time (Scully et al. 1996).

This dissertation focused on DOC delivery to two arid-land stream ecosystems, one native desert and one urban. The overall objectives of this work were (1) to document patterns in DOC quantity and chemical composition, (2) generate and test hypotheses explaining variation in DOC quantity and quality and (3) relate this variation to microbial activity. The overarching theme of the dissertation was the role of spatial and temporal variability in DOC quantity and complexity in controlling carbon cycling in stream ecosystems.

The first chapter documents DOC patterns in a native desert stream over four years with both high and low rainfall periods (Objective 1). Two important storm characteristics created much of the variation in DOC chemistry in upland runoff (Objective 2). One was the intensity of rainfall, with higher intensity rain producing more quickly moving surface runoff that spent less time in contact with upland soils or mixing with antecedent water in the mainstem (highest order stream in catchment) channel. Second, the frequency of small rainstorms preceding a large runoff event controls soil moisture content in the uplands, which in turn may influence the rate of biological mineralization of soil organic matter pools. The variation in DOC chemical complexity documented in this chapter most likely is important to microbial community activity within the stream sediments, creating temporal variability in C and nutrient cycling. To establish a link between variation in DOC chemical complexity and microbial activity, laboratory bioassays using microbial stream sediment communities were performed using sources of DOC with varying chemical complexity (Objective 3).

The second chapter compares native desert and urban stream ecosystems by examining differences in concentrations of DOC, nutrients, and conservative ions between desert stream sites that are unregulated, regulated, and highly modified by the urban environment. Changes in water chemistry over time and with respect to disturbance by flooding indicated that carbon and nutrient cycling have changed as a result of human modification of the landscape, including lowered hydrologic and chemical variability and increased baseflow C and N loading (Objective 1 and 2). This work suggests that biogeochemists working in an urban setting may need to shift their

focus from more traditional spatial and temporal scales of study by increasing both the spatial and temporal extent.

The third chapter again documents DOC patterns and mechanisms creating them, but in an urban stream with highly modified flowpaths that are actively managed by humans (Objective 1). Human alteration of geomorphology and hydrologic flowpaths in the Phoenix metropolitan area has significantly influenced stream water chemistry in comparison to low-impact streams in the Sonoran Desert. Mechanisms of nutrient retention and transformation were shifted from dominance by biotic to abiotic ones, severely dampening the influence of climate regime and substituting instead the maintenance of food production and waste management as the dominant large-scale controlling factors (Objective 2). The urban stream exhibited temporally consistent gradients in organic matter chemistry, which could provide an opportunity for ecologists to test theory concerning microbial community structure and stability under a hydrologic and chemical regimen that sits at one end of the spectrum between a highly disturbed and extremely stable ecosystem.

The fourth chapter links variation in DOC stream chemistry with microbial activity (Objective 3). Community respiration was temporally and spatially variable along the urban flowpath, but not strongly predicted by DOC quantity or complexity. Extracellular enzyme analysis indicated that microbial communities at each site along the flowpath were distinct in the composition of their suite of enzymes, and that they responded to changes in DOC complexity.

Following this short introduction, each of the four chapters is presented as a separate manuscript that stands on its own. The dissertation ends with a synthesis of the work as a whole.

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CHAPTER 1: TERRESTRIAL-AQUATIC LINKAGES IN A DESERT STREAM AND THEIR IMPORTANCE FOR DISSOLVED ORGANIC CARBON CYCLING

ABSTRACT

Spatial and temporal patterns in the delivery of dissolved organic carbon (DOC) to Sycamore Creek, AZ, were used to identify and quantify DOC sources to floodwaters and baseflows. The relative contribution from each hypothesized source to the total floodwater DOC load was calculated using mass balance equations. There were equivalent contributions from rewetting of unsaturated riparian soils and dry mainstem channel sediment, that when summed together, contributed significantly to floodwater DOC loads. Based on a two-endmember mixing model using chloride concentrations, the contribution of water and salts from these two sources was larger during winter floods than monsoon (summer) floods and was a function of rainfall intensity (r^2=0.47). Floodwater DOC chemical complexity (measured using specific ultraviolet absorbance) increased with increasing contributions from upland soil organic matter (SOM) pools. In addition to mass balance calculations for the catchment, DOC chemistry along the flowpath from precipitation to the mainstem was monitored to identify where on the landscape DOC transformations occurred and how upland SOM sources varied temporally. Upland soils contributed high-complexity DOC to runoff, which was then reduced both in complexity and DOC concentration as water moved from small to large tributaries. Temporal variation in water delivery and DOC chemical complexity along the flowpath was created by variation in antecedent moisture conditions, expressed as cumulative rainfall 30-120 days prior to sampling (depending on season). An increase in the antecedent moisture conditions resulted in low concentrations of high-complexity

DOC being exported from upland soils and small tributaries, and low-complexity DOC when antecedent conditions were dry. Of the three additional sources identified as possible contributors to baseflow chemistry, only one (algal exudates) was found to be important for stream DOC. This low complexity, high quality DOC may be the dominant source of DOC during monsoon months, but its influence was less evident in winter baseflow chemistry. Laboratory bioassays suggested that DOC in upland runoff could be the primary fuel for microbial respiration during winter months. The results from this work have important implications for ecosystem carbon cycling, the functioning of heterotrophic microbial communities associated with mainstem channel sediments, as well as the export of DOC to recipient ecosystems.

INTRODUCTION

Dissolved organic carbon (DOC) is often a large percentage of the carbon budget of freshwater ecosystems. Once considered relatively invariant, almost conservative in nature, DOC has gained attention as an important regulator of microbial community activity (Kaplan and Bott 1989, McKnight et al. 1993, Sobczak 1996, Findlay 2003). But the impact of DOC on ecosystem processes such as respiration and nutrient retention is not merely a function of pool sizes, as has been emphasized in previous work. Mapping the cycling of DOC through an ecosystem also requires an understanding of the quality (defined here as the ability of the microbial community to utilize a DOC source for respiration or reproduction) of DOC and the factors influencing its spatial and temporal variation. Evaluating the chemical structure of organic compounds is important to predict their fate, whether cycled through abiotic (photolysis, adsorption) or biotic

(microbial utilization) reaction pathways. The fate of DOC in lotic ecosystems is particularly important to downstream recipient systems where DOC inputs may fuel microbial production of greenhouse gases (e.g. CH_4, CO_2, N_2O), increase the release of inorganic nutrients during mineralization, and facilitate contaminant transport.

Factors controlling the delivery of DOC to streams are still poorly understood, despite much recent attention. The quantity and quality of organic matter coming from the terrestrial portion of the watershed differs from that derived from primary production within the surface stream. Leaf litter from trees is a significant organic matter source in mesic, forested streams. Once leaf material begins to be leached and decomposed in the stream, it can provide a strong pulse of DOC that stimulates energy flow through microbial communities as well as higher trophic levels , (Fisher and Likens 1973, McDowell and Fisher 1976, Hall and Meyer 1998). In contrast to terrestrial primary production, exudates from in-stream algal production have been identified as an important source of DOC in well-lighted streams (Minshall 1978, Kaplan and Bott 1982, Jones et al. 1995a) But most of the DOC inputs to streams derive from terrestrial soil organic matter (SOM) pools, created when plant material is altered by microbial activity, abiotic oxidation/humification, and consumption/excretion by insects. SOM carbon content and carbon to nitrogen (C:N) ratio have been identified as strong predictors of stream DOC concentrations in several studies, suggesting that this terrestrial material is the predominant source of DOC to the stream (Cotsaris et al. 1993, Hope et al. 1997, Aitkenhead and McDowell 2000) The extent to which SOM enters the stream is

dependent on several factors, including the flowpath water takes before arriving (Boyer et al. 1997b, Boyer et al. 1997c, Mulholland and Hill 1997).

In arid ecosystems, terrestrial-aquatic linkages are episodic and short-lived, and depend on the pattern of rainfall and runoff. Thus, the climatic regime has a strong influence on the movement of materials within the catchment (Butturini and Sabater 2000). Ephemeral or intermittent tributary networks deliver water to the mainstem only during large rain events; therefore, aquatic-terrestrial linkages are limited to these storms. Between large rain events terrestrial SOM pools accumulate solutes, particularly on the soil surface. Biological activity in upland soils may slow down as moisture content drops, then accelerate again after rewetting from rain. Smaller rain events may not only stimulate biological activity, they move accumulated materials downslope with short, episodic runoff that infiltrates soils or evaporates before reaching the mainstem. Biogeochemical transformations that occur in upland soils and small tributary channel sediments between episodes of runoff to the mainstem most likely influence temporal patterns in water chemistry.

Terrestrial-aquatic linkages in desert stream ecosystems are still relative unexplored. (Fisher and Grimm 1985) found antecedent conditions influenced both runoff chemistry and nutrient budgets in three small Sonoran Desert watersheds, but did not measure DOC. (Jones et al. 1996) calculated annual DOC exports from Sycamore Creek, a Sonoran Desert stream, over five years and found larger export values during high-flow El Nino-Southern Oscillation (ENSO) years. These two studies were completed during relatively wet years and were some of the first studies to explore

linkages between climate and organic matter cycling in the desert southwest. However, they did not consider the chemical complexity of the DOC in stream water, which we feel is vital for understanding carbon cycling in lotic ecosystems. We know of only two studies that have examined patterns in chemical complexity of DOC as it relates to possible sources during flooding (Aiken 1993, Westerhoff and Anning 2000), only one of which focuses on arid-land DOC chemical complexity.

The objectives of this research were: (1) to determine the sources of DOC to a Sonoran Desert stream, Sycamore Creek, during floods and during baseflow, (2) to identify factors influencing the contribution and chemical complexity of different DOC sources to mainstem (largest order stream in catchment) floodwaters, and (3) to assess which sources are most likely fueling sediment-associated microbial respiration. Our conceptual model of DOC sources to the stream includes a shift from atmospheric and terrestrial-derived DOC during flooding to a stream ecosystem dominated by sources located in the stream during baseflow (Fig. 1). Our approach compared patterns in catchment inputs and outputs to infer possible mechanisms controlling DOC delivery, then tracked changes in water chemistry at several points along its path from precipitation to the mainstem of Sycamore Creek to locate positions at which changes in DOC chemistry occurred.

In arid systems, floodwater flowpaths begin when episodic storms produce intense rains that quickly exceed upland soil infiltration capacity and runoff as overland flow. Overland flow (sheetflow) collects in small channels, or rills, which then coalesce into larger and larger tributaries within the stream network, where it is the main

contributor to the flood peak (Fetter 1994). Runoff to the stream is primarily overland, which prevents water from interacting with the rooting zone of terrestrial vegetation while in transport. Once in the mainstem channel, floodwaters enter the riparian zone via subsurface flowpaths (Marti et al. 2000). Floods bring distinct DOC sources from varying portions of the catchment, and not all floodwater exits the catchment as surface flow (i.e. water storage in riparian, shallow groundwater, or deep groundwater can be significant). These flood-associated DOC inputs represent material that may fuel microbial metabolism between floods when it is released back into the surface stream from storage zones. Therefore, flood DOC inputs to arid-land streams are contributors to baseflow chemistry and should be considered alongside more locally-derived sources. We captured water for chemical analysis at several points along the flowpath from precipitation, through upland rills and small tributaries, into the largest tributaries and finally, into the mainstem of Sycamore Creek.

Data analysis included calculating seasonal averages, creating water and carbon budgets for individual floods, and using regression analysis to test whether characteristics of each flood (such as precipitation intensity), or the activity in the uplands between floods (i.e. time since previous runoff event and rainfall accumulation leading up to a sampling event), explained temporal variation in DOC chemistry. A chloride (Cl) mixing model analysis was applied to quantify old (water already present in the stream-riparian corridor) versus new (precipitation/runoff) water inputs to floods, and these results were compared to independent calculations of DOC contributions from SOM pools. We

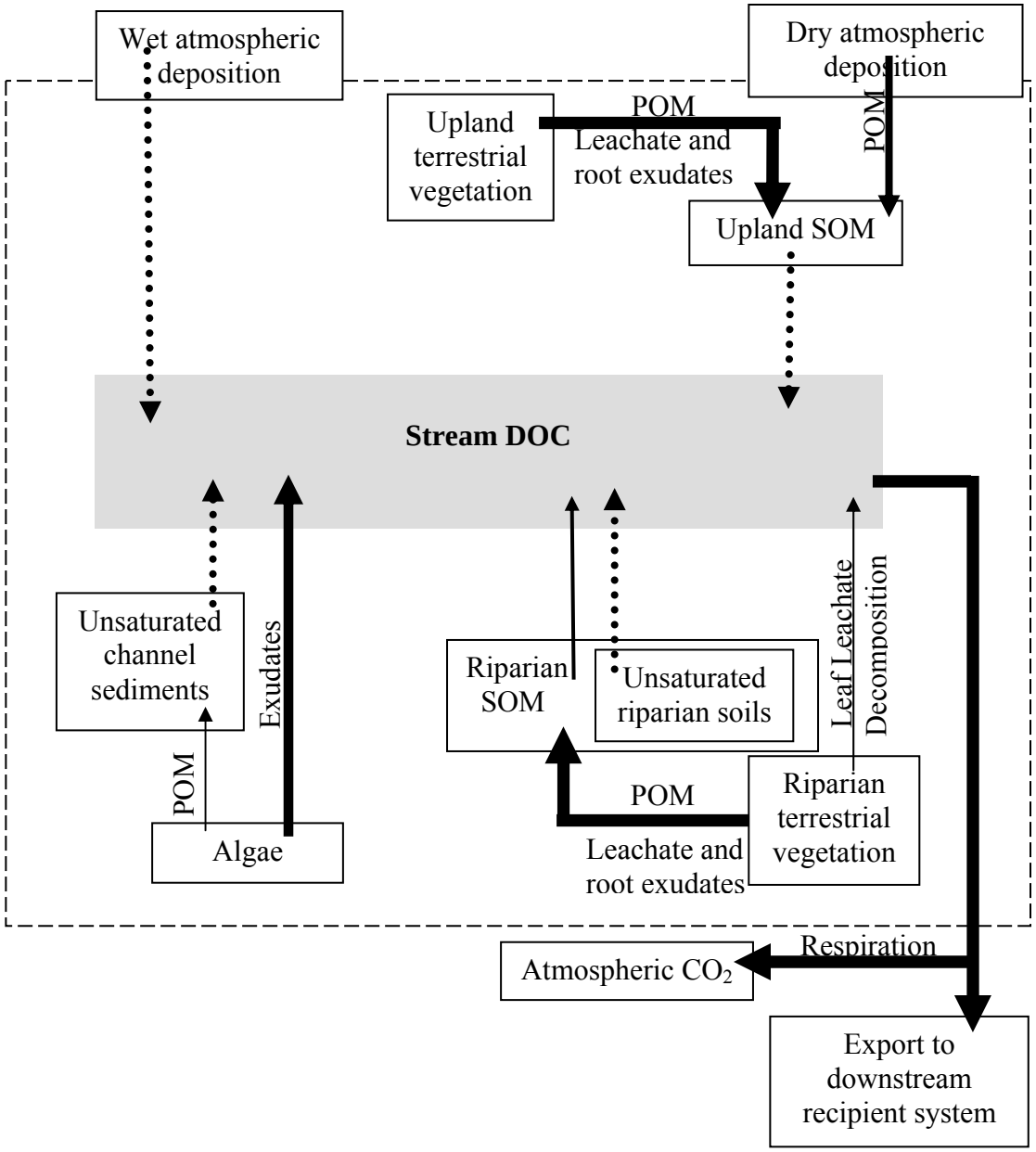

FIG. 1. Conceptual model of hypothesized sources of dissolved organic carbon (DOC) to the surface stream of Sycamore Creek, AZ. Dashed box indicates watershed boundaries. Dotted arrows enter the stream DOC box as runoff during floods as water flushes soil organic matter (SOM) and atmospheric particles. Solid arrows are dominant during baseflow, and their weight indicates the relative importance of each vector. Terms associated with arrows indicate the form the organic matter takes or the mechanism by which it is transferred to another pool; POM is particulate organic matter.

identified changes in DOC chemistry during an event, inferred what may be happening between events, and looked for trends on seasonal and annual time scales. Once we established the relative importance of each source to stream DOC, we used laboratory assays to test the quality of the sources for microbial activity.

METHODS

Site Description

Our study was conducted between 1997 and 2001 in the Sycamore Creek watershed, an intermittent Sonoran Desert stream located 32 km northeast of Phoenix, Arizona, USA (Fig. 2a). The stream drains a 505 km^2 catchment varying in elevation from 427 to 2164 m (Fig. 2b). The catchment is composed of igneous and metamorphic rocks with shallow overlying soils and unconsolidated sediments (Thomsen and Schumann 1968). Ponderosa pine and piñon-juniper woodlands predominate at higher elevations and Sonoran desert scrub at lower elevations. Precipitation is bimodal with winter and summer (monsoon season) maxima; slightly more than half falls in the winter. Annual means are 58.4 and 33.9 cm/year at higher and lower elevations, respectively (Thomsen and Schumann 1968). The two distinct rainy seasons have very different rainfall characteristics. Monsoon precipitation tends to come during intense, localized and short-lived storms, while winter rains are generally longer but less intense. Water moves rapidly to stream channels because of the low porosity of the soils and the steep topography of the catchment. From 1997-2001, rain gages were secured at five locations

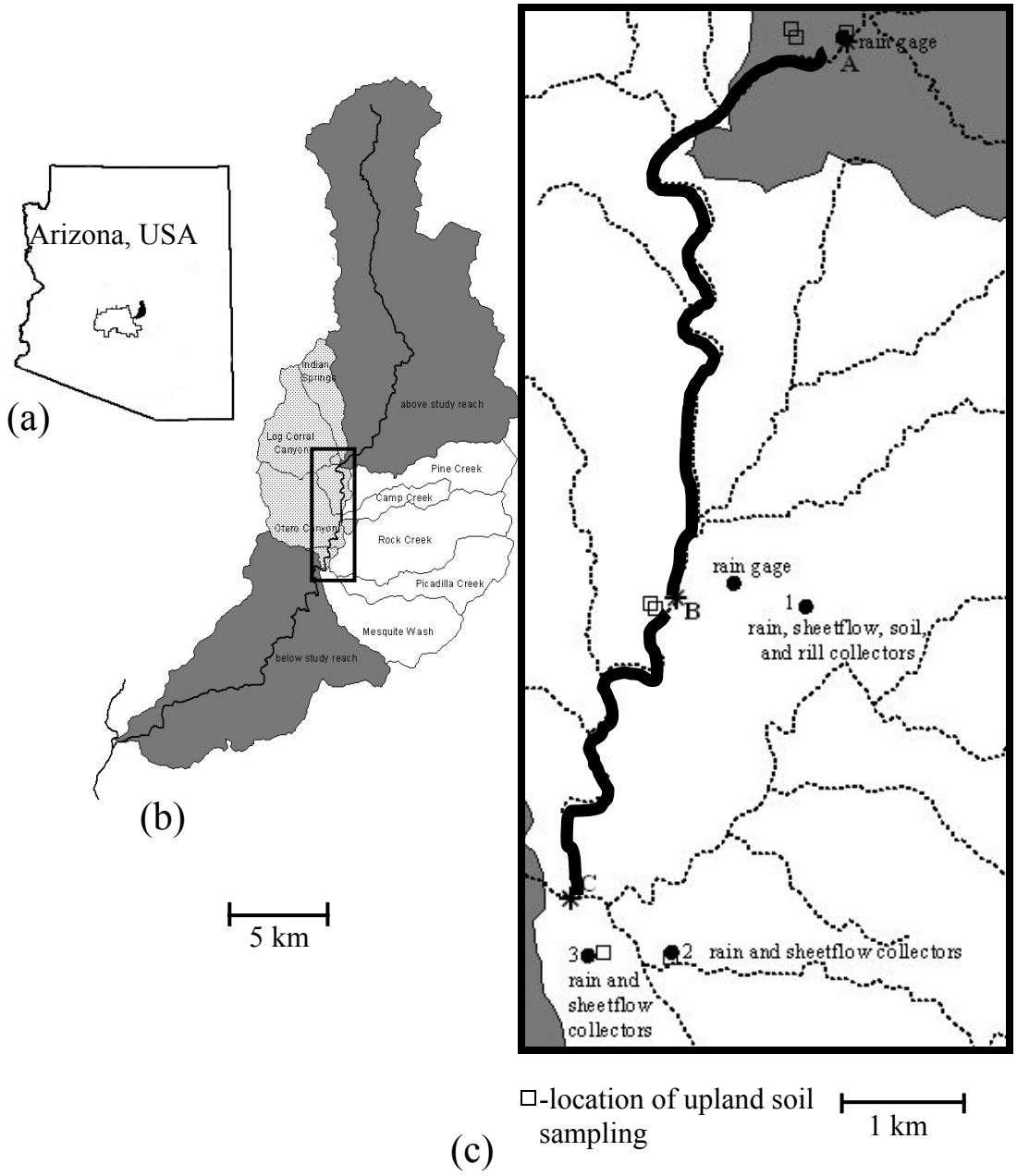

Figure 2. (a) Position of Phoenix metro area within Arizona, showing the Sycamore Creek catchment to the northeast (black figure). (b) Detail of the Sycamore Creek catchment, showing the boundaries of the subcatchments. Dark gray areas are outside our study reach and shaded catchments were not sampled. (c) Map of 12-km study reach (mainstem indicated by bold line); open boxes indicate soil sampling sites, filled circles are locations of rain gages and various water collectors, asterisks indicate mainstem sampling sites; dotted lines are stream channels, watershed boundaries not shown.

along a 12-km study section and were emptied after each rain (Fig. 2c). Annual rainfall from 1997 to 2001 (Oct-Oct) was 45, 50, 19, 39 cm at site A (Fig. 2c), and 41, 31, 16, and 38 cm at the bottom of the catchment.

Sycamore Creek discharge was highly variable all years, with 11, 9, 2, and 13 mainstem floods in each of the years of the study (Fig. 3). Of these 35 floods, 16 were sufficiently sampled from 1999-2001 to be used in the budget calculations presented here. In mid-elevation runs of Sycamore Creek (ranging in elevation from 600 to 760 m), mean stream depth is 5 cm and average wetted channel width is 5-6 m. The wetted channel is bounded by an active channel of alluvium that is over 20 m wide (Fisher et al. 1982). Stream substrata consist primarily of sand and fine gravel with a mean depth to bedrock of 62 cm (Valett et al. 1990). Riparian trees are restricted to the high-flow stream margin, consequently the stream receives full sunlight most of the day and has in-stream gross primary production as high as 12 g $O^2m^{-2}d^{-1}$ and algal biomass (*chl a*) as great as 350 mg/m^2 (Grimm 1987). Attached heterotrophic microbial communities are spatially patchy. Highest cell abundance, percentage of cells actively respiring, and rates of microbial respiration are associated with locations where surface water infiltrates streambed sediments (Holmes et al. 1998, Jones 1995). Jones et al. 1995 measured rates of aerobic respiration in channel sediments ranging from 0.05 – 4.41 $mgO_2 \cdot L\ sediments^{-1} \cdot h^{-1}$. Saturated riparian soils also have been found to be a location of high rates of microbial denitrification and methane production (Holmes et al. 1996, Jones et al. 1995b).

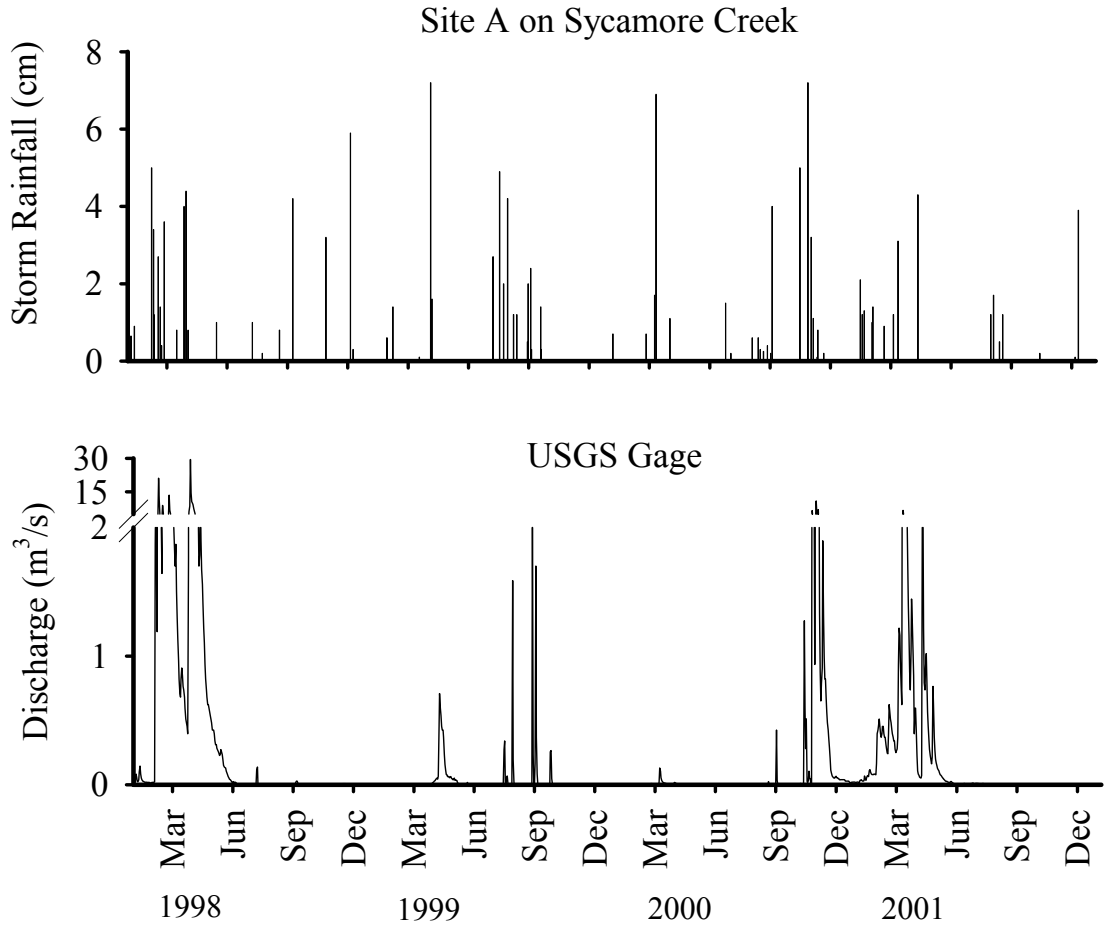

FIG. 3. (a) Rainfall amount measured for every storm event from 1998-2002 using a rain gage located at the top of the 12-km reach of Sycamore Creek (Site A) (b) mean daily discharge in Sycamore Creek from 1998-2001 (data from the U.S. Geological Survey).

The 12-km section of Sycamore Creek running from site A to C was the focus of our work (Fig. 2c). Twenty-three percent of the total Sycamore Creek watershed is below site C, and 40% is above site A. Three upland sites (1,2,3 on Fig. 2c) were instrumented for collection of precipitation and sheetflow samples. Of the three sheetflow sites, only the one in the Rock Creek subcatchment (site 1) was maintained past August 1999. Rill collectors were placed in the Rock Creek subcatchment starting in July 1999 to capture channel runoff in low-order tributaries. Floodwater samples were taken from the largest tributaries whose watersheds are unshaded in Fig 2b, but we were unable to sample the gray-shaded watersheds west of the mainstem due to their inaccessibility. Three sites were designated for collection of water samples along the mainstem of Sycamore Creek (sites A, B, C on Fig. 2c).

Sample collection and analysis

To characterize organic matter along the flowpath from precipitation to the mainstem, we collected samples of five types. The first type was atmospheric deposition, for which we employed two methods of collection. One method, used at all three rain collection sites, comprised a funnel connected to a nalgene bottle by plastic tubing. This generated a bulk deposition sample, defined here as wet deposition plus any dryfall accumulation within one week of the storm. Water used to rinse the funnels after a 1-3 week period of no rain was analyzed as a dry deposition sample. Atmospheric deposition was also collected at site 3 using National Atmospheric Deposition Program (NADP) standard methods (http://nadp.sws.uiuc.edu/). The second sample type, sheetflow, was collected using 3.7-L plastic jugs connected to v-shaped aluminum flashing installed

level with the ground surface at site 1. This design integrated the entire area upslope of the flashing, while at sites 2 and 3 sheetflow collectors were tear-shaped and collected water from only inside the flashing. The third type of samples along the upland-stream gradient was rill samples collected using buried bottles with a mesh-covered opening secured directly above the rill sediments at site 1 (Fig. 2c). The fourth type of gradient sample, from the largest tributaries, was collected as a grab sample as soon as possible after flooding began. And finally, for the mainstem of Sycamore Creek, a battery-powered autosampler was programmed to start sampling surface water once a co-axial cable positioned directly above the water's surface came in contact with the rising floodwaters at site C (Fig. 2c). From 1999-2001, nine of the sixteen floods for which mainstem water samples were taken had corresponding samples taken by this autosampler, the other seven were collected as grab sample. Only events associated with a flood in the mainstem of Sycamore Creek were used in our analyses. Sampling of surface water continued between flood events to characterize baseflow chemistry. Riparian wells and subsurface channel piezometers were sampled from 1997-1999 at site C for water chemistry analysis.

We used radar precipitation data and rain gages on the ground to quantify rainwater volume. Although not indicated on Fig. 2c, every location with precipitation collectors had a rain gage as well. Radar data (available for 10 of the 16 floods) were used to quantify total rainfall to the catchment, because they capture the high spatial variability of the rainfall patterns throughout the storm. For these 10 storms, 6-52% of the total rainfall during any one event fell below site C, and 10-57% fell above site A.

Accumulated rainfall was calculated from rain gage data for a consistent number of days preceding every sampling date using several different windows of time (14, 30, 60, 90, 120, 150, 180, 245, and 365 days of previous rainfall). Fifteen-minute interval discharge data from a USGS stream gauging station located on Sycamore Creek were used to quantify floodwater volume. To determine the importance of antecedent and new water to floodwaters, mass balance calculations were completed for the floodwater Cl. Chloride concentration in the tributary samples was used as the new water endpoint and baseflow surface water concentration was used as the old water signature. The contribution from each source was then calculated using the following two equations, where Q is discharge, C is concentration, s is antecedent mainstem water, p/r is tributary inputs, and f is floodwaters.

Equation 1 $Q_s = Q_f \times [(C_f - C_{p/r})/(C_s - C_{p/r})]$

Equation 2 $Q_{p/r} = Q_f - Q_s$

To begin to bracket the contribution of DOC to floodwaters from solubilization of material on previously dry soils and sediments, we performed several water extractions in the laboratory. Soil was collected in the uplands by coring to 5 cm after removing surface debris. Dry channel sediments were collected to a depth of 5 cm using a trowel, and riparian soils were extracted using a soil auger to a depth of 10 cm. Soil/sediment extractions were performed in plastic sample bottles using nanopure water and shaking for one hour.

Water samples collected in the field were stored on ice and returned to the laboratory where they were filtered through a pre-ashed Whatman GF/F ashed filter (0.7

μm pore size), and the filtrate was analyzed for DOC concentration, DOC chemical complexity, and nutrients. DOC was measured using high-temperature combustion on a Shimadzu 5000-TOC autoanalyzer. In addition to quantifying DOC concentration in the water, a simple measure of DOC chemical complexity was used. Specific ultraviolet absorbance (SUVA) is the absorbancy of a filtered, acidified water sample at 245 nm, divided by the DOC concentration in the sample. SUVA is an indicator of the quantity of double-bonded C atoms (unsaturated sp^2-hybridized carbon atoms). An aromatic carbon ring has half of its carbon as C=C, and since most natural organic matter is aromatic, not aliphatic, SUVA is a strong measure of the aromaticity of a DOC sample (Edzwald 1993).

Bioassays were completed by adding water with 5 mg/L of various DOC sources plus N and P greater than 5 mg/L to containers filled with washed Sycamore Creek sediments. The first bioassay monitored dissolved oxygen (DO) over a period of eight hours using a DO meter. This short-term bioassay was used to capture the faster respiration rates, associated with more labile organic carbon, that often occur initially in bottle experiments. A longer bioassay was completed in amber bottles containing the same sources of DOC as in the short-term experiment, excess nutrients, and bubbled with air. In this long-term bioassay changes in DOC concentration were monitored for 10 days. In addition to determining the relative quality of different DOC sources, we tested Sycamore Creek sediment respiration for limitation by carbon quality using sediments collected 4 days following an August 2003 flood. This test involved adding acetate, an organic compound of low chemical complexity, to bottles with sediment and subsurface

water, then measuring oxygen depletion in the bottles with and without acetate over 18 hours.

RESULTS

Budget analysis

Wet/dry deposition and mainstem floodwater samples were collected to characterize and quantify the DOC chemistry of inputs and outputs to the Sycamore Creek catchment. Wet deposition (as rain) brought low complexity (measured using SUVA) DOC into the catchment. This material was then transported to Sycamore Creek, where it left the ecosystem with much higher DOC concentrations and higher SUVA values. To compare DOC loads in inputs and outputs, a budget was constructed for each flood using catchment area above Site C on Sycamore Creek. For storms for which radar data were available, >87 percent of the water entering the ecosystem during a rainstorm was retained within the catchment, with an average of 96.7 percent retention (defined here as material not exported). The amount of water retained in the catchment during a storm was negatively correlated with rainfall accumulation, meaning more rainfall over a given time interval resulted in more runoff during episodic floods and, therefore, less total water retention per storm. More specifically, 65% of the variation in the percentage of water retained during winter floods was negatively correlated with the total amount of rainfall that fell 30 days prior to the flood, while 40% of the variation in monsoon water retention was negatively correlated with 120-day rainfall accumulation (Fig. 4). Other

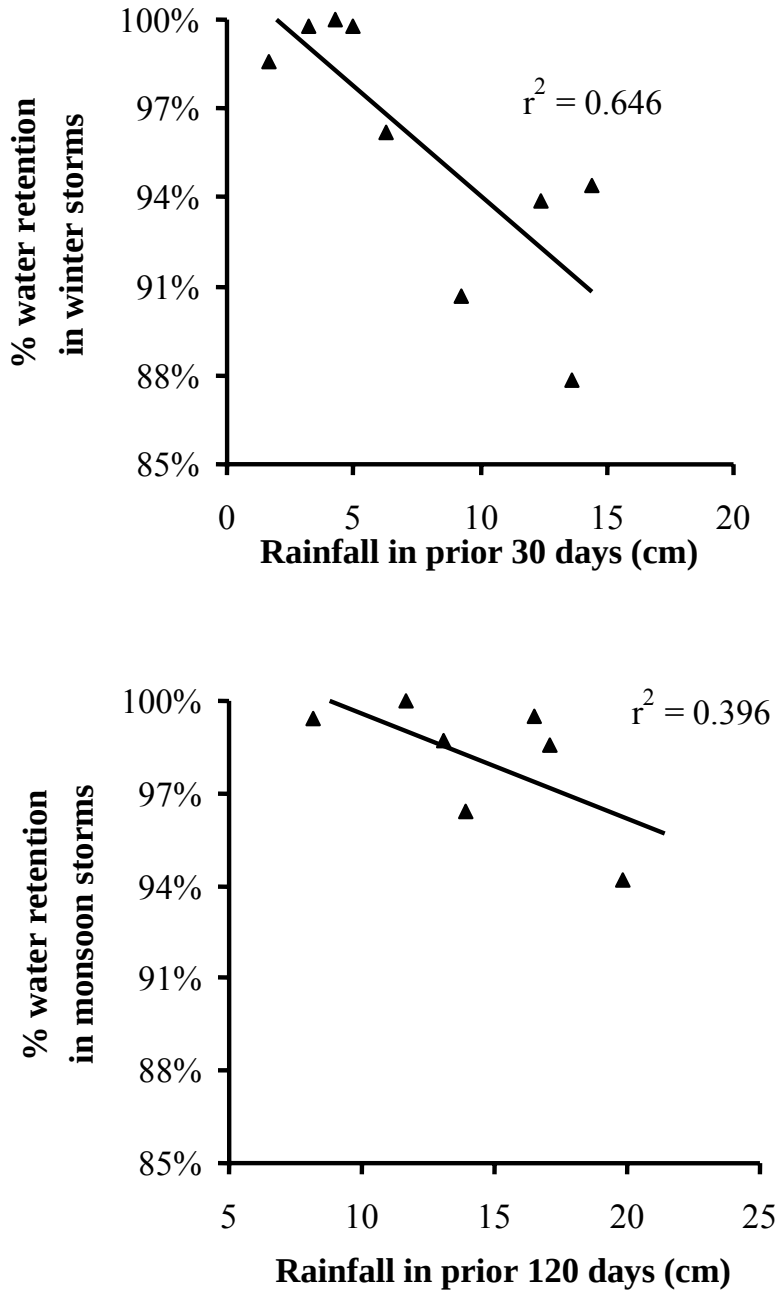

FIG. 4. Percentage of rainfall retained in the catchment for the each of the 16 floods monitored (broken into seasons) from 1999-2001 versus the amount of rain that fell in the preceding (a) 120 days (monsoon) and (b) 30 (winter) days.

storm characteristics, such as storm intensity and rainfall volume of individual storms, were unrelated to percentage water retention during the event.

Using average rainfall DOC concentrations for each storm, we calculated the total DOC load in precipitation. Regression analyses did not include storms without radar data or water chemistry samples because of the low accuracy of the calculations, however, we did include them in our calculations of seasonal DOC loads (Table 1). Of the three monsoon seasons monitored, two delivered higher DOC loads than the winter season that occurred immediately before (Table 1). Therefore, more rain-derived DOC entered the catchment during monsoon storms, on average, than during winter storms. This changed as an extended drought began in 1998, and by 2001 DOC loads were greater in the winter rainy season than in the monsoon season, which saw no flooding.

As with water retention during floods, the most rainfall DOC was retained in the catchment as water moved from the uplands into the mainstem of Sycamore Creek. Seasonally, the percentage of rainfall DOC load retained was lower than the percentage water retention for every flood, with an average of 85.5% of the DOC load retained (compared to 97% for water). Water retention explained much of the DOC retention during monsoon and winter floods (93% and 64%, respectively), and more DOC was exported during monsoon storms than in winter storms. The difference in DOC retention between the two seasons suggests greater accumulation of DOC in runoff as it moved along the upland flowpath in the winter. We concluded that rainwater accumulated DOC as it moved across the landscape based on: (1) the lower retention of DOC as compared to water, and (2) the increase in SUVA values when comparing precipitation to mainstem

TABLE 1. Summed dissolved organic carbon (DOC) loads in precipitation and mainstem floodwaters for the Sycamore Creek catchment during winter and monsoon floods from October 1998 to June 2002.

Water year	Precipitation DOC load (metric tons C)	Floodwater DOC load (metric tons C)	% retention
Oct 1998-Oct 1999			
Winter	7.03	2.06	71
Monsoon	289.3	6.89	98
Annual Total	296.3	8.95	97
Oct 1999-Oct 2000			
Winter	4.39	0.29	93
Monsoon	72.0	30.0	58
Annual Total	76.39	30.29	60
Oct 2000-Oct 2001			
Winter	82.5	28.3	66
Monsoon	0	0	
Annual Total	82.5	28.3	66
Oct 2001-Oct 2002			
Winter	5.74	3.00	48
Monsoon	NA	NA	

chemistry. Floodwater DOC could derive from several SOM pools in the catchment, including upland soils, unsaturated riparian soils, or dry channel sediments. Analyses using laboratory water extractions found different SUVA values associated with several SOM sources; therefore their relative contribution should influence the chemical complexity of the floodwater DOC (Fig. 5).

To determine the importance of SOM pools as contributors to floodwater DOC, we estimated the DOC load riparian soils and channel sediment could contribute and compared that to the mainstem flood DOC load. We also calculated the maximum contribution from precipitation for each flood, based on percent water retention. By difference, the remaining unexplained DOC load must be from upland soils or tributary channel sediments. Our estimates involved several assumptions: (1) 25% of active channel is sandy runs (Stanley et al. 1997), (2) the average width of the active stream channel is 25 m (Fisher et al. 1982), (3) the average values for soil/sediment organic matter and bulk density from samples taken from site A, B, C, is appropriate to apply to the entire 12-km stream section, (4) the average width of the riparian zone is 13 m (Schade et al. 2002), and (5) 10% of the DOC load resolubilized from dry soils in the riparian zone during a flood moves back into the surface stream. We then used stage readings at the USGS gage to estimate the volume of previously dry soil/sediment that was inundated during each flood (Fig. 6).

Values for the DOC load from channel sediments and riparian soils ranged widely (Table 2). Once riparian soils and channel sediments are flushed, the chemistry of the

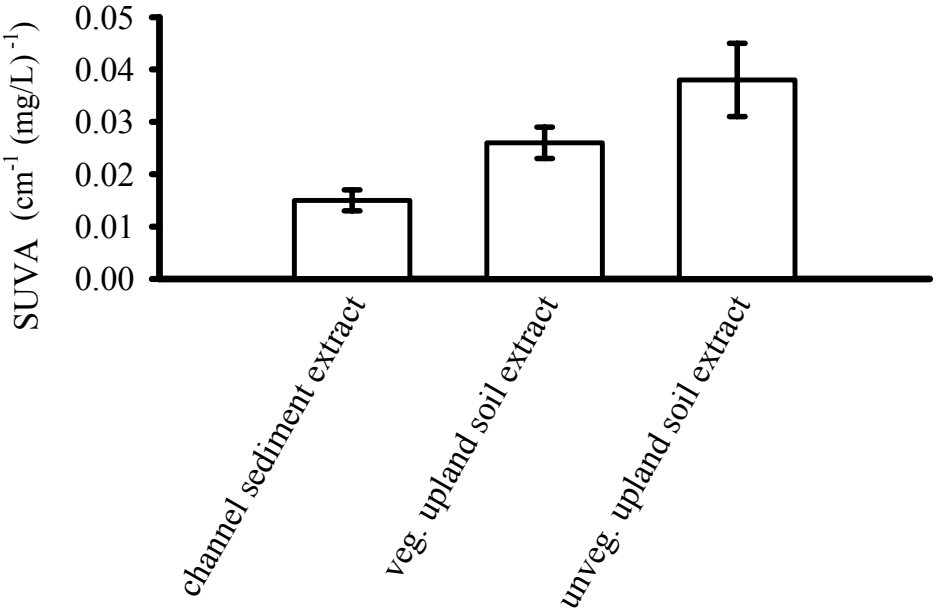

FIG. 5. Specific ultraviolet absorbance (SUVA) for laboratory water extractions on channel sediments and vegetated and unvegetated upland soils. Statistical difference determined using a one-way ANOVA (F= 6.447, df=2, p=0.001).

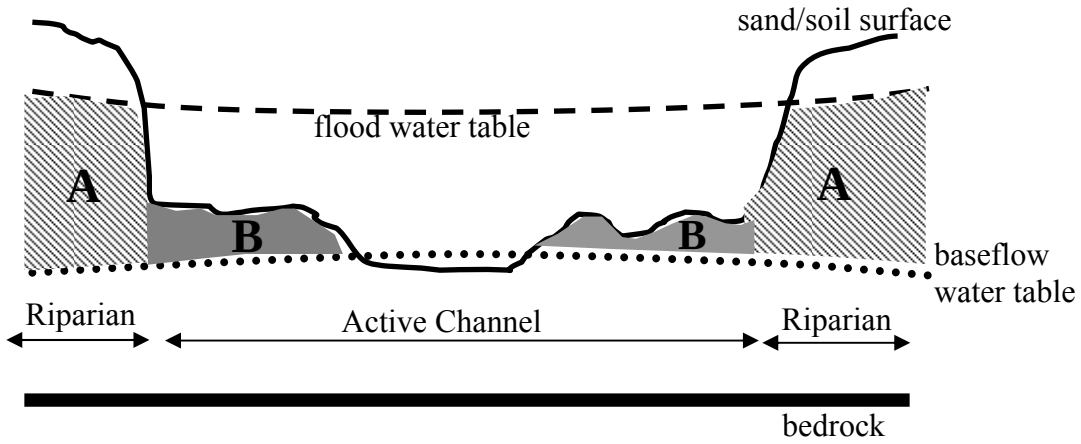

FIG. 6. Diagram of stream cross-section demonstrating how a rise in water table due to flooding creates zones of rewetting of previously unsaturated riparian soils (A) and channel sediments (B).

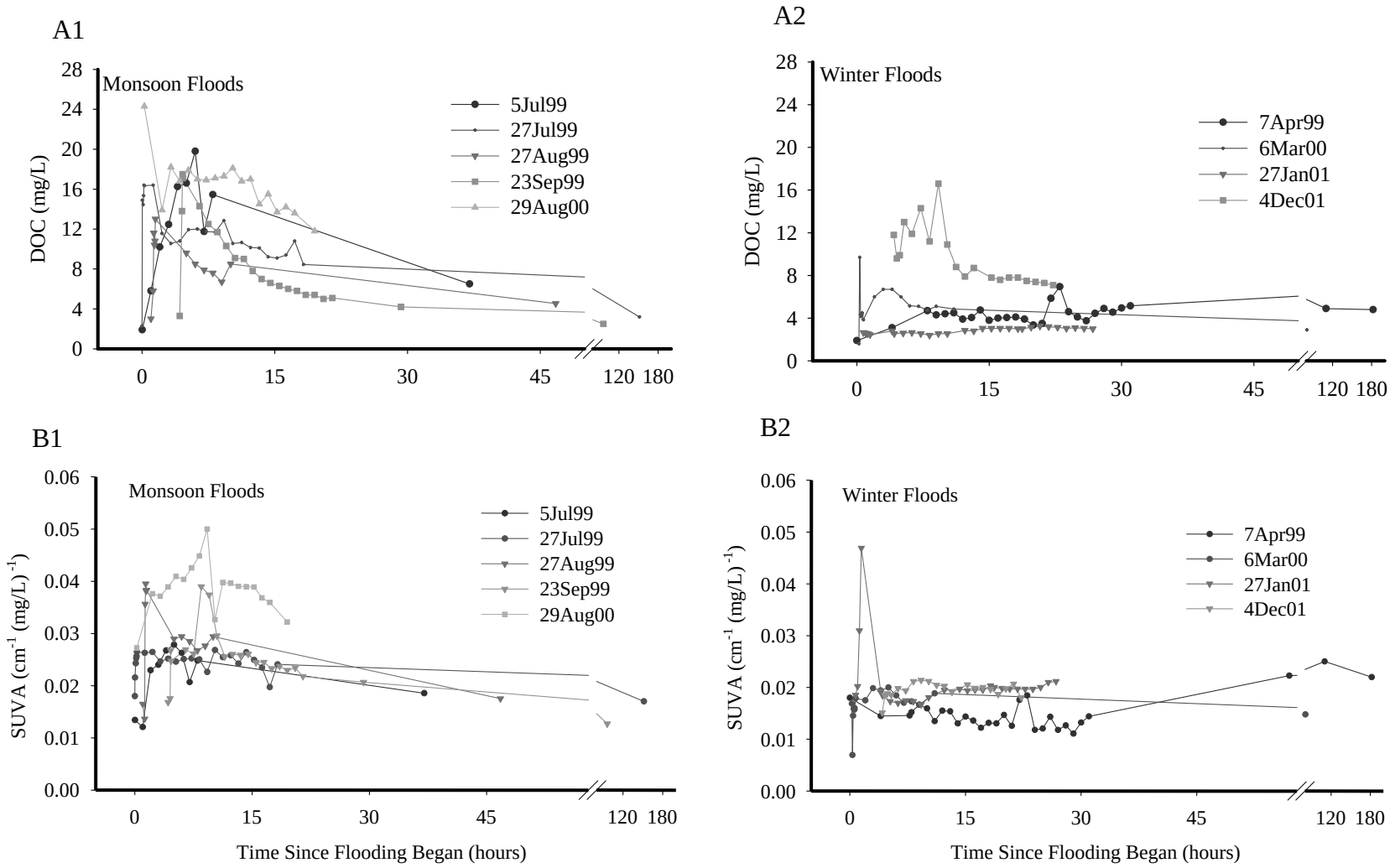

FIG. 7. Monsoon (A1, B1) and winter (A2, B2) floodwater samples collected at site C on Sycamore Creek using a stationary autosampler. (A) DOC concentrations, (B) SUVA values.

water equilibrates with that of floodwaters, and this source does not contribute to subsequent flood DOC loads until sufficient time has passed for organic carbon to once again accumulate. The contribution from these two sources was approximately equal, and added together comprised a substantial percentage to the total DOC load in Sycamore Creek floodwaters, with a median value of 23%.

To complement the budget approach just described, we examined variation in the chemistry of mainstem floodwater over time as an indicator of variation in DOC sources to the stream. The primary temporal trend was seasonal, with higher DOC concentrations and SUVA values in monsoon floods across all years (Fig. 7). At the scale of a single flood, SUVA and DOC concentrations rose with the rising limb of the hydrograph (Fig. 7). In addition to DOC chemistry itself, chloride concentrations in mainstem floodwaters were used to infer the origin of materials carried in runoff to the stream (Buttle 1998, Kendall and McDonell 1998). Mainstem Cl values dropped as low-Cl floodwaters from the watershed mixed with the preexisting water in the stream (Fig. 8). Although upland runoff has lower Cl concentrations than baseflow, runoff values were higher than precipitation, because salts and organic material accumulated in the rainwater as it came in contact with soils and sediments. The largest contribution of inorganic salts appeared between the smallest rills and the largest tributaries (Fig. 9). Winter storms had much less variability in Cl throughout the flood, and higher minima in Cl concentrations as compared to monsoon storms (Fig. 8).

To quantify the contribution of new (precipitation and runoff) water versus mainstem baseflow water to the total floodwater load, we used chloride concentrations in

TABLE 2. Sycamore Creek catchment budget calculations for 16 floods from 1999-2001. Dissolved organic carbon (DOC) load in precipitation (corrected for water retention in uplands), DOC load from rewetting of previously dry channel sediments and riparian soils, and the contribution from upland soils by difference. Values in parentheses are the percentage contribution to the total DOC flood load from each source. Last column generated from two-endmember mixing model using Cl concentrations when available, showing percentage of total floodwater load that was derived from precipitation/runoff.

Flood Date	SYC DOC load (kg C)	Peak discharge (m^3/s)	Rainfall DOC load in exported water (kg C)	DOC load from channel sediment (kg C)	DOC load from riparian soils (kg C)	DOC load from upland soils (kg C)	% new water
7 April 1999	2,061	0.9	654 (32)	24 (1)	27 (1)	1,356 (66)	insufficient data
5 July 1999	7.29	<0.003	8 (100)	4 (58)	5 (66)	0	insufficient data
15 July 1999	805	1.0	305 (38)	108 (13)	124 (15)	268 (33)	57%
27 July 1999	1,252	6	637 (51)	61 (5)	99 (8)	456 (36)	insufficient data
27 August 1999	2,197	42	658 (30)	90 (4)	372 (17)	1,077 (49)	73%
31 August 1999	2,224	6	1,222 (55)	0	0	1,002 (45)	45%
23 Sep 1999	409	2	147 (36)	0	0	262 (64)	95%
5 March 2000	286	0.3	62 (22)	66 (23)	76 (26)	82 (29)	32%
30 August 2000	1,402	6	221 (16)	132 (9)	189 (14)	860 (61)	97%
28 Oct 2000	18,551	35	1,573 (8)	0	182 (1)	16,796 (91)	84%
31 Oct 2000	4,849	16	834 (17)	0	0	4,015 (83)	30%
6 Nov 2000	1,120	2	426 (38)	0	0	694 (62)	insufficient data
12 Jan 2001	35	0.1	19 (53)	0	0	16 (47)	insufficient data
16 Jan 2001	42	0.15	21 (51)	9 (21)	10 (24)	2 (4)	insufficient data
27 Jan 2001	1,073	0.5	819 (76)	46 (4)	53 (5)	155 (14)	56%
4 Dec 2001	3	0.003	0.20 (7)	9 (100)	10 (100)	0	insufficient data

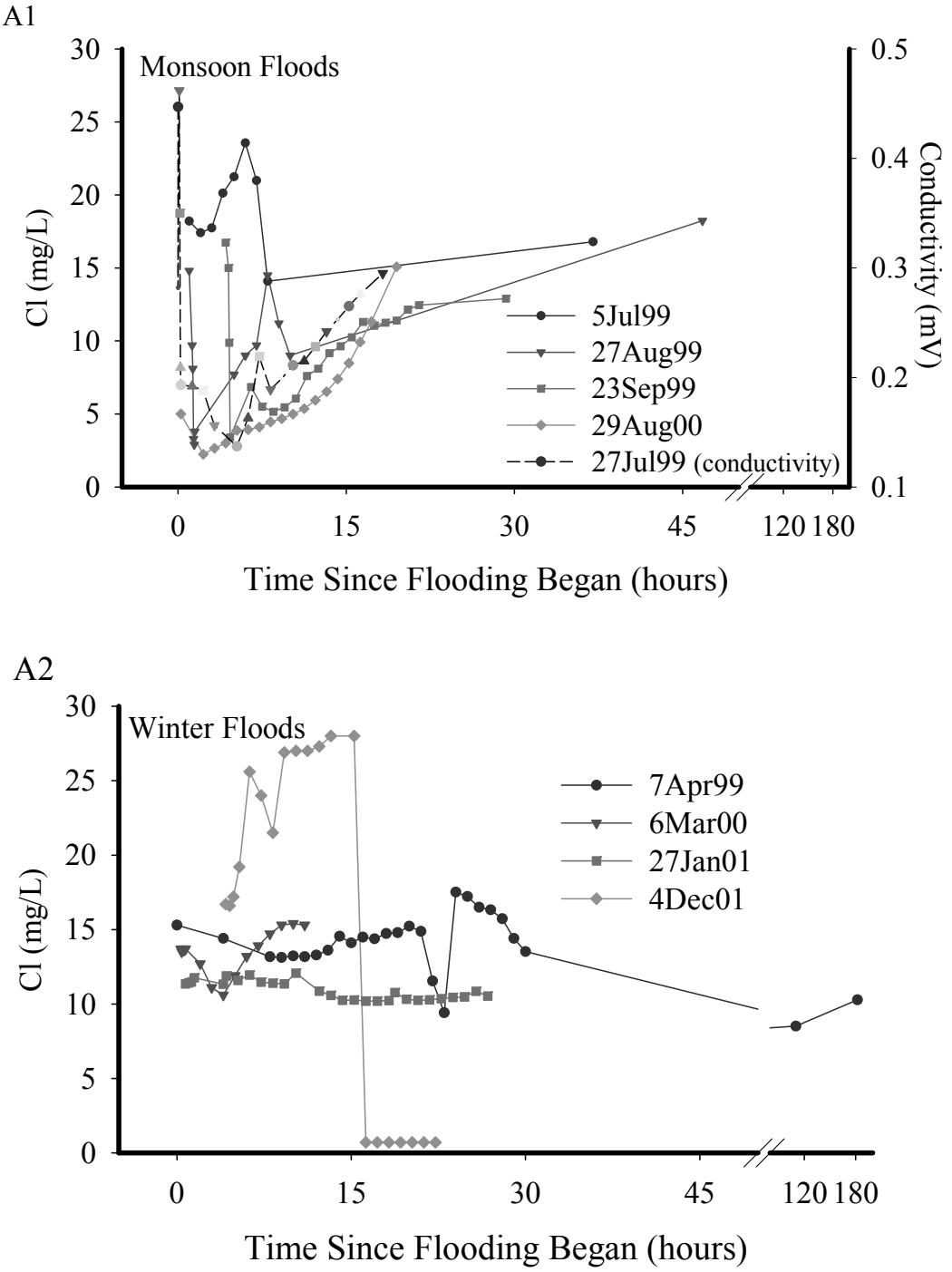

FIG. 8. Monsoon (A1) and winter (A2) floodwater samples collected at site C on Sycamore Creek mainstem using a stationary autosampler. Data are chloride (Cl) concentrations, with the exception of 27 July 99 where conductivity was substituted for Cl.

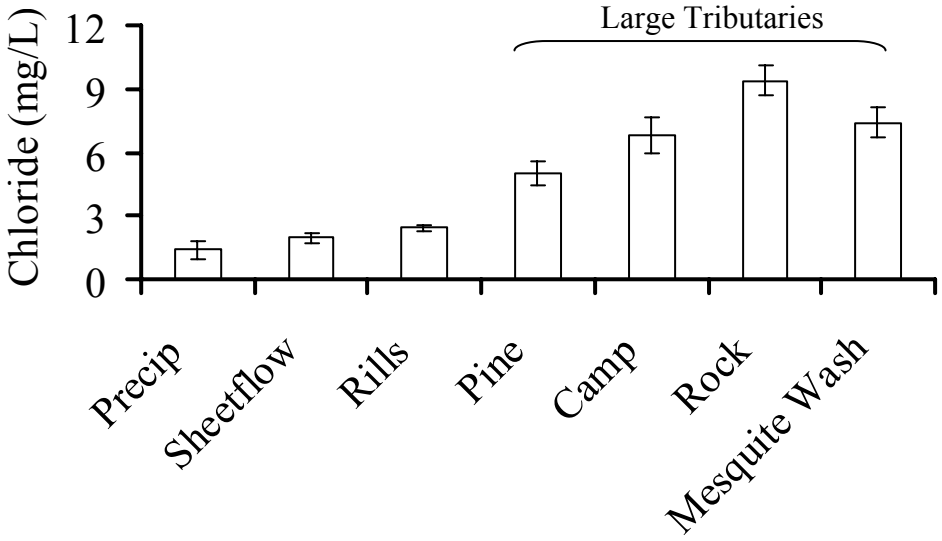

FIG. 9. Chloride concentrations in samples collected along the upland-stream gradient within 24 hours of flooding in Sycamore Creek. Tributary samples were taken just upstream of junction with Sycamore Creek.

a two-endmember mixing model as described in equations 1 and 2. We found significant variation in the percentage of new water in floods. This variation was related to rainfall intensity, with more water from the mainstem contributing to the flood when rainfall intensity was lower (r^2=0.47, p=0.028) (Table 2). As a check of our mass balance calculations, the percentage of the DOC load that came from precipitation and upland SOM (r^2=0.42, p=0.01) increased as the percentage of new water (as predicted by the mixing model) in the flood increased.

Following flood sampling we continued monitoring baseflow surface stream chemistry. Mainstem DOC concentrations and SUVA values decreased as floodwaters receded and baseflow patterns established (Fig. 7). The decline in SUVA values suggests a less chemically complex DOC source began to dominate the surface DOC pool (Fig. 10). Variation in winter baseflow SUVA values was not as strongly related to number of days postflood as for the monsoon season, indicating that the low complexity DOC source present in the warm months was not as dominant in the winter.

Flowpath analysis

The black box approach was useful for establishing a framework for an analysis of DOC delivery to Sycamore Creek; however, it lacks spatial information that could better describe the changes in DOC as water moves across the landscape from the uplands to mainstem. Therefore, samples along a hypothetical flowpath were taken to begin to quantify these changes. As indicated previously, there were very strong and consistent seasonal differences found in DOC concentrations and SUVA values. DOC

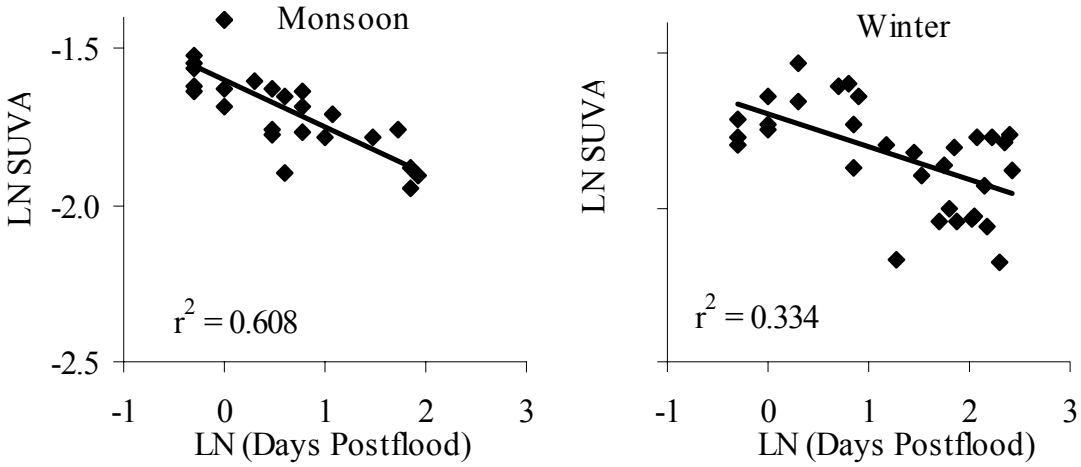

FIG. 10. Seasonal SUVA values from samples collected from 1998-2001 at site C on the mainstem of Sycamore Creek. Data were transformed to meet assumptions of normality; scales on graphs are the same.

concentrations were on average higher at all locations along the flowpath during the monsoon season as compared to winter storms (Fig. 11, 12). SUVA was not seasonally different for the upland precipitation, sheetflow, and rill samples, but was higher in monsoon samples in the largest tributaries and the mainstem of Sycamore Creek as compared to winter samples (Fig. 11, 12). Because of these seasonal trends, all analyses were completed keeping data from each season separate so as not to mask spatial patterns or patterns at shorter time scales.

Transformations in rainwater DOC chemistry along the path to the mainstem were substantial (Fig. 11 and 12). Bulk precipitation DOC concentrations varied with rainfall amount, but SUVA did not and was consistently very low, indicating low chemical complexity. None of the other sample types showed a relationship with per-event rainfall amount. Moving from precipitation to the mainstem, the overall trend was an initial increase in DOC concentration and SUVA from rainfall to sheetflow, a continued increase in DOC concentrations but decrease in SUVA from sheetflow to rills, and a decrease in DOC concentration and SUVA values from rills to the largest tributaries and the same from tributaries to the mainstem of Sycamore Creek (Fig. 11 and 12). Variation in rill chemistry and sheetflow chemistry was correlated, particularly for SUVA values (Fig. 13). Rill DOC concentrations were higher than those of sheetflow samples during the winter season and had lower SUVA values than sheetflow samples during both seasons (Fig. 13). Rill chemistry, therefore, was dependent on sheetflow chemistry and consistently lowered the complexity of the DOC pool once in the rills. We looked for the same pattern between rill samples and the large tributaries, and found variation in

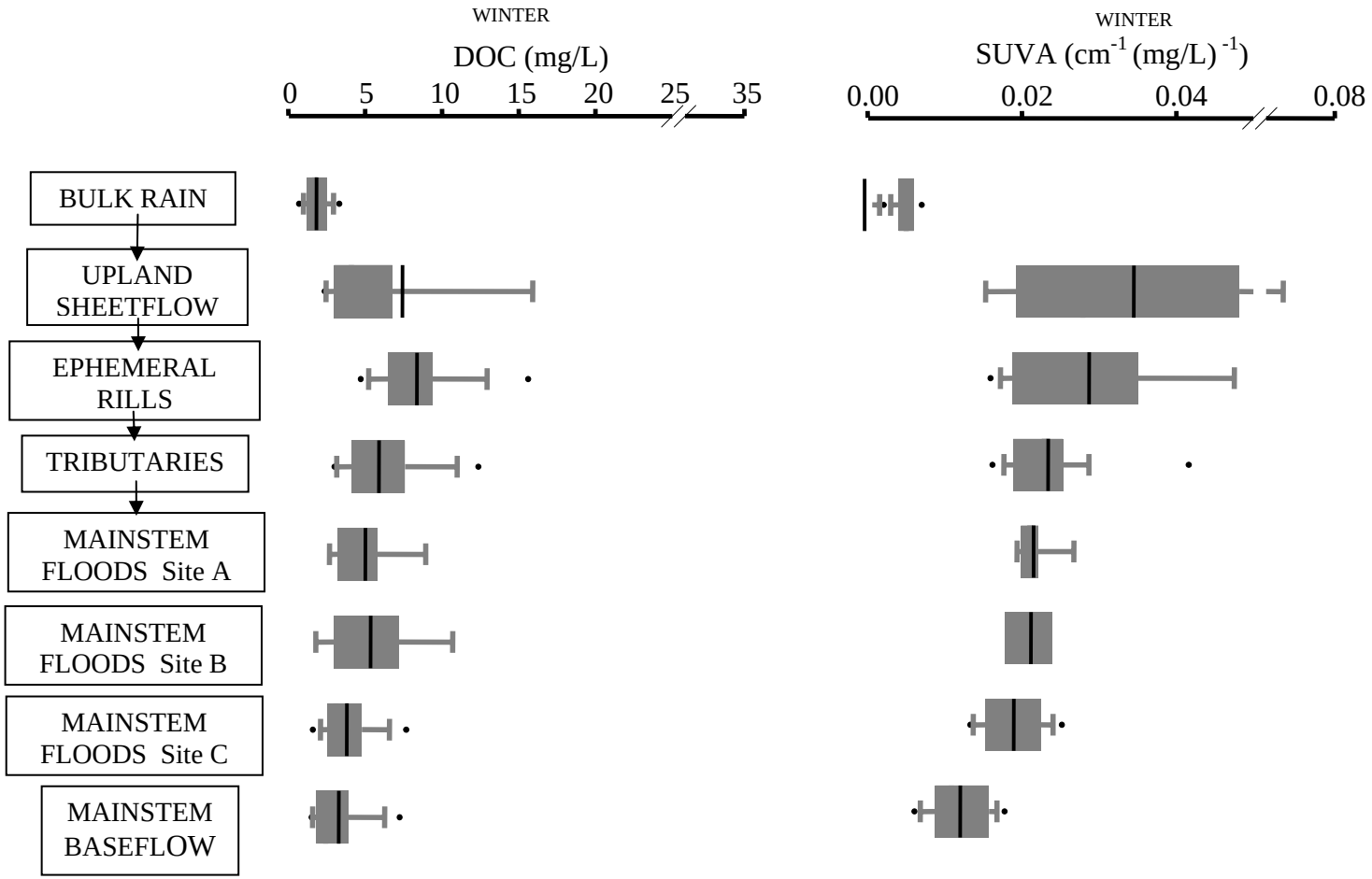

FIG. 11. Water chemistry of winter samples collected from 1998-2001. The boundary of the box closest to zero indicates the 25th percentile, and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers above and below the box indicate the 90th and 10th percentiles, the mean is the dark line and outlying points are graphed.

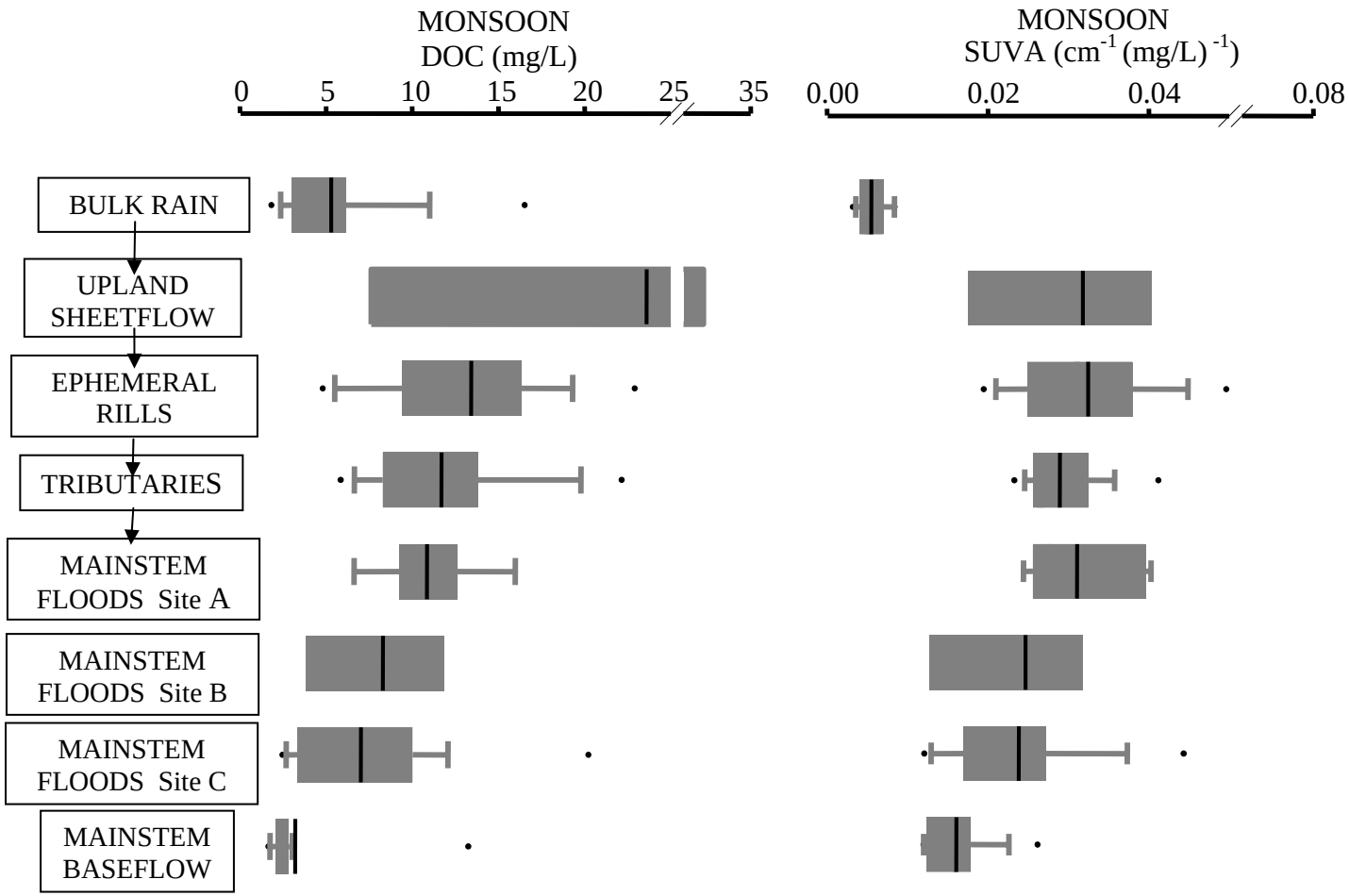

FIG 12. Water chemistry of monsoon samples collected from 1998-2001. The boundary of the box closest to zero indicates the 25th percentile, and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers above and below the box indicate the 90th and 10th percentiles. The mean is the dark line and outlying points are graphed.

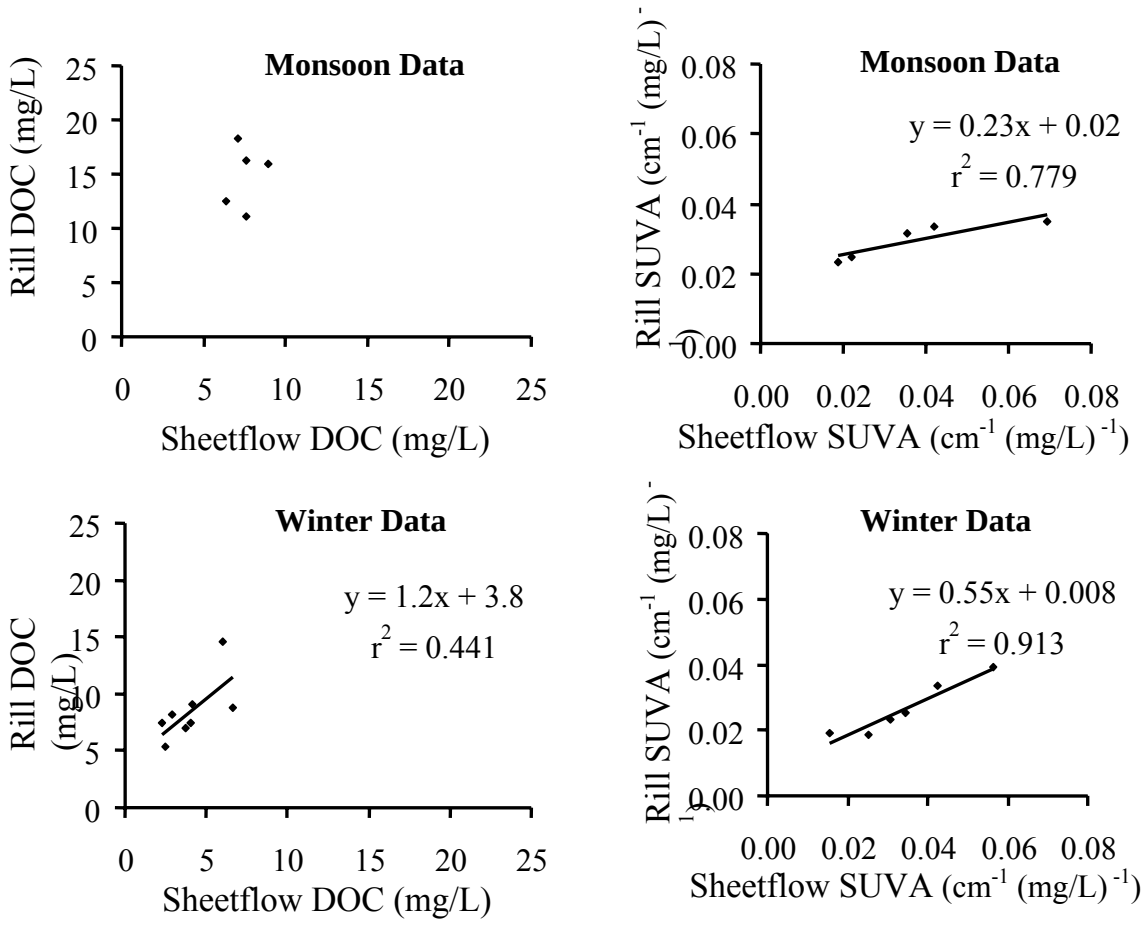

FIG. 13. Seasonal rill DOC concentrations and SUVA values versus sheetflow chemistry collected for the same rain event. Data were collected from 1999-2001 in one sub-catchment of the Sycamore Creek watershed (Site 1).

tributary DOC concentrations was explained by rill DOC concentrations (r^2=0.313), but that SUVA values were not positively correlated (Fig. 14).

Interflood dynamics

Two correlative measures of between-flood activity were used to help explain temporal patterns in DOC chemistry along the flowpath: the relationship between chemistry and (1) the number of day since the last runoff event, and (2) the accumulated rain that fell prior to a given sampling date. Days since last runoff is a measure of the amount of time material has remained in the uplands, under varying conditions, without any flushing of the soil by storm rainwater. Accumulated rainfall indicates several conditions prior to a runoff event including; the extent to which upland soils have been moist (and most likely biologically active), the accumulation of small runoff events that did not generate mainstem floods, and/or the legacy of past storms that replenished subsurface reservoirs in larger tributaries. We did not expect activity between rain events to influence rain chemistry during a storm, so interflood dynamics were not evaluated for rain chemistry. Number of days since the last runoff event was positively correlated with only a few chemical parameters; DOC concentrations in sheetflow samples collected during the winter, winter DOC in two large tributaries (Pine and Camp Creek), and winter SUVA values in Pine Creek.

Rainfall accumulation patterns for DOC concentrations followed a general trend of less DOC export when more rain fell prior to sampling (Table 3). We found this negative relationship between DOC concentrations and rainfall accumulation in all sample types and for both seasons in all but the rills (for which only winter data were

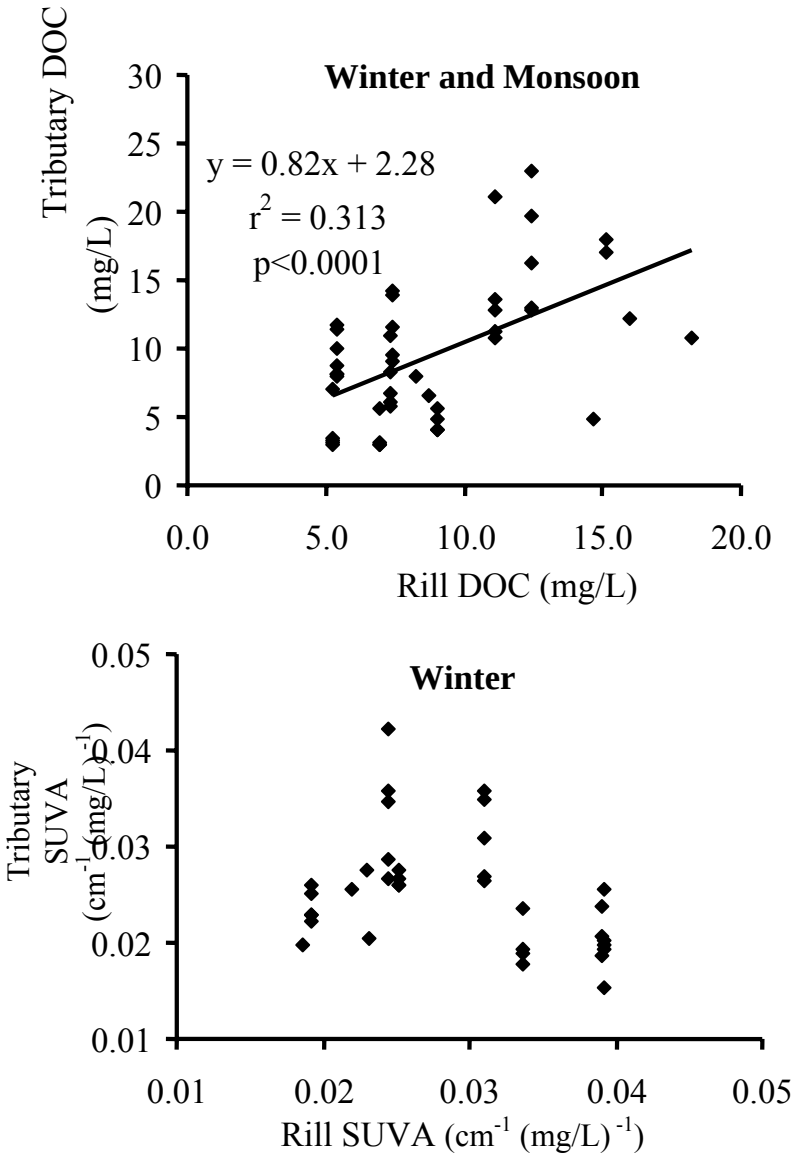

FIG. 14. Tributary (a) DOC concentrations vs. rill DOC concentrations (data from both rainy seasons and (b) Tributary SUVA vs. rill SUVA for samples collected during the same storms. Data include both rainy seasons and span from 2000-01.

TABLE 3. Statistically significant ($p<0.05$) regressions of seasonal dissolved organic carbon (DOC) concentrations and SUVA values (measure of chemical complexity) as a function of rainfall accumulation prior to sampling event. Time intervals ranging from 14 days to 365 days were tested, but if more than one interval was significant the two intervals with the highest r^2 values are presented. Data for three types of samples along a presumed flowpath through the catchment: sheetflow, rills, and the largest tributaries. +/- signs indicates direction of relationship; numerical values in () indicate sample size. Only Mesquite Wash had a sufficient sample size from monsoon storms to regress water chemistry with rainfall accumulation.

Season	Analysis	Sheetflow		Rills		Large tributaries			Sycamore Creek mainstem	
		Rainfall accumulation days (n)	r^2	Rainfall accumulation days (n)	r^2	Tributary name	Rainfall accumulation days (n)	r^2	Rainfall accumulation days (n)	r^2
Monsoon	DOC	30 (11) 90 (11)	0.687 (-) 0.499 (-)	No significant relationship (n=5)		Mesquite Wash	240 (5) 365 (5)	0.929 (-) 0.936 (-)	No significant relationship	
Winter	DOC	90 (16)	0.377 (-)	180 (8) 240 (8)	0.555 (-) 0.575 (-)	Pine Creek	150 (10) 180 (10)	0.733 (-) 0.885 (-)	60 (15)	0.639 (+)
						Camp Creek	120 (9) 150 (9)	0.796 (-) 0.835 (-)		
						Rock Creek	180 (5) 365 (5)	0.943 (-) 0.902 (-)		
						Mesquite Wash	30 (15) 60 (15)	0.395 (+) 0.580 (+)		
Monsoon	SUVA	90 (9) 240 (9)	0.855 (+) 0.967 (+)	90 (5)	0.745 (+)	Mesquite Wash	No significant relationship (n=5)		No significant relationship	
Winter	SUVA	90 (18)	0.373 (+)	180 (8) 365 (8)	0.524 (+) 0.745 (+)	Pine Creek	150 (10) 180 (10)	0.682 (-) 0.707 (-)	60 (15)	0.492 (+)
						Camp Creek	365 (9)	0.646 (-)		
						Rock Creek	120 (5) 150 (5)	0.937 (-) 0.947 (-)		
						Mesquite Wash	150 (12) 365 (12)	0.378 (+) 0.360 (+)		

significant). Mesquite Wash and the mainstem of Sycamore Creek had a positive, not negative, relationship between DOC concentrations and rainfall accumulation, indicating higher DOC with higher total rainfall prior to sampling (Table 3). In contrast to DOC concentrations, SUVA values in sheetflow and rill samples increased with increasing rainfall accumulation, meaning more complex material was exported the greater the cumulative rainfall prior to sampling. This pattern was consistent for both seasons for sheetflow and rill samples. For the largest tributaries and the mainstem of Sycamore Creek (excluding Mesquite Wash), the direction of the relationship between SUVA and rainfall accumulation was the reverse of that for sheetflow and rill samples.

Bioassays

Using laboratory bioassays with Sycamore Creek sediments as the source microbial community, we tested the relative bioavailability of several DOC sources. An eight-hour, short-term incubation indicated that simulated upland runoff was higher quality (more easily decomposed) material than algal or leaf leachate or Sycamore Creek surface water (Fig. 15). However, the same upland source was less bioavailable than algal leachate when the incubation period was extended to ten days (Fig. 16a). During the incubations, microbial communities utilized the more labile, less complex material (low SUVA), leaving a DOC pool with a higher average SUVA value (Fig. 16b).

DISCUSSION

Contribution from various DOC sources (Objective 1)

Upland and riparian soil water contributions to floodwaters have been documented in

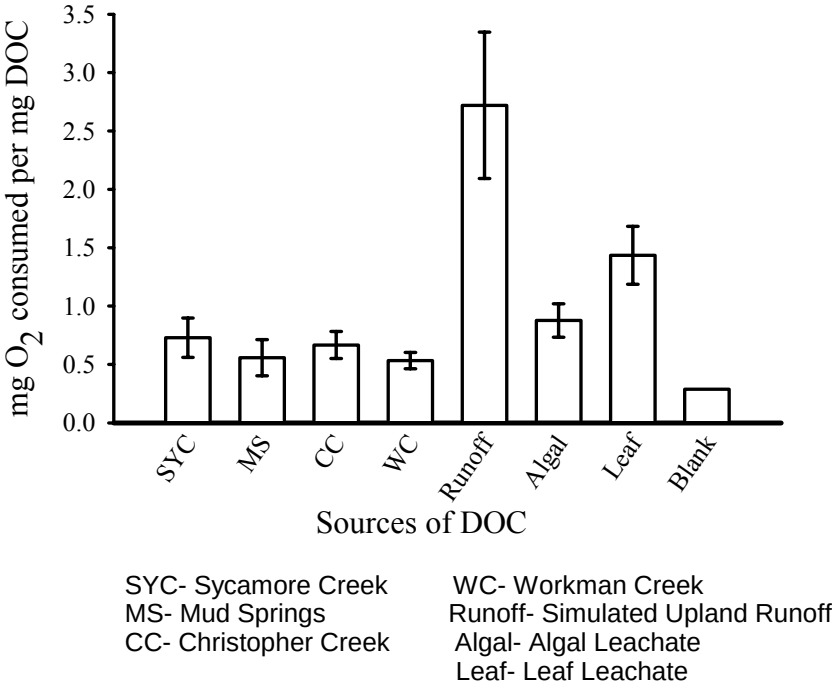

FIG. 15. Eight-hour bioassay using Sycamore Creek sediments incubated with varying DOC sources. Blank was sediment plus buffered nanopure water.

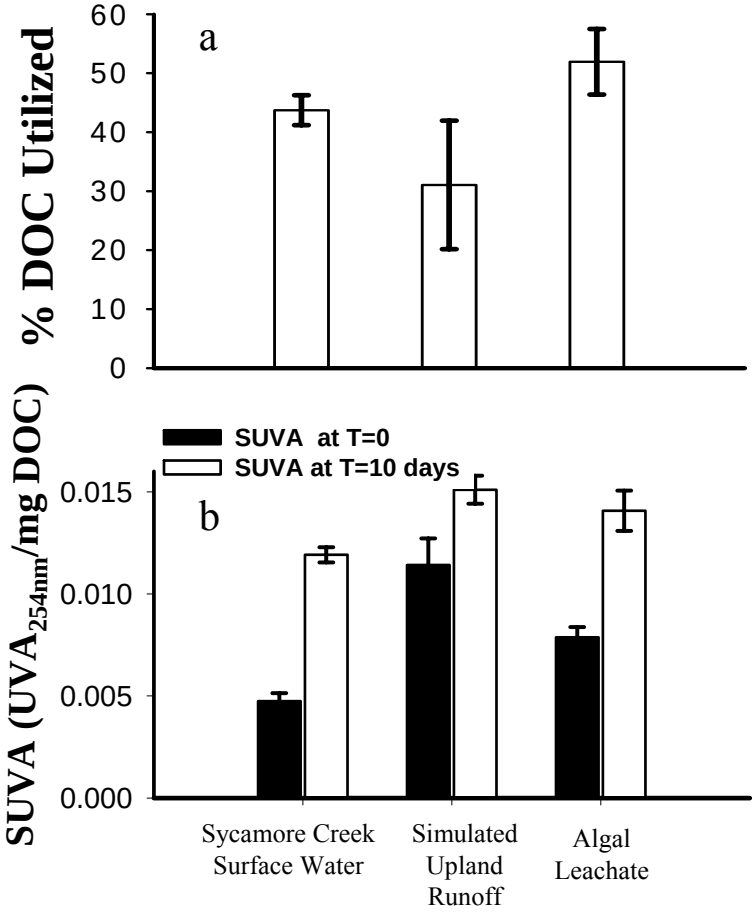

FIG. 16. Ten-day incubation of Sycamore Creek sediments with three DOM sources; (a) per cent of DOC in water that was utilized over the 10 day period; (b) change in average SUVA value of incubation water from day one to day 10.

forested catchments using a variety of approaches (Aiken and Cotsaris 1995, Boyer et al. 1997a, Soulsby et al. 2003). Some of these studies focused on the role of hydrology in influencing DOC delivery to streams; others focused on identifying the source of the DOC coming from different locations in the catchment. Our approach differed from these studies in two ways. First (in addition to considering the quantity of DOC), we considered the chemical complexity of DOC sources. This is an important regulator of the fate of stream water DOC and has been relatively unexplored in watershed studies. Second, we not only used stream chemistry as an indicator of DOC sources, we followed water along its path from precipitation to the mainstem to better understand how upland runoff and the stream-riparian corridor interact as suppliers of DOC.

Relative contribution of DOC to Sycamore Creek floodwaters from sources identified in Fig. 1 varied greatly (Table 2). Our Cl mixing model found that, for storms following dry periods, much of the inorganic salt load in floodwaters was derived by displacing water from saturated mainstem sediments or by solubilization of previously dry material, particularly in the winter. There was less displacement of mainstem water when rainfall intensities during a storm were high, because runoff moved more quickly through the stream system, inhibiting interaction with subsurface water. Mass balance calculations of DOC source loads confirmed the importance of material from channel sediments and riparian soils as indicated by the mixing model, with a relatively equal contribution from these two sources (Table 2). Our laboratory extractions suggested that floodwater SUVA values should vary as a function of the contributing DOC sources. The average SUVA value in floods did increase with an increase in the contribution from

the more chemically complex upland SOM pool (r^2=0.61, p=0.023). Establishing that variation in DOC sources had a direct effect on the quality of DOC in the mainstem adds new information to our previous understanding of organic matter export from arid catchments. This finding has broad implications for relating variation in DOC sources to in-stream microbial respiration rates, which could translate into a better understanding of downstream export of DOC.

The complexity of DOC in upland runoff was not only different from the complexity of channel-derived DOC, it varied along the flowpath to the mainstem. After sheetflow coalesced into the smallest orders of the channel network, chemical complexity of the DOC pool was significantly lowered, either by the addition of low-complexity material stored in the rills and/or through adsorption of large, complex DOC compounds to rill sediments (and hence removal of high complexity DOC from solution). DOC was then further reduced both in concentration and chemical complexity as runoff reached large tributaries, possibly through the same two mechanisms. Documenting changes in water chemistry along the stream network structure emphasizes the importance of a more spatially explicit approach to studying transformations in DOC en route to the mainstem. A spatially explicit approach has rarely been used in empirically-based catchment studies, (Leff and Meyer 1991, Hedges et al. 2000) and yet we found water chemistry patterns varied considerably at every location monitored.

An alternative explanation for changes in DOC chemical complexity and quantity when comparing sheetflow to rill and tributary samples is that the chemistry changes as a reflection of the larger catchment area being integrated by the sample. There is, of

course, not one flowpath but many bringing water to the mainstem using a network of tributaries. Rill samples are integrating an area of the uplands whose chemistry may or may not be represented by the sheetflow samples, and large tributary samples integrate an area whose chemistry may or may not be represented by the rill samples. This is much less of a concern when comparing sheetflow and rills versus rills and tributaries, because the sheetflow and rill samples were in the same subcatchment.

Runoff from uncharacterized areas contributing to tributary flow may have a diferent DOC concentration and/or SUVA value. As a first approximation of the spatial variability in upland SOM pools, we sampled soil in four locations within the larger Sycamore Creek watershed (locations indicated on Fig. 2c). Neither the amount of dissolved organic carbon extracted per unit of soil (average=27 mgC/kg soil; $F=3.204$, $df=3$, $p>0.05$) nor the SUVA value of the extract (average= 0.039 cm^{-1} $(mg/L)^{-1}$; $F=1.354$, $df=3$, $p>0.05$) was different for soil samples taken in unvegetated areas at these four locations. The lack of runoff samples located at an intermediate tributary size between the smallest rills and the large tributaries makes mechanisms of DOC transformation in the stream network difficult to distinguish.

Baseflow sources of DOC to the stream were in sharp contrast to those found during floods. Unlike mesic streams, leaf fall and its associated DOC production are relatively insignificant in the carbon budget of Sycamore Creek (Schade and Fisher 1997). The decline in SUVA values following a flood could not be explained by lateral inputs of riparian water, because SUVA values in water samples from riparian wells were the same as or higher than surface water SUVA values (data not shown). Seasonal

differences in the SUVA decline following floods suggests algal regrowth in the surface stream was the primary DOC source, as biomass accrual was faster and reached a higher standing stock in the summer due to higher ambient temperatures (Grimm and Fisher 1989).

Variation in DOC source chemistry (Objective 2)

The majority of the rain entering the Sycamore Creek catchment was not exported from the ecosystem. This is an important characteristic of arid and semi-arid streams that is underappreciated given that the location of much of the world's population and approximately 25% of its land cover is in deserts, yet we know very little about desert stream hydrology. The repeated process of water runoff, infiltration, and evaporation concentrated salts in lowland areas of the catchment topography, such as tributaries channels. Similar to research in other ecosystems, we found water export (and hence, DOC export) from the catchment was a product of antecedent soil moisture conditions (Bernal et al. 2002), (Herron and Wilson 2001), (Ceballos and Schnabel 1998), (Dick et al. 1997). Longer-term climate regime (precipitation accumulation over prior month(s)) and not individual storm characteristics were most important in determining export of water. These findings suggest that changes in regional rainfall patterns due to global warming may drastically change the timing of rain delivery to the catchment and ultimately the quantity and chemical complexity of DOC exported from it.

Antecedent conditions not only influenced water delivery to the stream, but the DOC chemistry of upland runoff was also a function of patterns in rainfall leading up to an event. Accumulated rainfall at varying durations leading up to a flood event explained

a large amount of the variation in both DOC and SUVA values in runoff chemistry along the flowpath. This suggests a link between short-term processing of SOM in upland soils between floods, and the chemistry of water carried to the mainstem. Ecologists working in ecosystems with large fluctuations in soil moisture content have identified patterns in nutrient and carbon cycling that relate to water availability for microbial communities (Rudaz et al. 1991, Schlesinger and Peterjohn 1991, Stark and Firestone 1995, Herman et al. 2003). Based on these studies, SOM in dry desert soils is most likely undergoing very little biological processing. Photo-oxidation through exposure to UV radiation may break down organic carbon compounds at the soil surface, but conversion to CO_2 by microbes is slow under water stress conditions found during periods between rain storms in deserts and grasslands (Fierer et al. 2003). This inactivity results in large pools of organic carbon sitting on dry soils and channel sediments that may generate low complexity DOC upon rewetting (Fierer and Schimel 2002).

Our results suggest that during periods with larger rainfall accumulation, higher soil moisture stimulates conversion of low complexity organic matter to CO_2 through microbial respiration, leaving smaller pools of high-complexity organic matter that are then partially solubilized and transported to the stream network during runoff. This hypothesis assumes that a pool of low-complexity DOC exists initially, which could be derived from dryfall accumulation at the soil surface, the lysing of microbial cells upon rewetting, or from UV breakdown of surface-associated organic matter. If SOM mineralization in the uplands is primarily limited by water supply, then the balance between rainfall that infiltrates soils and stimulates *in situ* processing versus a storm that

creates runoff and transports material to the mainstem will drive where in the catchment mineralization of low complexity DOC occurs, and ultimately whether DOC in runoff is exported as CO_2 or DOC. The relationship between rainfall accumulation and SUVA in the largest tributaries, with the exception of Mesquite Wash, was negative, not positive as in sheetflow and rill samples. The change in the direction of the relationship from small order to large order tributaries implies a shift in the controlling mechanism(s) with increasing spatial extent.

Bioavailability of DOC sources (Objective 3)

The working hypothesis for Sycamore Creek is that the activity of microbial communities living in channel sediments are limited by the supply of labile (high quality, low complexity) organic matter (Jones 1995, Jones et al. 1995a). Floodwaters, and the baseflow they generate, are considered a relatively unavailable source of DOC to microbes (but see (Holmes et al. 1998). In contrast to this current model, short-term bioassays showed upland runoff to be better quality material for microbial respiration than any other source tested. This is surprising given the high SUVA value of this material. But the 10-day incubation found that algal leachate could support more respiration (evidenced by a larger DOC decline) than upland runoff. Our conclusions is that there is a small pool of labile DOC contained in the upland runoff that was quickly spent, leaving more complex material of lower quality as compared to algal leachate. While the majority of upland material appears to be lower quality, on average 30 percent of the material was utilized over the ten-day experiment, versus 50 percent with algal leachate. This is not a large difference, suggesting upland material may be more easily

utilized than expected. Therefore, floodwaters to the mainstem may fuel rates of sediment respiration that are high on the short term, and lower, yet still ecologically significant, on longer time scales. Algal exudates released by periphyton in the surface stream will be preferentially used to fuel respiration, when the material is available. Baseflow chemistry patterns suggested that algal material was not as abundant in wintertime, in which case sediment respiration may depend more heavily on terrestrial-derived DOC.

Conclusions

Previously published work has established that DOC cycling in arid-land ecosystems is closely aligned with the climate regime. We provide a more detailed account of spatial and temporal differences in patterns of DOC delivery to the stream from the catchment, and a measure of its associated chemical complexity. We found a seasonal difference in our dataset, indicating that monsoon storms produce larger DOC loads of higher chemical complexity, possibly because the flowpath the water follows is different than in the winter. In fact, our mass balance calculations combined with results from a Cl mixing model demonstrated that larger contributions from upland soil DOC sources produced higher complexity floodwaters, and that monsoon floods were often dominated by upland runoff due to high rainfall intensities. We also identified previously unrecognized sources of DOC to floodwaters, namely mid-complexity DOC washed from riparian and mainstem channel sediments.

Within each rainy season, runoff chemistry from upland soils and rills appears to be highly dependent on the moisture regime of the soils. Frequent rainfall during the months prior to sampling resulted in runoff chemistry that was lower in DOC concentration and higher in chemical complexity than would be characteristic of drier periods. This may have consequences for where in the catchment the majority of carbon mineralization and CO_2 production occurs throughout the year. If rainfall is frequent but not abundant enough to create floods in the mainstem, then the labile organic carbon is mineralized in the upland soils and intermittent tributaries. In this scenario the remaining, unutilized DOC from the catchment is eventually transported into Sycamore Creek, where it is more likely to continue downstream rather than being taken up biologically. If rainfall is infrequent but intense enough to create mainstem flooding, the less complex DOC stored in the uplands is transported into the stream network, where the high quality material may be mineralized or exported downstream.

Our laboratory assays suggest that these patterns in DOC delivery to the stream may have implications for the microbial community living on channel sediments. Winter communities receive higher quality material in floodwaters with fewer supplements of algal exudates, while summer communities experience lower quality material but larger algal exudate pools. This combination of sources of varying chemical complexity may translate into higher than expected winter respiration rates and CO_2 production.

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CHAPTER 2: LONG-TERM CHANGES IN STREAM-WATER CHEMISTRY AS A FUNCTION OF URBAN ACTIVITY IN ARID LANDS

ABSTRACT

This work compares native desert and urban stream ecosystems by examining differences in concentrations of DOC, nutrients, and conservative ions among desert stream sites that are unregulated, regulated, and highly modified by the urban environment. Water retention by the city was particularly high during severe drought, and climatic variability was poorly related to river hydrology during these dry periods. Due to the city's large water retention capacity, material loads were much higher entering the city then exiting. However, the city was a source of carbon, nutrients, and salts to the river ecosystem.

Changes in water chemistry over time and with respect to disturbance by flooding indicate that carbon and nutrient cycling have changed as a result of human modification of the landscape, including lowered hydrologic and chemical variability and increased baseflow C and nutrient loading. Biogeochemists working in an urban setting may need to increase their spatial and temporal scales of study to better understand the feedbacks between human decision-making and carbon and nutrient cycling.

INTRODUCTION

Urbanization is a pervasive and growing land-use and cover change on the Earth's surface (UN Population Division, 2002). In particular, the desert southwestern US is experiencing rapid conversion of previously agricultural or native desert land to urban landcover, with important implications for water use in the region. Because runoff is low

in the desert Southwest, humans have engineered methods for collecting, using and reusing water before it leaves the ecosystem. Just as water quality in non-urban rivers integrates processes occurring in the whole watershed (Hynes 1975), rivers draining urbanized catchments similarly reflect the dominant processes occurring within the cities they drain.

Interest in the effects of urbanization on water quality has increased dramatically over the past 50 years in the United States. Modification of the physical and chemical attributes of rivers by agricultural activity, construction of water-retention structures such as dams, and urbanization have been documented in the literature (Westerhoff and Anning 2000, Paul and Meyer 2001). The National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS) was established in 1991 to collect and distribute water quality data to inform federal policy. The program expanded to document the effects of urbanization on stream ecosystems in 15 metropolitan areas in 1999. The NAWQA findings to date, like almost all studies investigating the effect of urban centers on stream-water quality, document higher concentrations of nutrients, salts, metals, suspended solids, and organic pollutants in urban streams as compared to non-urban streams. These increased loadings to rivers are often accompanied by a decrease in the geomorphic complexity of the river channel, which can increase sediment bed load and reduce the hydrologic exchange of surface water with the riparian zone and subsurface sediments (Jones and Mulholland 2000). Obvious concern surrounds the impact of these changes in water quality on fauna living in and around the streams, on

recruitment and longevity of riparian vegetation, and the ability of humans to find a safe drinking water source.

Variation in the regional and historical context between cities may be important in determining the influence of urbanization on water quality (Pickett et al. 2001). This variability can result from differences in climatic regime; the presence or absence of a history of agriculture; the damming of rivers; the density of residential, commercial, and industrial land uses; or the development of white-collar versus blue-collar industry. Additional complexity arises when there are multiple urban activities or physical attributes acting in concert to influence water quality, such as federally-legislated reductions in chemical loads to surface water; completion of a dam or tertiary wastewater treatment facility; initiation of industrial point source waste additions; or population growth and the associated increase in automobile exhaust, fertilizer application to lawns, and water delivered to wastewater treatment plants (Findlay et al. 1998). Water chemistry is an integrator of all these human activities, as well as a reflection of biological processing in the stream itself.

Not only are temporal patterns in stream-water chemistry in urbanized catchments integrations of the ontogeny of the city, they reflect the mechanisms of material transport and transformation in the ecosystem. Comparison of temporal patterns of low-impact ecosystems (outside the influence of the city) stream-water chemistry and discharge to that of streams in an urban center may suggest ways in which human modification in the city has altered terrestrial-aquatic linkages. This would be most apparent when comparing periods of high flow, as terrestrial-aquatic linkages are strongest during storm

runoff (Fisher et al. 1998). Our objective was to analyze long-term temporal patterns in stream-water chemistry above and below the metropolitan area of Phoenix, AZ, with a focus in three areas: 1) the influence of dams on water chemistry entering the urban ecosystem, 2) changes in spatial, seasonal, and discharge-related patterns in water chemistry as an indicator of how biogeochemical cycling may have been altered by urbanization and 3) to look for any "signal" in water chemistry indicating a response to abrupt shifts in, for example, policy, water sources, or treatment technologies. We compared short- (5-year) and long-term (decades-long) patterns in biologically conservative and reactive compounds. The Phoenix area is an ideal location for these types of analyses, because its history of rapid urbanization and expansion is short and relatively recent. Our datasets include water chemistry analyses collected over 40 years ago, when the population was a fifth of what it is today and urban land cover was a third of present extent. Phoenix is also ideal because of the regional climate regime. Rainfall is sparse and highly variable both in space and time, making runoff events more easily identified.

Our work was part of a larger study at Arizona State University known as the Central Arizona Phoenix Long Term Ecological Research (CAP LTER) project. The CAP LTER is examining the Phoenix metropolitan area as an integrated ecosystem that includes human-ecosystem interactions and feedbacks in its conceptual framework (Collins et al. 2000, Grimm et al. 2000). For this study we used a combination of two datasets, one from the USGS and the other from the CAP LTER, containing chemistry data for the three main surface water inflows to the city and two locations along the

hydrologic output from the entire metropolitan area. In addition, we analyzed discharge data from USGS stream gauging sites at similar locations (details below). We compared patterns over time and in space to draw conclusions regarding the interaction of urban activity and stream-water chemistry in this arid-land city.

METHODS

Site description

The Phoenix metropolitan area is located in Maricopa County, AZ, and surrounded by the Sonoran desert scrub of the southwestern US (Fig. 17). The valley floor consists of deep alluvial deposits from the Salt-Gila River complex. Most streams and rivers in this area are ephemeral, flowing only for short periods of time during large rainstorms. The confluence of several large perennial rivers in the valley now occupied by the Phoenix metropolitan area has supported agricultural activity since the late 1800's, as well as from the 5th to 15th centuries. The Verde River joins the Salt River just east of the city (Salt river flow is from east to west), and the Salt and Gila Rivers converge in the western edge of the city. The Salt River has five dams upstream from the Phoenix metropolitan area, the first built in 1911, the last one completed in 1930. The Verde River has two dams, finished in 1939 and 1946. These reservoirs are engineered and managed for flood control, water storage, and recreation. Supplemental water began entering Phoenix from the Colorado River in 1985. Water is transported approximately 400 miles via the cement-lined Central Arizona Project (CAP) canal, to Granite Reef dam, where a portion of the water is mixed with the flow from the Salt and Verde Rivers.

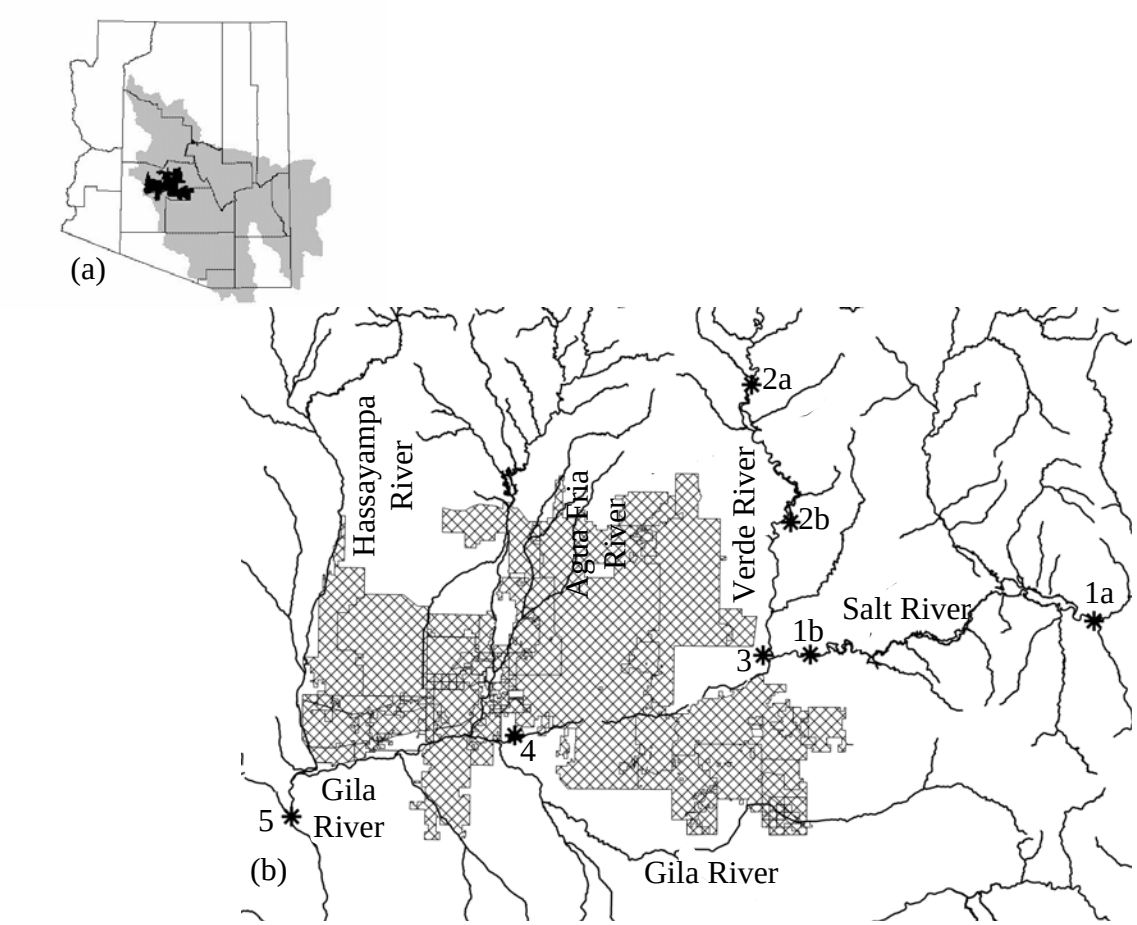

FIG. 17. Map (a) shows the location of the Phoenix metropolitan area (in black) within Maricopa County. Superimposed on Phoenix is the area drained by the Gila River watershed above its outflow from the city. Map (b) is more detailed, indicating the location of sampling points upstream of the city on the Salt River (1a, b), Verde River (2a, b) and the CAP canal (see text) (3); and downstream of the city at the 91st Avenue wastewater treatment plant (4) and the Gila River (5). Sites "a" and "b" on the Salt and the Verde Rivers are above and below the dams.

Groundwater pumping in the eastern portion of the city has been used to supplement municipal and industrial water needs since since the early 1900s.

The Salt and Verde Rivers do not enter Phoenix via the natural Salt River channel (i.e. the channel is dry inside the city), but since 1908 have been mixed and diverted into canals at Granite Reef dam where the water enters a distributary system of canals that feed water treatment plants (Site 3, Fig. 17). Downstream of the main metropolitan area water is reintroduced into the riverbed as treated effluent from the 91st Avenue wastewater treatment plant (WWTP) (Site 4, Fig. 17). Approximately 5 km downstream from the 91st Avenue WWTP inflow, Gila River water enters the river channel from the south, predominately as subsurface discharge (low flows here are due to water withdrawals upstream). The Gila River (as the combined flow is now called) then travels approximately 70 km through agricultural fields where groundwater wells augment flow while at the same time water is removed for irrigation. At the end of this 70 km flowpath, the water is again diverted into canals for irrigation purposes further downstream (Site 5, Fig. 17).

Phoenix's precipitation is bimodal with winter and summer (monsoon season) maxima; slightly more than half the annual total falls in the winter. The two distinct rainy seasons have very different rainfall characteristics. Monsoon precipitation tends to come during intense, spatially localized and short-lived storms, while winter rains are generally longer, spatially more widespread, but less intense. Annual mean rainfall in the city is 19 (±1) cm, calculated from the previous 50 years of rainfall data. Local precipitation, however, does not adequately describe runoff patterns, because the majority

of streamflow for the Salt, Verde, and Gila Rivers is derived from higher elevation rainfall and snowfall. Runoff patterns over the past 40 years have included a very dry period from approximately the early 1940s to the early 70s, followed by an above average rainfall period from the early 1970s to the mid 1990s (with very large floods in the late 70s, mid 80s, and early 90s); currently the area is experiencing another period of drought (Fig. 18). For purposes of this work, data before 1973 were considered part of the "dry" climatic period, and data after 1973 are part of the "wet" period. Floods occurred during the dry period, but at a reduced frequency and magnitude.

Historically, Phoenix was an agricultural community, with abundant cotton farming and livestock activity, but in 1955 population growth in this area has risen exponentially from approximately 300,000 to over 3 million inhabitants today. As a city with virtually no limitations on land availability, Phoenix maintained a pattern of low-density commercial and industrial development (Gammage 1999), as well as rapid conversion of agricultural and native desert land into residential neighborhoods.

Sample collection and analysis

USGS NAWQA sampling sites were located upstream of the city on the three main surface-water inflows- the Salt River, Verde River, and CAP Canal- and at two locations downstream of the city on the lower Gila River. Long-term datasets were available from the USGS for the NAWQA sampling locations. The CAP LTER maintained selected parts of the pre-existing USGS NAWQA surface water sampling in early 1998. The Salt and Verde Rivers were sampled above the dams by the NAWQA

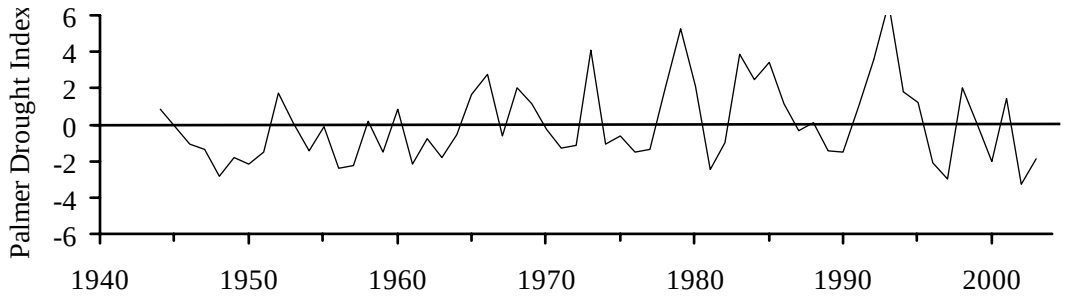

FIG. 18. Annual Palmer Drought index ratings for Maricopa County, which includes Phoenix, AZ. Index reflects average conditions over a year using a combination of rainfall patterns and soil moisture conditions. Negative values suggest below average conditions, positive values suggest above average conditions.

program (site1a and 2a, Fig. 17), but the LTER chose to sample below the dams due to the difficulty in getting to the original NAWQA sites (site 1b and 2b, Fig. 17).

The sampling protocol that was developed by the USGS for the NAWQA program was modified slightly by the CAP LTER. A depth-integrated, channel-wide sample was collected at each site into a 3-L nalgene bottle, transported to the laboratory on ice, and then split into 10 subsamples. Three subsamples were filtered through a Whatman GF/F ashed filter, and the filtrate was used for DOC analysis using high-temperature combustion on a Shimadzu TOC-5000 carbon analyzer. Materials remaining on the GF/F filter were used for ash-free dry mass determination and elemental analysis using a Perkin-Elmer 2400 Series II CHNS/O analyzer. Three other subsamples were filtered through a membrane filter of porosity 0.45 μm, followed by cation (Ca, Mg, Na, K) analysis using a Varian SpectrAA 400 Flame atomic absorption spectrometer, dissolved nutrient analyses using colorimetric methods on a LACHAT 'Quick Chem' 8000 flow-injection autoanalyzer, and sulfate analysis using a Dionex 4000i ion chromatograph. The remaining subsamples were filtered through a Whatman GF/F filter and a known volume of filtrate was placed in a pre-weighed glass beaker, dried at 100°C, and reweighed. The difference in mass between beakers before water addition and after evaporation was used to calculate total dissolved solids (TDS). In addition, samples for total inorganic carbon and pH were collected in the field with no headspace and transported to the laboratory for analysis. Conductivity and water temperature were measured at each site using an Orion field meter.

Data from the LTER, NAWQA, and other previous USGS sampling efforts, along with discharge data from USGS gauging stations located at the same sites on the Salt, Verde and Gila Rivers, were included in our analyses. Daily discharge data from the 91st Avenue WWTP and the CAP canal were obtained from the City of Phoenix and the Central Arizona Water Conservancy District. Analytes for which there were more than 2 samples per year over multiple years were used to calculate several measures of temporal variability, including 95% confidence intervals, coefficients of variation, and aggregated means through time. We used regressions among conservative elements and reactive elements, and discharge to infer possible pathways by which major ions reached the river.

RESULTS

Influence of dams on river hydrology

Before considering how urbanization has influenced the chemistry of the Salt and Gila Rivers, we first examined the influence of dams on the delivery of water to the city. Discharge measurements extend back > 60 years at sites 1a, 2a, and 5 (Fig. 17). The Salt River is dammed at five locations, and water release from the most downstream reservoir is based partially on water demands. Agricultural activity and human activity (including maintenance of lawns and swimming pools) accounts for a large portion of the water use in the region, hence flows are augmented and maintained at their highest levels during the summer when plants are most water stressed and evaporation and transpiration are highest. When water demand is low, flow is restricted to a level far below that seen above the dams. Since 1934, 29% of the daily average flows below the dams were < 2.1

m^3s^{-1}. This level of flow is significant, because it is the lowest discharge recorded, since 1913, upstream of the dams on the Salt River. The Verde River site below the dams also experiences a reduced baseflow as compared to upstream sites, with discharge lower than that historically found at the unregulated site.

In addition to reducing baseflow, the dams have also reduced variability in discharge for the two rivers. For the previous 6-7 decades, discharge was less variable (measured using coefficient of variation) below the dams as compared to above the dams (Table 4). This difference was much smaller during wet years (1974-98) when more of the high flow events were allowed to exit the reservoirs. The hydrograph of the Verde River above and below the dams maintains a very similar shape, although average discharge above the dam in consistently higher than below (Fig. 19). In contrast, the Salt River below the dams had a more regular, less flashy hydrograph than the upstream site during the dry period (1934-74) (Fig. 20b). Once wetter years arrived, average discharge below the dams was often higher than upstream, and the shape of the two hydrographs became more similar.

A third surface-water input to the city comes from Colorado River water, delivered through the Central AZ project canal. For the Phoenix metropolitan area, this water source is only important when it is mixed with the Salt and Verde River flows. If not needed, the Central AZ project canal carries the water downstream of the city. Flooding, climatic variation, and management of reservoirs do not influence the chemistry of the CAP water, therefore discussion of its influence on nutrients delivered to the city is reserved for later.

TABLE 4. Coefficient of variation (CV) for daily discharge measurements (m^3/s) at USGS gauging sites above and below the dams on the Salt and Verde Rivers.

	Salt River		Verde River	
Time Frame	Above Dams	Below Dams	Above Dams	Below Dams
	CV	CV	CV	CV
1934-44	232	96		
1944-54	258	78	264*	113*
1954-64	216	96	204	121
1964-74	226	151	296	166
1974-84	276	247	370	348
1984-94	242	192	413	361
1994-03	188	129	397+	363+

* does not include 1944
+ ends in 1998

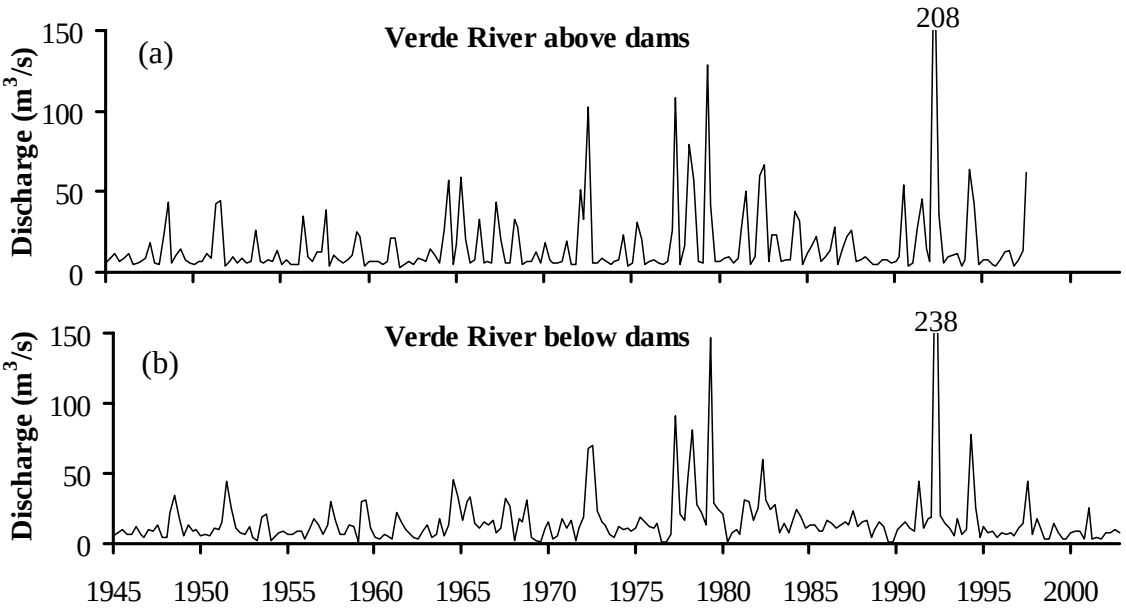

FIG. 19**.** Discharge averaged every 3 months for gauging stations upstream (a) and downstream (b) of dams on the Verde River.

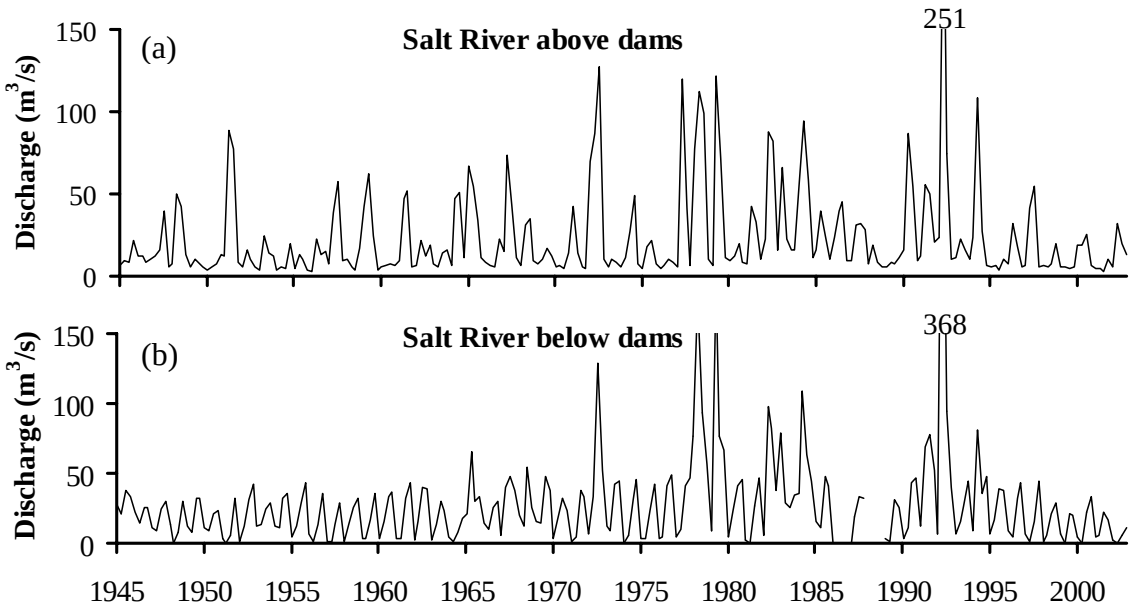

FIG. 20. Discharge averaged every 3 months for gauging stations upstream (a) and downstream (b) of dams on the Salt River.

Influence of dams on river water chemistry

The influence of the reservoir system and the alteration of the flow regime on water chemistry may be inferred from comparing data from sites above and below the dams. To make valid comparisons, we analyzed data from the same time periods. This limited the number of chemical parameters we could evaluate, because the record of observations was not always consistent for the sites above and below the dams. In our analyses we used conductivity, total dissolved nitrogen (TDN), inorganic phosphate, and dissolved organic carbon (DOC). Conductivity varies as a function of variation in all species dissolved in the water, but is most closely correlated with changes in cations, chloride, sulfate and bicarbonate. It represents, therefore, a biologically conservative measurement. Biological communities, in contrast, readily utilize N, P, and use or produce DOC. Nitrogen has been found to limit primary production in Sonoran desert streams and carbon has been found to limit heterotrophic respiration (Grimm 1987, Jones 1995).

Long-term, average conductivity downstream of the dams on the Salt River was slightly less than half of the upstream average, and the CV was smaller downstream (Table 5). For both the Salt and Verde Rivers, values decreased with increasing discharge, and there was no relationship between day of year and conductivity. We calculated the 90% percentile interval around the variance at the downstream site, superimposed that on the data from upstream, and found 80% of the upstream values exceeded these percentiles (Fig. 21). These results demonstrate a significant reduction in conductivity and its variability in the Salt River as water moved through the

TABLE 5. Average concentration and CV for conductivity, total dissolved N (TDN), inorganic phosphate, inorganic phosphate, and dissolved organic carbon (DOC) at sites upstream and downstream of dams. ±1 SE are in parentheses.

	Salt River						Verde River					
	Time Frame	n	Above Dams		Below Dams		Time Frame	n	Above Dams		Below Dams	
			AVG mg/L	CV	AVG mg/L	CV			AVG mg/L	CV	AVG mg/L	CV
Conduc-tivity (as uS/cm)	1976-92, 1996-01	144	2127 (100)	57	1014 (26)	34	1980-92, 1996-01	93	584 (12)	19	465 (11)	22
TDN	1984-89	38	0.49 (0.06)	75	0.38 (0.05)	75	1985-92	24	0.59 (0.09)	75	0.55 (0.06)	51
	1998-03	10	0.11 (0.07)	197	0.44 (0.14)	100						
Phosphate	1976-77	11-13	0.023 (0.004)	64	0.016 (0.003)	66	1981-86	17-19	0.022 (0.004)	68	0.024 (0.003)	60
	1986	2-5	0.020 (0.01)	71	0.016 (0.005)	68						
DOC	1978-81	14			6.2 (0.9)	52	1978-81	12			6.9 (1.5)	73
	1996-98	32	2.2 (0.2)	57			1982-98	29	2.1 (0.3)	75		
	1998-03	42			3.9 (0.3)	56	1998-03	37			3.0 (0.3)	67

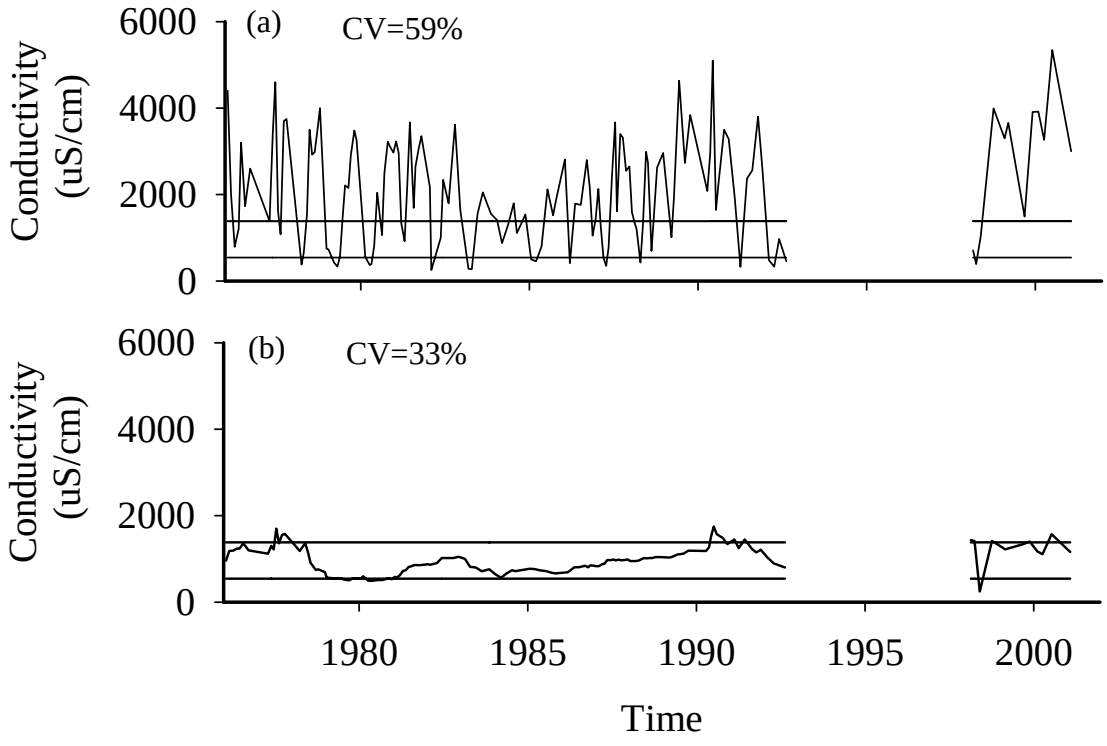

FIG. 21. Salt River conductivity data (a) upstream and (b) downstream of the dams. Lines indicate the 90th percentile calculated from data downstream of the dam and applied to both graphs. The coefficient of variation (CV) was calculated for each data set.

reservoir system. These same patterns were not found with Verde River conductivity. The long-term average, while higher upstream of the dams on the Verde, was only 25% higher, and the CV of the data set was approximately the same (Table 5). In the Salt River, the number of measurements outside of the 90% percentile intervals decreased downstream of the dams, whereas the opposite occurred on the Verde River. Thirty-nine per cent of the values at the downstream site on the Verde River are outside of the 90% percentile limits generated by the upstream conductivity data. Therefore, changes in conductivity due to the presence of reservoirs were somewhat different for the Salt and Verde Rivers, with relatively little change on the Verde, compared to reduced variability downstream of dams on the Salt. This may at least in part reflect much higher background concentrations that occur naturally in the Salt River (hence its name).

Nutrient concentration data upstream and downstream of the dams had different trends from that of conductivity. The 6-year average TDN concentration for the Salt River remained the same from upstream to downstream of the dams in the 80s and increased (4 times higher than upstream) over the past 6 years (Table 5). There was no change in the long-term average TDN concentration on the Verde River, but the CV was lower downstream of the dams (Table 5). Inorganic phosphate concentrations and CVs were not different above versus below the dams on the Salt or Verde Rivers for similar time periods (Table 5). While there were no overlapping time periods for which DOC data above and below the dams existed for both the Salt and Verde Rivers, upstream concentrations were lower than downstream, and the CV remained relatively constant (Table 5).

Changes in water chemistry brought about by damming upstream of the Phoenix metropolitan area varied between the two rivers. The five dams on the Salt River drastically reduced discharge values between floods, the number and magnitude of high flow events, and variability in average discharge, particularly during dry periods. Conservative element concentrations were reduced by half and nitrogen concentrations increased, but mass balance calculations of major ions showed production of some of the conservative elements and retention of others (Table 6). A greater than 5-fold increase in N loading and much smaller production of DOC suggest that biological activity within the reservoirs influenced water chemistry. The Verde River dams resulted in a similar reduction in baseflow discharge and the overall variability in the hydrograph, but more flood peaks were maintained below the dams. Similar to the Salt River, average conductivity dropped below the dams as compared to above them, but there was an increase in loads of all major conservative ions (except Ca) (Table 6). Reservoirs on the Verde River did not significantly change average TDN concentrations or loads, but did decrease its variability. In contrast to the Salt River, DOC was consumed in the reservoirs on the Verde Rivers. It appears, then, that the reservoirs have an influence on both hydrology and chemistry in the Salt and Verde River systems.

Influence of metropolitan area on river hydrology

Comparisons of hydrographs above and below the city (sites 1b, 2b, and 5) show Gila River discharge was the smallest of the three streams during low-flow periods, even though it has the largest catchment area (Fig. 22). Upstream variation in discharge was not related to variations in downstream discharge from 1945-77, but upstream and

TABLE 6. Water and material loads at sites upstream and downstream of the dams on the Salt and Verde Rivers. Values for Salt River were calculated from March 1998 through April 2001, and values for Verde River were calculated from March 1998 through October 2000.

	Site #	Water Volume ($m^3 \times 10^8$)	DOC Loading (kg x 10^6)	N Loading (kg x 10^6)	Ca Loading (kg x 10^6)	Na Loading (kg x 10^6)	Mg Loading (kg x 10^6)	K Loading (kg x 10^6	Cl Loading (kg x 10^6)	SO_4 Loading (kg x 10^6)
Inputs										
Salt River	1a	16.1	4.7	0.12	77.9	430	24.7	9.93	688	103.9
Verde River	2a	10.5	5.0	0.60	34.6	22.4	20.1	2.01	13.6	34.9
Outputs										
Salt River	1b	13.5	4.9	0.62	73.9	269	22.6	7.59	451	97.5
Percent of Input		84	105	527	95	63	91	76	66	94
Verde River	2b	10.0	3.7	0.59	31.5	25.1	19.8	2.23	14.3	67.5
Percent of Input		96	74	98	91	112	99	111	105	193

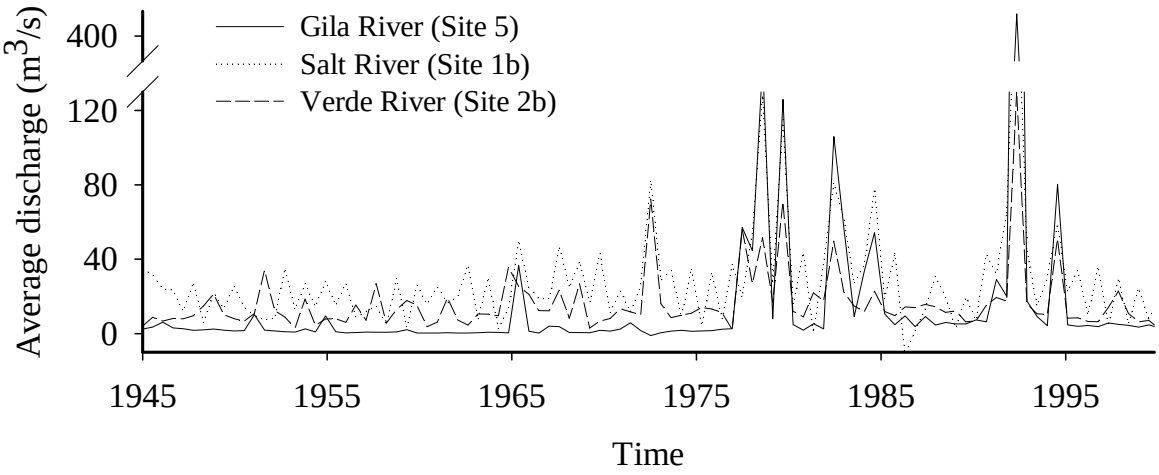

FIG. 22. Discharge averaged over 3 months at the two gauging stations upstream of city (and downstream of all dams) compared to the hydrologic output from the city on the Gila River.

downstream discharge were highly correlated during the period that included the major high flow events of the late 70s, mid 80s and early 90s (r^2_{Salt}=0.789, r^2_{Verde}=0.882). During these high-flow periods, discharge was highest downstream of the city on the Gila River as compared to the Salt and Verde River discharge, as would be expected from the large catchment area drained by the former (Fig. 22).

Influence of metropolitan area on river water chemistry

As with almost all cities, concentrations of dissolved constituents are higher downstream of the Phoenix metropolitan area as compared to upstream. In this study, there are two important downstream sites to consider for water chemistry analyses, the one directly below the outfall from the wastewater treatment plant on the Salt River (site 4, Fig. 17), and the one 70 km downstream (site 5, Fig. 17). Between these two sites, shallow and deep groundwater enters the river and water is extracted from surface flows for irrigation of crops. In general, considering both downstream sites, average DOC concentrations over the past five years (1998-2003) were approximately 2-3 times higher below the city than above (Table 7). Nutrient concentrations were 1-2 orders of magnitude higher downstream; TDN and nitrate increased, while ammonium, TDP, and SRP decrease between the two downstream sites (Table 7). Conservative ions were comparable at site 4 as compared to upstream, but there was an approximately three-fold increase in concentrations of conservative ions (except K^+) between the two downstream sites (Table 7).

Whereas material concentrations (mass per volume) increased as water moved through the city infrastructure, water retention within the city from 1996-98 was high

TABLE 7. Average concentration of DOC, nutrients, and conservative ions at sites upstream and downstream of the city. Data averaged from 1998-2003, ±1 SE is in parentheses.

Constituent	Upstream of Phoenix Metropolitan Area			Downstream	
	Salt River (Site 1b)	Verde River (Site 2b)	CAP Canal (Site 3)	Salt River (Site 4)	Gila River (Site 5)
DOC (mg/L)	4.0 (0.4)	2.8 (0.4)	4.1 (0.4)	9.5 (1.0)	6.9 (1.5)
TDN (mg/L)	0.218 (0.034)	0.237 (0.027)	0.317 (0.031)	4.747 (0.342)	8.696 (0.362)
Nitrate-N (mg/L)	0.008 (0.002)	0.036 (0.011)	0.162 (0.022)	2.698 (0.195)	8.808 (0.226)
Ammonium-N (mg/L)	0.017 (0.002)	0.023 (0.005)	0.020 (0.003)	2.049 (0.220)	0.223 (0.032)
TDP (mg/L)	0.017 (0.002)	0.021 (0.002)	0.012 (0.002)	3.682 (0.693)	0.900 (0.156)
Phosphate-P (mg/L)	0.029 (0.004)	0.029 (0.004)	0.014 (0.002)	2.958 (0.151)	0.813 (0.076)
Calcium (mg/L)	60.5 (2.8)	47.0 (1.8)	74.7 (2.3)	70.3 (2.5)	212.6 (9.7)
Magnesium (mg/L)	18.6 (0.5)	30.6 (0.9)	27.7 (0.8)	31.1 (0.8)	92.7 (3.6)
Sodium (mg/L)	229.9 (8.0)	36.4 (1.4)	86.2 (3.6)	220.0 (7.6)	698.4 (20.6)
Potassium (mg/L)	6.5 (0.3)	2.9 (0.1)	4.5 (0.2)	18.1 (0.6)	12.7 (0.3)
Chloride (mg/L)	381.7 (10.6)	24.6 (2.3)	75.8 (0.8)	274.9 (15.0)	959.8 (27.0)
Sulfate (mg/L)	72.7 (4.4)	52.7 (3.1)	245.9 (7.7)	201.6 (5.0)	587.4 (25.8)
TDS (mg/L)	931 (23)	293 (11)	615 (18)	945 (18)	3265 (367)

(Table 8). A comparison of surface water input and output loads (total mass) to and from the city found significant retention of DOC and total dissolved salts (TDS). The percentage retention of these two components was lower than the water retention value, which indicates that water accumulated DOC and salts as it was routed through the city. And while N and P stream loads were higher downstream of the city versus upstream, N loads were less than double that of upstream, not an order of magnitude higher as with the concentration data (Table 8).

Differences in water chemistry upstream and downstream of the city may be caused by differences in the residence time of the water in the catchment before joining surface flow. For instance, whether surface water recently moved overland during runoff events, or seeped from groundwater storage, dictates the extent to which biological uptake and exchange with soils have influenced the chemistry. To determine how much of the variability in water chemistry above and below the city was due solely to changes in discharge due to flooding, we examined patterns in conservative elements (Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}) taken at varying discharge levels. We constructed a correlation matrix of bivariate plots of every combination of ions, dividing the data into pre-1978 (dry) and post-1978 (wet) data sets to account for the differences in low and high precipitation years (Fig. 23). A linear relationship between any two ions indicates conservative mixing between the flood endmember and the baseflow endmember, and that the sources of the ions are similar. A line that passes through the origin indicates that flow-related variations in ion chemistry were the result of simple dilution of the baseflow signal by storm flow and that the baseflow ratio was not different from the flood

TABLE 8. Water and material loads for January 1996-March 1998 at sites upstream and downstream of the Phoenix metropolitan area.

	Site #	Water Volume ($m^3 \times 10^8$)	DOC Loading (kg x 10^6)	N Loading (kg x 10^6)	P Loading (kg x 10^6)	TDS Loading (kg x 10^6)
Inputs						
Salt River	1b	14.9	5.6	0.32	0.025	1387
Verde River	2b	6.0	3.0	0.15	0.013	177
CAP canal	3	10.5	3.2	0.33	0.013	646
Outputs						
Salt River	4	2.9	2.4	1.38	1.07	274
Percent of Input		9	20	173	2098	12
Gila River	5	1.36	0.94	1.18	0.12	444
Percent of Input		4	8	148	235	20

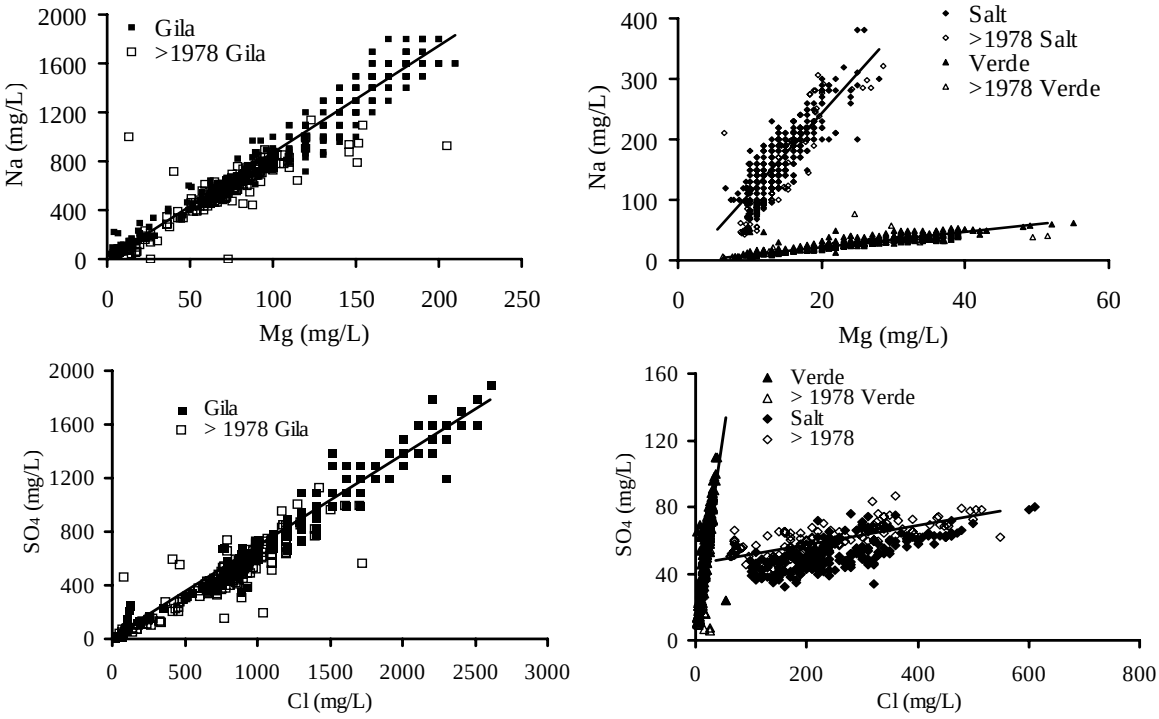

FIG. 23. Example of conservative element plots for the Salt, Verde, and Gila River, sites 1b, 2b, and 5 (Fig. 1). Data are divided into two groups, values generated before 1978 (indicated in legend by the name of the site, only), and those generated after 1978 (indicated by ">1978"). A linear relationship between ions indicates dilution of baseflow ion ratio during floods, and one that passes through the origin indicates the same signature ratio for both baseflow and floods.

endmember.

Ion ratios for all three sites consistently resulted in three positive linear relationships (one for each site), most of which passed through the origin. Hence, catchment characteristics seem to play a dominant role in controlling both baseflow and stormflow endmember composition, rather than flow path routing changes under different rainfall regimes. There were exceptions to the general pattern. For instance, none of the ion ratios containing K^+ showed significant correlations for the Gila River data set (with the exception of Mg^+ vs. K^+, which had a low r^2). Additionally, ratios with SO_4^{2-} (and the plot of Mg^+ vs. Cl^-) resulted in a linear relationship that did not pass through the origin at the Salt River, indicating a different signature ratio at low and high flow periods.

Only on the Gila River were there different ranges in values for the pre- and post-1978 data. For every ion ratio plotted, the values before 1978 maintained the same ratio, but with higher concentrations for each individual ion (Fig. 23). These higher concentrations were recorded under drought conditions, with 75% of them collected in months with a negative Palmer Drought Index (Fig. 18). These values were not associated with a particular month or season, and some low flow samples collected before 1978 did not have these very high concentrations although discharge was very low for most of these measurements. Patterns in ion concentrations (as measured by conductance) appear to have been consistent for several decades, although conductance was higher in the Gila River downstream of the city during the drought years of the 60s (Fig. 24).

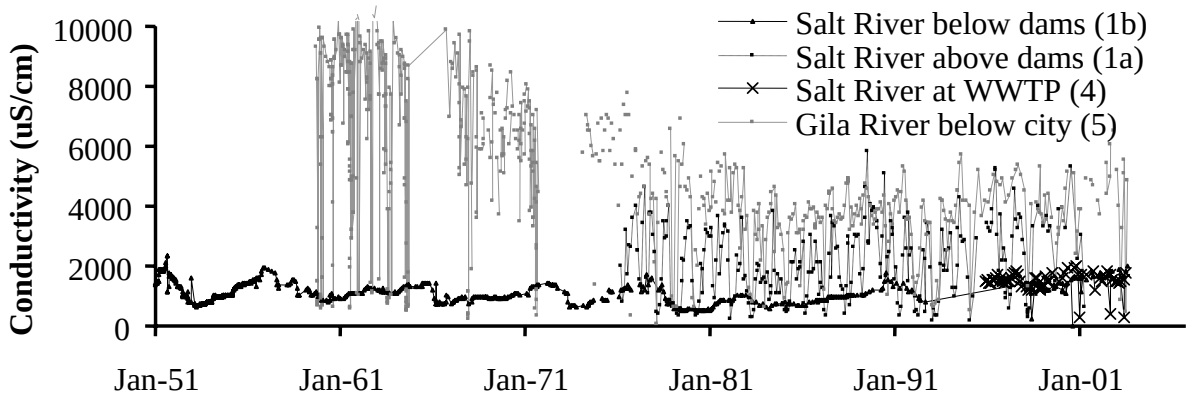

FIG. 24. Conductivity plotted over time for the two sites above and below the dams on the Salt River upstream of the city (site 1a, b) and the two sites downstream of the city on the Salt and Gila Rivers (site 4, 5).

In summary, aside from K^+, major ion concentrations upstream and downstream of the city appear to be a function of hydrologic dilution during flooding. Correlations with discharge support this interpretation, as all major ions were negatively correlated with discharge at the Verde River and Gila River sampling locations ($p<0.0001$). This relationship was stronger downstream of the city where post-1978 data were better predicted by discharge than pre-1978 data (r^2= 0.35-0.4 for pre-1978, r^2=0.4-0.8 for post-1978), compared to r^2 values of only 0.10-0.20 upstream of the city. There were no significant relationships between conservative ions and discharge at the Salt River site. While the chemical composition of baseflow water remained consistent with that of the unregulated stream, management of the dams on the Salt River has resulted in baseflow concentrations well below those ever recorded upstream of the dams, effectively decoupling discharge and water chemistry at this site.

The conservative nature of the ions discussed above leads us to suggest mechanisms influencing patterns in reactive ions. On the Salt River (site 1b, Fig. 17), we found, for post-1978 data only, that NO_3^- decreased when concentrations of Mg^{2+}, Na^+, K^+, and Cl^- increased, suggesting that water with low conservative ion concentrations coincided with an inflow of water with high nitrate concentrations into the river ($p<0.05$, r^2 ranged from 0.46-0.53). Similarly, upstream of the city on the Verde River, TDN, DOC, and total phosphorus (TP) were negatively correlated with conservative elements (excluding K^+) using data post-1978, but with less than 30% of the variance explained. Conversely there was a positive relationship between all conservative ions and total

nitrogen and nitrate, suggesting that water delivering salts is also carrying high N concentrations on the Gila R. downstream of the city.

Correlations of conservative and reactive constituents provide evidence that flooding influenced water chemistry. However, not all nutrient and DOC data co-varied with conservative element concentrations. Thus, temporal variation in water chemistry downstream of the city was not always due to changes in discharge. As a next step we examined concentration data through time to look for possible explanations for the observed changes in water chemistry as a function of changes in "baseflow" water sources or changes in city ecosystem engineering. As water is diverted away from the riverbed at the edge of the city and becomes part of the urban canal network, three major water sources can be identified: (1) baseflow from the Salt, Verde, and Colorado Rivers, (2) surface runoff during floods (discussed above), and (3) groundwater pumped into canals through wells (Edmonds and Grimm 2004), Ying et al., in preparation). Each of these sources has its own unique chemical signature, and variation in the contribution from each has implications for biogeochemical cycling.

To detect changes in water sources, SO_4^{2-}/Cl^- and Ca^{2+}/Na^+ ratio at the two sites downstream of the city were compared to patterns upstream of the city (but below the dams). The contribution of water from the Salt and Verde Rivers to the urban ecosystem varied from year to year (Table 9). The Salt River was more frequently the primary source of water, but there were months (Nov-April) where the Verde River was the sole water source. Water from the Colorado River, delivered by the CAP canal, has become a larger contributor to the city water supply in the last 5 years (Table 9). All three sources

TABLE 9. Annual contribution to Phoenix canal distribution system from primary water sources for Phoenix from 1980 to 2002.

Year	Salt River (m^3 x 10^8)	Verde River (m^3 x 10^8)	Groundwater pumping (m^3 x 10^8)	Colorado River_ CAP Canal (m^3 x 10^8)
1980	41.23	25.65	15.25	
1981	8.88	2.08	22.38	
1982	6.28	8.99	15.65	
1983	36.31	14.48	9.86	
1984	11.81	6.70	15.20	0
1985	24.16	10.18	11.97	0.0014
1986	7.99	5.81	11.87	0.19
1987	9.20	5.31	10.82	0.94
1988	7.90	8.45	11.62	1.13
1989	17.38	3.97	12.33	1.32
1990	4.93	2.03	14.86	1.81
1991	8.94	3.94	10.83	0.95
1992	19.59	10.28	8.53	1.11
1993	69.03	36.91	9.87	1.26
1994	7.37	3.29	11.19	2.75
1995	17.80	14.94	10.47	3.14
1996	7.77	2.51	10.41	4.01
1997	6.67	2.75	11.93	5.31
1998	4.87	8.00	…	4.05
1999	4.97	2.82	…	5.84
2000	3.63	1.91	…	8.32
2001	0.11	1.25	…	6.24
2002	…	…	…	8.22

had distinguishing conservative ion characteristics (Fig. 25). CAP water was calcium and sulfate-dominated. Verde River water was low in chloride, making sulfate to chloride ratios high, and sodium and calcium were low and comparable to each other, creating ratios centered around 1. NaCl dominated Salt River water. Almost half of the variation in cation ratios for the Verde River was explained by discharge, indicating that Na and Ca did not behave similarly during flood events. Discharge did not explain any of the variation in SO_4^{2-}/Cl^- ratios on the Verde River, or Salt River ion ratios. Temporal patterns in cation/anion ratios were synchronous on the Salt River, with decreasing ratios since 1980.

SO_4^{2-}/Cl^- ratios below the city were slightly higher than Salt River values but much lower than CAP canal and Verde River ratios, and Ca^{2+}/Na^+ ratios were comparable to Salt River values (Fig. 26). Variability in ion ratios was lower downstream of the city, on average, although the CAP canal data had the lowest CV of all sites upstream or downstream. At both of the two downstream sites, there was an annual pattern of summer maxima in SO_4^{2-}/Cl^- ratios. Inter-annual changes in source waters were undetected despite the dramatic increase in the contribution from Colorado River water since 1985 and the significant decline in ratios in the Salt River (Table 9). Temporal variation in these ratios at the downstream sites was not related to changes in discharge; however, concentrations of each ion were (see above).

Biologically reactive ions downstream of the city were also evaluated as a function of upstream chemistry. TDN concentrations at the Salt River downstream of the city (site 4, Fig. 20) were predicted from upstream TDN ($p<0.05$, $r^2=0.36$). At this same

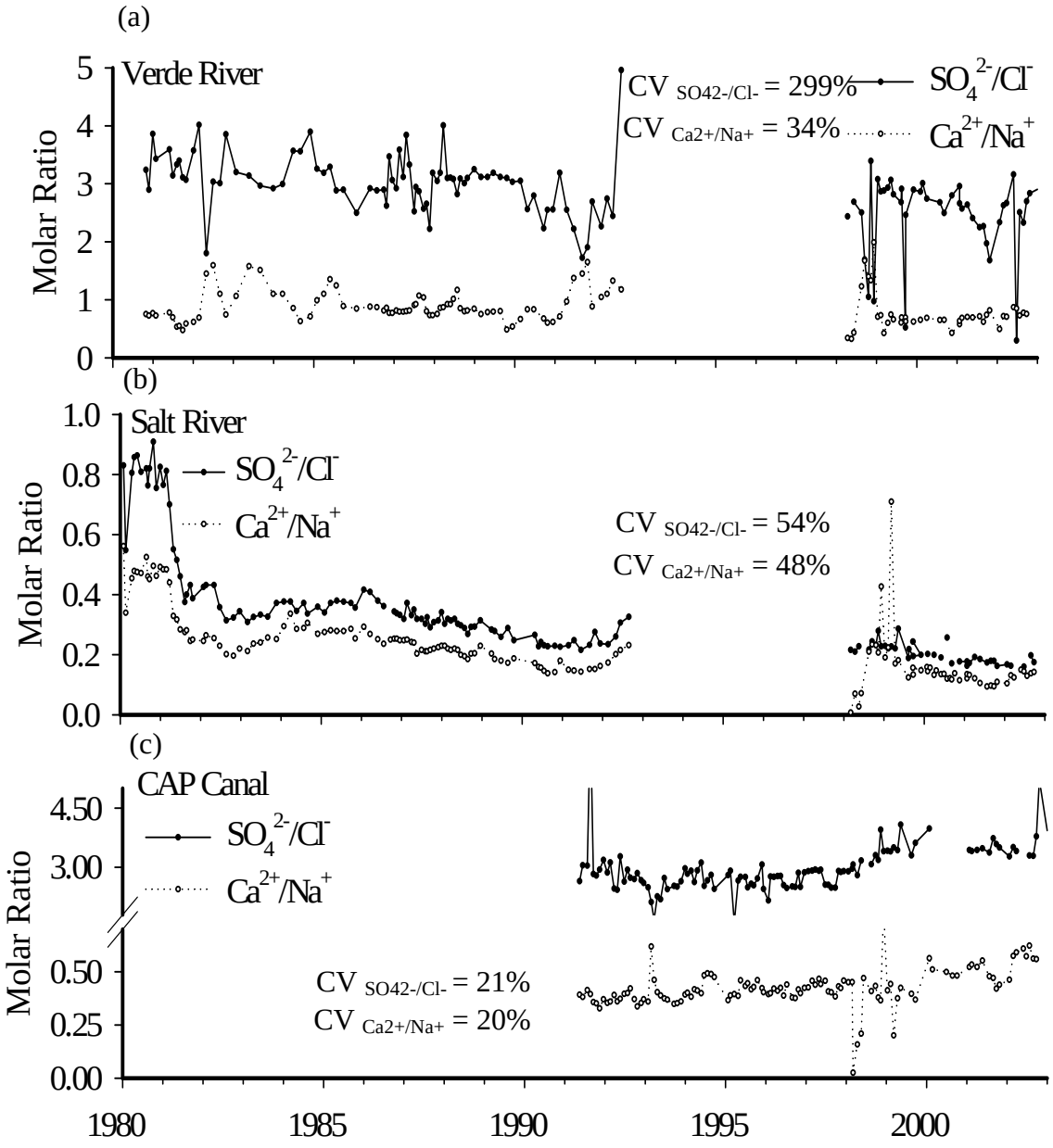

FIG. 25. SO_4^{2-}/Cl^- and Ca^{2+}/Na^+ molar ratios plotted over time for the three sites upstream of the city, the (a) Verde River (site 1b, Fig. 1), (b) the Salt River (2b, Fig. 1) and (c) the CAP Canal (site 3, Fig. 1). CV is the coefficient of variation for the raw data used to generate averages.

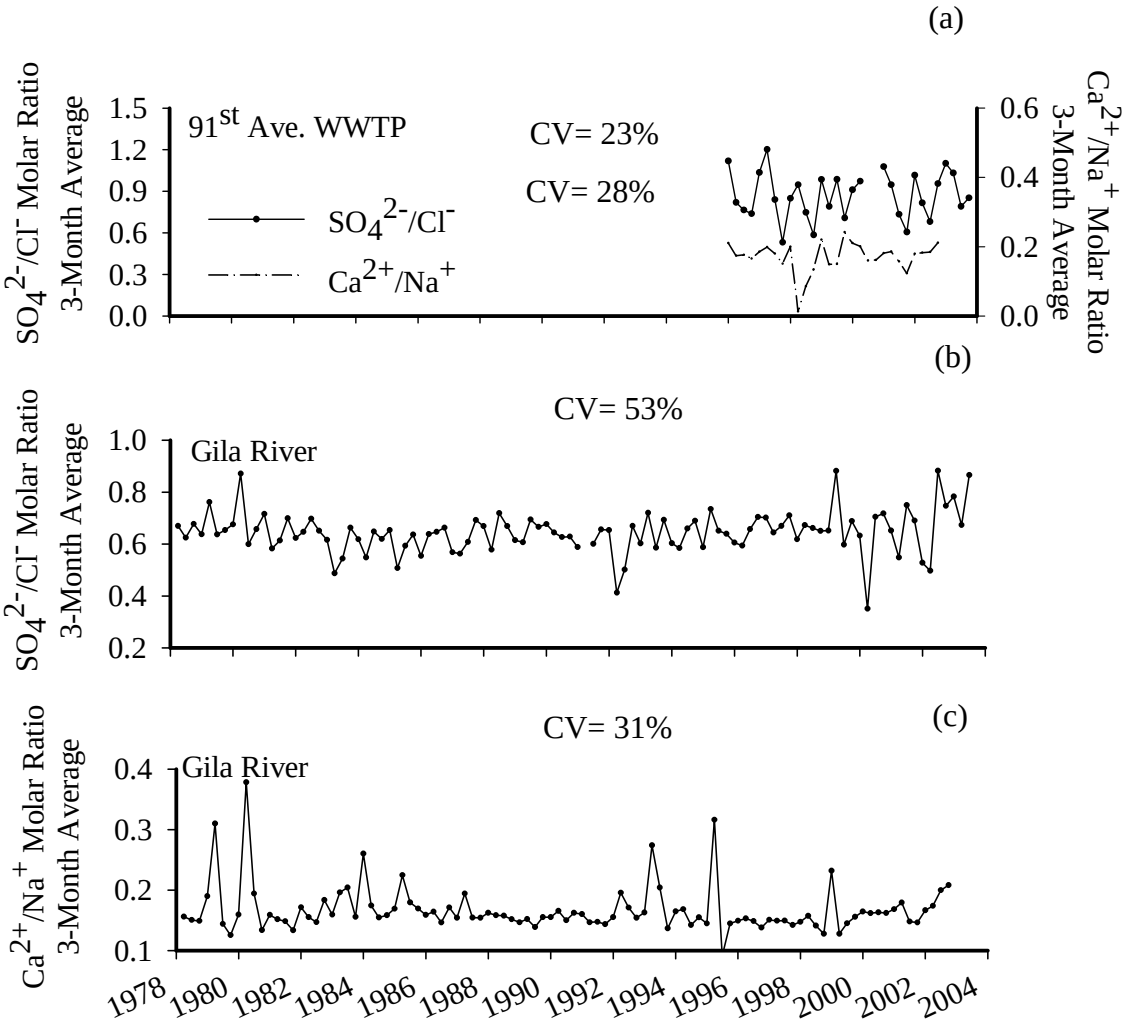

FIG. 26. 3-month averages of SO_4^{2-}/Cl^- and Ca^{2+}/Na^+ molar ratios plotted over time for the (a) Salt River downstream of the city, (site 4, Fig. 1) and (b) and (c) the Gila River (site 5, Fig. 1). CV is the coefficient of variation for the raw data used to generate averages.

site, upstream chemistry did not explain TDP, DOC, or Cl concentrations. Calcium at this site was correlated with CAP canal concentrations, Mg^{+} and SO_4^{2-} ions were correlated with Verde River concentrations, Na^{+} was explained by concentrations on theSalt River, and K^{+} was correlated with both Salt and Verde concentrations.

The Gila River site (site 5) had very different temporal patterns due to the extensive groundwater additions that occurred along the flowpath from site 4 to site 5. Pumping of groundwater to supplement river discharge was highest in the summer; therefore, nutrients and salts exhibited annual maxima in the summer months. However, above the annual pattern there was a significant negative relationship between TDN and time on the Gila River starting in 1986 ($p<0.0001$, $r^2=0.39$) (Fig. 27). This drop in concentration coupled with the reduction in water export during drier years created a temporal trend of decreasing flux of N from the city (Fig. 28). TDP and conservative ions (Na shown as example) also exhibited a decreasing trend in flux at the Gila River site downstream of the city (Fig. 28). The chemistry at Site 5 is important, because export of materials from the city to downstream recipient systems occurs here.

DISCUSSION

The first stated objective of this research was to evaluate the influence of dams on water chemistry entering the urban ecosystem. Dams can be considered part of the urban infrastructure, as they are often constructed to ensure water supply for a metropolitan area. In this paper we separate dam effects from city effects, because the maintenance and operation of the reservoirs does not include human-mediated chemical additions as

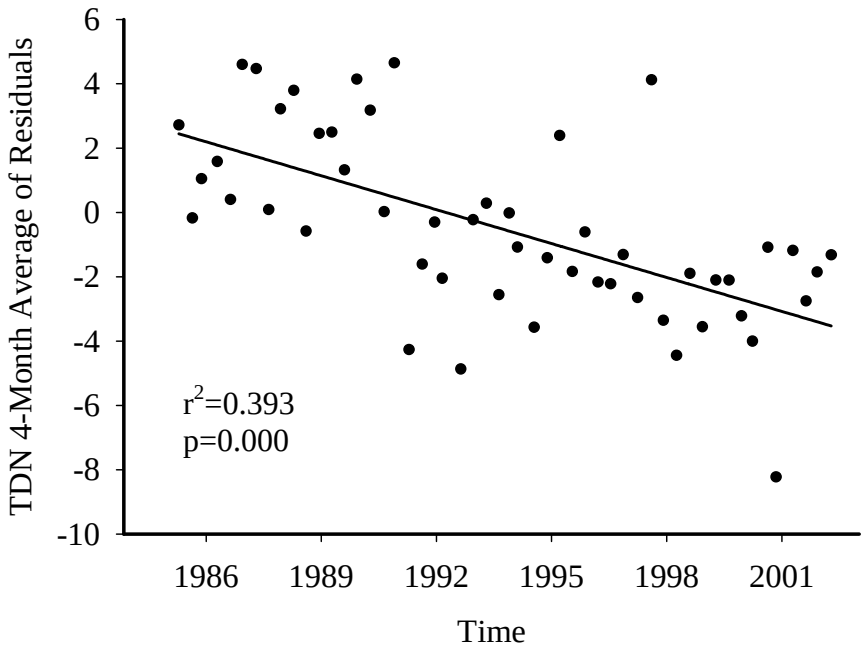

FIG. 27. Gila River TDN concentrations vs. time. The residuals of the regression of TDN vs. discharge at the site were averaged over 4-month increments and then used in this regression analysis.

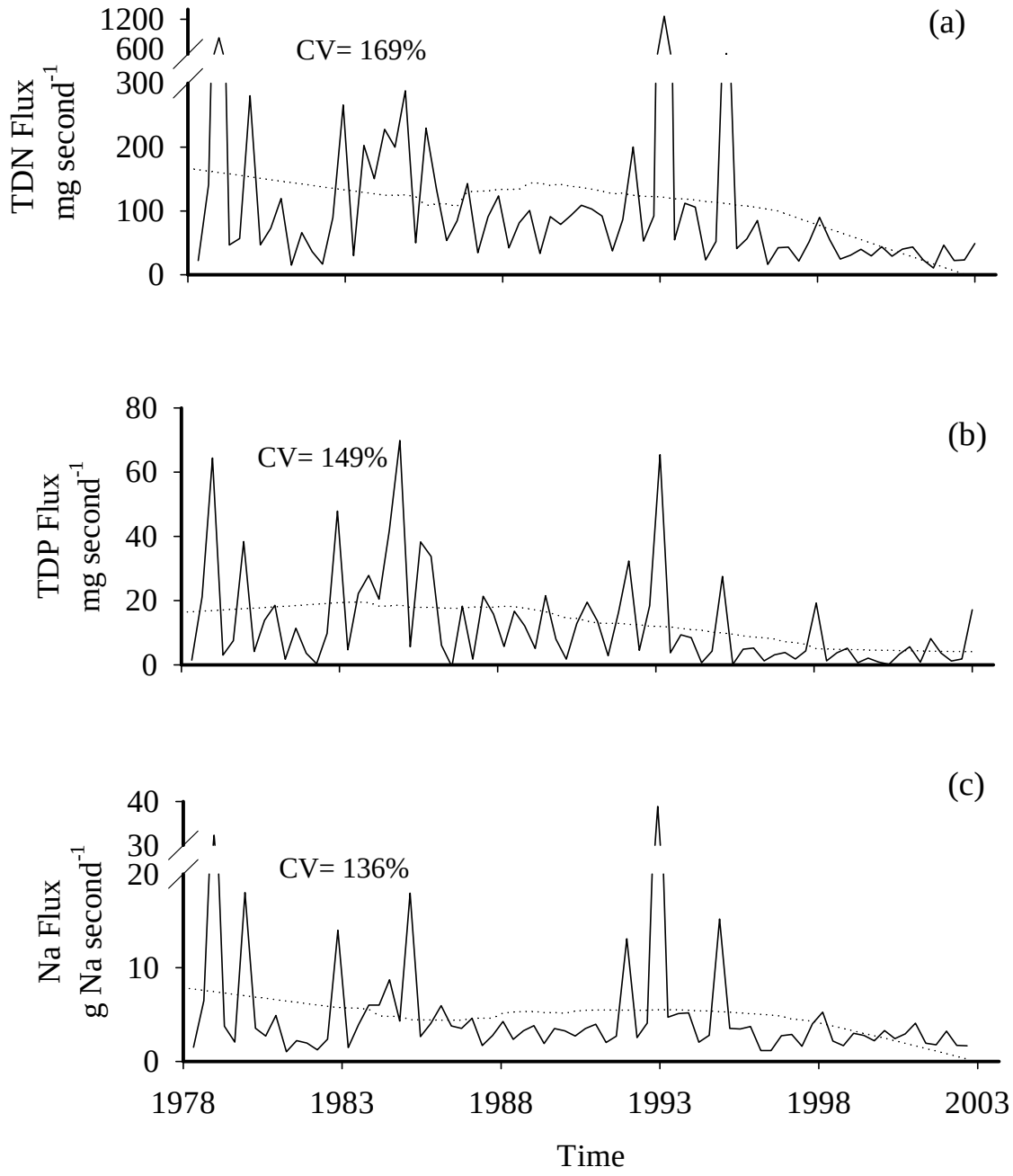

FIG. 28. Fluxes in (a) TDN, (b) TDP, and (c) Na on the Gila River vs. time. Data were averaged over 4-month increments and then smoothed with a 6-month moving average (solid line) and a 2-year moving average (dotted line).

are often found in cities. For the Phoenix metropolitan area, the dams upstream of the city altered the flux and concentrations of dissolved constituents by reducing downstream discharge variability, low flow discharge, and the variability of several chemical constituents. While other work has found similar hydrologic effects in other ecosystems, the importance of these changes to water chemistry in a downstream metropolitan area has not been extensively discussed in the literature (Parks and Baker 1997). The presence of dams upstream of the city dampened the variability and stochastic nature of water chemistry in the two rivers entering the city. For example, the Salt and Verde rivers are the primary sources of drinking water for the city. Therefore, the increase in C and N loads, as well as the amelioration of salt loading, could have important consequences for water treatment (Nguyen et al. 2002).

The second research objective was to identify how patterns in water chemistry upstream versus downstream of the city have changed, and the possible implications these changes might have for biogeochemical cycling. The Phoenix metropolitan area routes water through hundreds of urban flowpaths, including canals, pipes, and modified stream channels. These flowpaths coalesce downstream, but with a substantial reduction in water volume (<10% of the original amount (Fig. 20)). Climatic variability in the desert southwest has encouraged extraordinary measures for reusing and retaining water for irrigation of lawns, crops, and as a drinking water source, which eventually leads to evaporation of the water. Therefore, the city is very good at retaining water, particularly during extended drought periods (decades-long). This manipulation of water concentrates the dissolved materials. Thus downstream river water concentrations were

much higher than those found upstream of the city (Table 7). Water retention within the city was higher than the retention of salts, DOC, TDN, TP, indicating that these constituents accumulated in the water as it moved through the city.

These accumulated constituents are most likely from three sources. Each of these sources represents a unique link between the terrestrial and aquatic components of the urban ecosystem. First, urban surfaces experience high rates of atmospheric deposition of N and C. Therefore, runoff during rain events may have supplied very high nutrient concentrations to local waterways (Hope et al. in press). However, floodwaters upstream of the city were a source of N, while below the city concentrations of N dropped during floods and variation in C and P were not related to flooding. This represents a shift in the dominant mechanisms influencing nutrient concentrations downstream of the city as compared to upstream. Floods no longer serve as a primary source of biologically reactive ions as they do in desert stream (Grimm and Fisher 1992, Belnap et al. in press). Therefore, the importance of the climate regime on annual or seasonal time scales is reduced in the city.

A second source of dissolved material from the urban ecosystem is groundwater. The use of fertilizers and the evaporation of water during irrigation have elevated nutrient and salt concentrations in local groundwaters. Seasonal usage of groundwater to augment surface flows increased constituent concentrations. Our analysis of temporal variation in conservative elements confirmed that the source was most likely regulated and unregulated groundwater that was generating baseflow at sites both upstream and downstream of the city. In fact, upstream chemistry explained a large percentage of the

variation in chemistry at the downstream site just below the WWTP. And, although we do not have records of groundwater pumping before 1980, extensive groundwater usage most likely explains the high pre-1978 ion concentrations found at the Gila River site. Recent work along the flowpath between the two downstream sites supports the suggestion that groundwater pumping generated seasonal peaks in N, P, and salts seen in the time series data on the Gila River (Edmonds and Grimm, in preparation).

The third source of dissolved material is generated from the disposal of human food and waste. Human activity creates highly concentrated WWTP effluent, which is released into the river system. DOC and nitrate concentrations are typically high in effluent, and the streams downstream of the Phoenix metropolitan area receive significant inputs from the treatment plants. Of the three hypothesized source, the second two seem to be most important, suggesting that sources of C and nutrients to the urban stream ecosystem have shifted. Human activity and decision making has assumed primary control over variation in stream-water chemistry. This control was more pronounced during extremely dry climatic conditions, establishing a feedback between environmental change and ecosystem engineering by humans.

The third research objective was to link changes in urban ecosystem management or structure with changes in downstream-water chemistry. One way in which human activity could create temporal variability in water chemistry would be through variation in the mixing of different water sources at the upstream edge of the city. Yet, variation in upstream-water sources and their associated patterns in water chemistry had little relevance to the chemistry of water exported from the city. The significant increases in

contributions of Colorado River water, as well as the decline in ion ratios in the Salt River at site 2b, were not reflected in the long-term trends in ion ratios at the Gila River site. Therefore, there was no "signal" in the downstream-water chemistry as a result of the changes in water sources. There was a decline in nitrogen concentrations and loads, however, in the water exported from the city, suggesting a change in the functioning of the urban ecosystem. This decline coincides with the increase in the use of Colorado River water, but is most likely due to a reduction in N loads from the WWTP when tertiary treatment began in 1997. The pattern of reduced export was also found for P and conservative ions, suggesting that these declines are most likely a combination of the current drought conditions and greater awareness of water quality issues by city managers.

Patterns in upstream-downstream-water chemistry are related to the functioning of the Phoenix metropolitan area as a whole. Stream biogeochemical cycling has been significantly altered by the presence of this urban center. The city is exporting more biologically reactive ions than enter and retaining conservative ions. Climatic variability has a strong influence on urban water chemistry on the decadal scale, but less of an effect at shorter time periods. This work suggests that decisions regarding groundwater usage will feedback on chemistry patterns of water leaving the city. Therefore, a significant reduction in nutrients and salt concentrations should result as Phoenix begins to reduce agricultural activity and increase residential development in its place.

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CHAPTER 3: ABIOTIC AND BIOTIC CONTROLS OF ORGANIC MATTER CYCLING IN AN AGRO-URBAN WATERWAY

ABSTRACT

Cities are gaining attention as ecosystems well suited for testing ecological theory. Urbanization often alters the physical, chemical, and biological structure of aquatic ecosystems embedded within them. Our work focused on patterns in dissolved organic carbon (DOC) along an urban flowpath in Phoenix, AZ. DOC is an important source of carbon for microbial community respiration, and its presence in the water column influences contaminant transport. Recent work has emphasized the importance of DOC quality (defined here as chemical complexity) in influencing microbial activity. We documented longitudinal changes in DOC concentrations and chemical complexity (measured as specific ultraviolet absorbance at 254 nm- SUVA) along a 67-km flowpath dominated by wastewater treatment effluent. SUVA is a measure of carbon double bonds associated with aromatic organic compounds. DOC concentrations declined by an average 64%, and chemical complexity increased substantially. We posed 4 main hypotheses to explain these changes in downstream water chemistry; including hydrologic dilution, microbial decomposition, abiotic adsorption to suspended sediments, and UV photodegradation.

Our data most strongly supported predictions from the dilution hypothesis regarding the decline in DOC concentrations, but changes in DOC chemical complexity were attributed to both hydrologic additions and microbial respiration. Patterns in aerobic and anaerobic respiration rates supported the suggestion that DOC at the head of

the flowpath was higher quality (lower SUVA) than DOC found downstream. Temporal variability in water chemistry patterns was low, and reestablishment of baseflow water chemistry patterns following a flood occurred more quickly than in non-urban desert streams. Surface-subsurface water linkages were important but altered from non-urban streams, because deep groundwater was used to augment flows. The importance of abiotic mechanisms of DOC retention in this urban flowpath was a function of human-decision making and engineering related to water management in the area.

INTRODUCTION

Urban ecosystems are of interest to ecologists not only because they are home to almost half of the world's human population, but also because they provide a new arena for testing ecological theory (Grimm et al. 2000). Part of the urban landscape is comprised of aquatic ecosystems, which provide recreational opportunities for humans and habitat for animals, while also receiving higher loadings of inorganic and organic compounds than in non-urban areas (Mulholland et al. 1997, Muller et al. 1998, Senn and Hemond 2002). In particular, urban streams (defined here as a stream whose physical form or chemical composition has been, and is currently being, significantly altered by human activity from densely populated areas) are of interest because they drain the urban land area,. Therefore they are one transport vector for materials moving from a city to downstream recipient ecosystems.

It is important to consider whether the mechanisms influencing material cycling in urban streams are the same as those found in non-urban ecosystems. Paul and Meyer (2001) reviewed the current state of knowledge regarding changes in physical, chemical,

and biological attributes a stream may experience due to urbanization in the catchment. Those relevant to this study include changes in hydrograph behavior, channel geomorphology, nutrient and salt loading, microbial community structure and function, and nutrient and organic matter retention. The character of the changes reviewed by Paul and Meyer (2001) will be a function of the ecosystem in which the city is embedded, and the pattern of development the city follows. For example, cities in colder climates where salt is frequently applied to the roads to inhibit snow accumulation will have aquatic ecosystems with different chloride dynamics than cities where salting is unnecessary. Grimm et al. (2004) suggest five key characteristics of arid-land streams that are likely to be strongly modified in urban areas: flood disturbance, nutrient limitation, surface-groundwater interactions, land-water interactions, and landscape hot spots of nutrient retention. The biogeochemical implications of these types of alterations in urban ecosystems can be inferred from published work, but remain essentially unmeasured.

There is a large body of work examining the influence of cities on stream nutrient concentrations, but almost no published literature on the effects of urbanization on dissolved organic carbon (Westerhoff and Anning 2000). Many human activities result in export of N and P to local waterways; including agriculture, lawn fertilization, sewage disposal or storage, and atmospheric deposition of automobile emissions (Perakis and Hedin 2002, Baker et al. 2001, Faerge et al. 2001). But our understanding of the influence of human activity on organic carbon cycling in streams is relatively unexplored (Hope et al. 1994, David et al. 1999, Drewes and Fox 2000, Westerhoff and Anning 2000, Hyer et al. 2001). DOC is one of the primary sources of carbon fueling microbial

decomposition and respiration in aquatic ecosystems; therefore, nutrient cycling is often closely tied to DOC consumption (Findlay 2003, Kaplan and Bott 1982, Sobczak 1999). The quality of DOC, not simply quantity, is an important regulator of microbial activity in many disparate ecosystems (Craft et al. 2002, Baker et al. 1999, Vitousek and Hobbie 2000, Dahm et al. 2003, Pomeroy et al. 2000, Hopkinson et al. 1998). Therefore, mapping the cycling of DOC through an ecosystem also requires an understanding of the quality (measured here as chemical complexity) of DOC and the factors influencing its spatial and temporal variation. Complexity was measured using SUVA, which reflects the aromaticity of the sample.

Our overarching goal was to critically evaluate what processes important to DOC cycling might be lost or changed when streams are altered through human activity, by explaining longitudinal patterns in DOC concentrations in an agro-urban waterway. If we understand these changes as they relate to the cycling of carbon through the ecosystem, then we gain insight into streams in general and begin to be able to predict the dominant mechanisms of DOC retention (defined here as a removal of DOC from the water column) in altered arid and semi-arid land streams. Working in an urban waterway that exhibits significant changes in water chemistry provides an opportunity to explore how modifications to stream geomorphology and hydrologic flowpaths might influence nutrient cycling and retention in an important component of the urban landscape. Understanding mechanisms explaining downstream change in DOC is also important for managers who want to reduce export of excess materials that might stimulate pathogenic

or nuisance microbial populations in downstream recipient systems, or who hope to use the water for crop irrigation and/or human consumption (Pinney et al. 2000).

This study focuses on an urban waterway that represents the residual flow of the Salt and Gila Rivers, two large desert rivers that are tributaries of the Colorado River, after substantial modifications within the Phoenix metropolitan area of central Arizona. The waterway, or flowpath, originates as outflow from a tertiary wastewater treatment plant (Fig. 29) and terminates 67 km downstream at the hydrologic output for the lower Gila River in Maricopa County, AZ. Monthly sampling of water along this flowpath for 1.5 years by the Central Arizona- Phoenix Long Term Ecological Research Project (CAP LTER), revealed that concentrations of dissolved organic carbon (DOC) decreased by an average of 50% as water flowed downstream, while the average chemical complexity of the DOC pool increased (reflected as an increase in specific UV absorbance (SUVA) and a decrease in the fluorometric index (FI), Fig. 30a, b). This longitudinal pattern was a reduction in the organic matter concentrations in water exported to downstream systems and a concomitant reduction in the quality of the organic matter. The specific objective of this study was to test alternative hypotheses (not mutually exclusive) explaining the decline in quantity and quality of streamwater DOC along the urban flowpath, considering the role of geomorphology, hydrology, and in-stream processing. This will enable improved understanding of urban stream function for comparison to the state of knowledge for unregulated streams in non-urban areas.

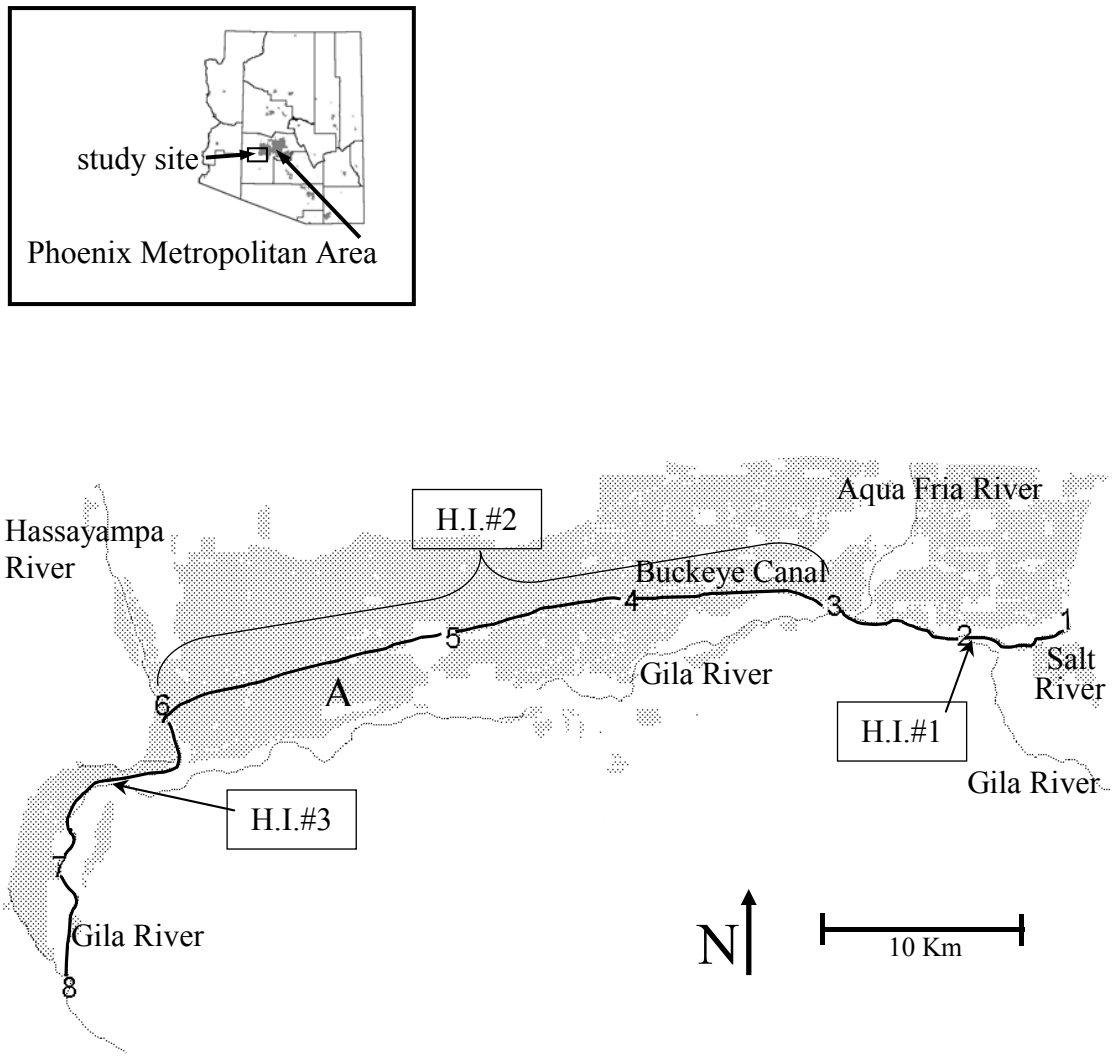

FIG 29. State map of Arizona indicating relative position of study site within Maricopa County. Larger map shows details of the study area. On the lower map, numbers mark locations of sampling points, the dark line indicates the flowpath (water flows from east to west), gray areas are agricultural fields. Hydrologic inputs (H.I) of water are found at three key locations indicated by the arrows. Reach from sampling sites 1 to 3 will be referred to as Reach 1, from sampling sites 3 to 6 is Reach 2, and sampling sites 6 to 8 is Reach 3. Letter A indicates the sampling location used to characterize water moving through the Gila River before it joins the Hassayampa River.

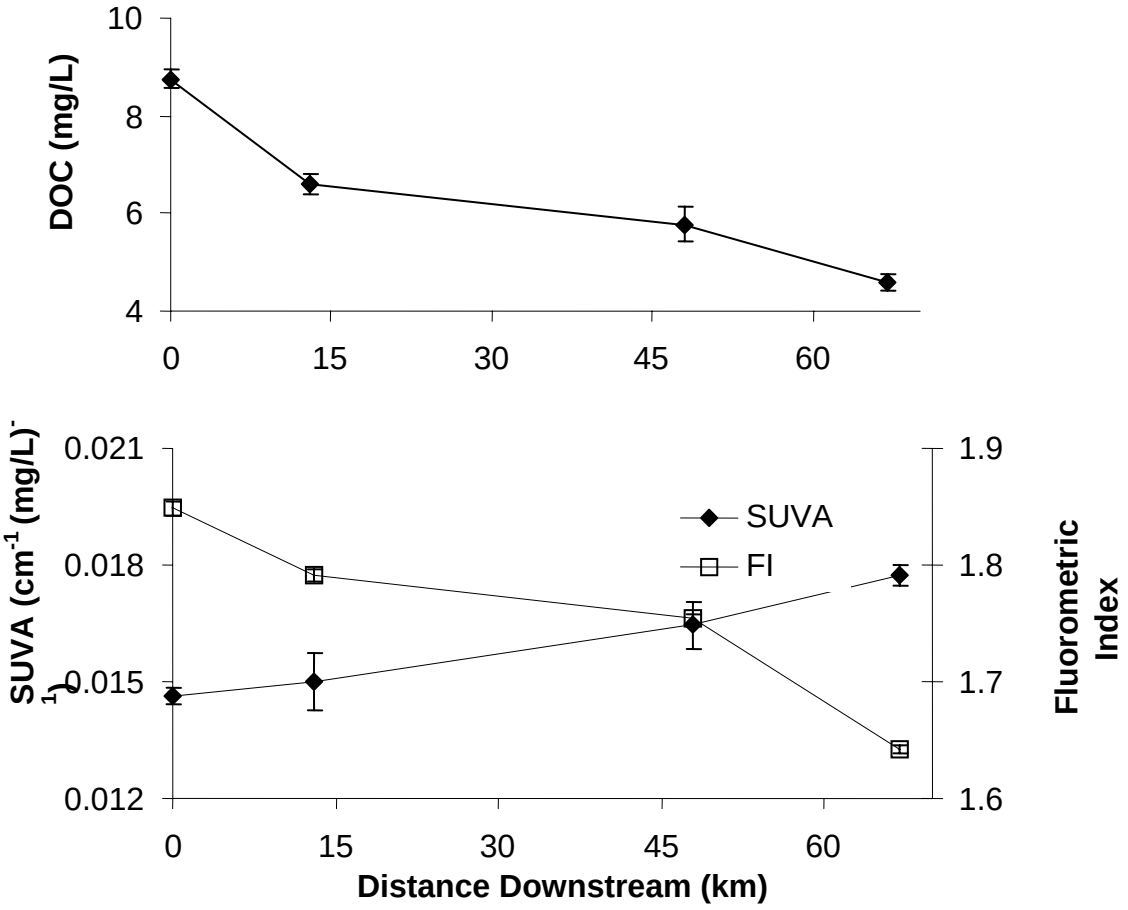

FIG 30. Average water chemistry of monthly samples collected by the CAP LTER from March 1998 – May 1999 along an urban stream flowpath beginning at the outflow of a tertiary wastewater treatment plant, all bars are ±1 SE. (a) dissolved organic carbon (DOC) concentrations, (b) patterns in DOC chemical complexity expressed as specific ultraviolet absorbance (SUVA) and fluorometric index (FI), which are discussed further in methods.

Four main hypotheses potentially answer the overall question of what causes the change in DOC concentration and chemical complexity as water moves downstream? These hypotheses and their resulting predictions are outlined in Table 10. Hypothesis testing was done with a combination of in-stream measurements, mass balance calculations, laboratory measurements, and the use of literature values to determine the most likely explanatory mechanism. In this paper, we develop a conceptual model of each hypothesis, which is then discussed in terms of its importance in this urban ecosystem versus native arid-land streams.

METHODS

Study site

This study was completed in the Sonoran Desert, Arizona, USA. The urban/agricultural waterway begins approximately 30 miles due west of Phoenix, AZ, in an agricultural community that is experiencing rapid urbanization. The population in the area's three incorporated cities increased 30, 102, and 202%, respectively, from 1990-2000 (US Census Bureau 2000), and as many as half a million homes are expected to be constructed in the area over the coming decade (Jackie Meck, personal communication, Buckeye Irrigation District). The 91st Avenue wastewater treatment plant (WWTP) receives approximately 56% of the municipal wastewater generated in the Phoenix metropolitan area (population 3.2 million; US Census Bureau 2000) (Lauver and Baker 2000). Sixty-four per cent of the effluent leaving the treatment plant is discharged directly into the Salt River (Fig. 29, site 1), which then joins the Gila River 5 km

TABLE 10. Summary of hypotheses (not mutually exclusive) and predictions concerning the decline in DOC quantity and quality along the 67-km urban flowpath.

Hypotheses	Predictions
HI: Hydrologic additions of low-DOC, high-complexity waters mixed with existing surface flow *(Dilution Hypothesis)*	P1a: Groundwater inputs, manifested as increases in surface water salt concentrations, will be positively correlated with changes in DOC concentrations and SUVA at different points along the flowpath
	P1b: Sampling dates with no groundwater well pumping into the system will not exhibit the same DOC decline and increase in SUVA
	P1c: Mass-balance calculations of groundwater additions to the surface stream will accurately predict changes in DOC concentrations and SUVA
H2: Microbial community respiration in channel sediments preferentially utilizes low complexity DOC, converting it to CO_2 and leaving higher complexity DOC to be exported by surface water flow *(Microbial Hypothesis)*	P2a: The extent of change in DOC quantity and complexity will be positively correlated with water temperatures due to the well-established temperature dependence of respiration and mineralization
	P2b: Measured sediment respiration rates will be sufficiently large to explain the decrease in DOC concentration in the surface waters
H3: DOC of low complexity adsorbs to suspended particles (*Adsorption Hypothesis*)	P3a: Concentration of total suspended solids will increase along the flowpath
	P3b: Percent organic matter of total suspended solids will increase along the flowpath
	P3c: Laboratory experiments will demonstrate DOC association with sediment particles and an accompanied change in SUVA values
H4: UV oxidation of the DOC changes the quantity and complexity *(UV Hypothesis)*	P4a: UV penetration through the water column can generate sufficiently high oxidation rates at all depths and sites to explain the DOC decline and the changes in chemical complexity
	P4b: Published rates of UV oxidation are sufficiently high as to explain conversion of DOC to CO_2 or to more complex organic matter during the time water spends in transport along the flowpath

downstream of the treatment plant (Fig. 29, site 2). All of this water is then diverted into the Buckeye Canal (Fig. 29, site 3) 7 km downstream from the confluence of the Salt and Gila Rivers (Fig. 29, site 2). The water travels 35 km in the canal before discharging into the dry riverbed of the Hassayampa River (Fig. 29, site 6). Once in the Hassayampa, the water travels 4.5 km back to the Gila River. The final leg (14.5 km) of the flowpath is in the Gila River, where it is then diverted into irrigation canals at a privately owned dam built in 1913 (Fig. 29, site 8). For ease of discussion, the 67-km flowpath has been divided into three reaches (Fig. 29). Reach 1 is the first 13 km of the flowpath (sites 1-3), before the canal begins. Reach 2 is the 35 km of the canal ending where it empties into the Hassayampa River (sites 3-6), and Reach 3 is the last 19 km of flow in the Hassayampa and Gila River (sites 6-8).

Groundwater wells are located throughout the area for water monitoring purposes and to supplement irrigation waters. Thirty-four wells are located along the Buckeye Canal to supplement water supplies during hot and/or dry periods (usually April to October). Ten drainage wells, located 1-2 km due north of the Gila River bed downstream of the Buckeye canal diversion, pump water year round into the dry Gila River bed to keep groundwater levels below the rooting zone of the crops in the area. This water creates some surface flow in the Gila River, which rejoins the flowpath at the confluence of the Hassayampa and Gila rivers. Because the water table is so close to the surface in this area of the Gila River watershed, both unmanaged and managed inputs of groundwater play a role in creating the hydrologic template for the ecosystem.

Channel width along the 67-km flowpath varied from 5 to 20 m, and channel depth ranged between 0.2 and 1.7 m. Riparian vegetation changed longitudinally both in composition and abundance. In Reach 1, to the confluence of the Salt and Gila River, the riparian plant community consisted of the exotic woody species *Tamarix ramosissima* and *T. chinensis* (common names: saltcedar or Tamarisk). The clay-lined canal (Reach 2) had no vegetation, while the Hassayampa River had a riparian strip of *T. spp.* approximately 2 m wide. The Gila River active channel was approximately 200-600 m wide, but the surface stream only occupied 5 to 20 m, and the remaining width was filled with *Tamarix*. Algal standing stock was moderate along Reach 1, but once water moved into the canal system chlorophyll a dropped to values that are low for arid-land streams, reflecting the high turbidity and velocity of the urban flowpath. Correspondingly, PAR irradiance reached 40-65% of surface value at a depth of only 20 cm at the three most downstream sites (Table 11). Nutrient concentrations in the ecosystem were very high. Average nitrate concentrations in the surface waters were consistently above 2 mg/L NO_3^--N and reached as high as 8 mg/L by the end of the flowpath, while phosphate concentrations ranged from 0.5-2.5 mg/L PO_4^{3-}-P.

The total amount of water moving through the system was dependent on irrigation demands, groundwater well pumping, diurnal flow variations from wastewater treatment plant discharge, and whether or not flooding had occurred recently. During extremely hot periods when irrigation needs were high, the last site on the Gila River contained only slow-moving pools of surface water, as most of the system's water was diverted into concrete canals upstream from the sampling location. Summer monsoon rains were

TABLE 11**.** Values are averages of all dates, VHG and DO were taken at a sediment depth interval of 10-15 cm, $^{+}$ Values in parentheses are standard errors followed by the number of samples (n). NA indicates parameter is not applicable at a site.

Distance Downstream (km)	Site Description	VHG (cm/cm)	DO (mg/L) (Temp, °C)	PAR at 20 cm depth (as % of surface)	TDS^{+} (mg/L)	TSS^{+} (mg/L)	%OM in TSS^{+}	TDN^{+} (mg/L)	TDP^{+} (mg/L)	N:P of DOM^{+}
0.01	Salt river bed	Data not available	Data not available	Data not available	0.97 (0.03, 5)	14 (7, 5)	33 (26, 3)	4.8 (0.6, 4)	1.83 (0.39, 4)	6 (3, 3)
5	Gila River below confluence with Salt	+0.27, -0.04, +0.05 -1.44	4.65 (30) 2.95 (30.6) 4.11 (30.2)	Data not available	1.29 (0.04, 9)	26 (4, 9)	24 (3, 8)	8.0 (1.0, 8)	2.33 (0.28, 8)	8 (4, 6)
13	Irrigation Canal	NA	NA	Data not available	1.34 (0.05, 3)	93 (52, 3)	15 (3, 3)	5.2 (0.9, 3)	1.76 (0.44, 4)	8 (4, 2)
20	Irrigation Canal	NA	NA	Data not available	1.74 (0.12, 11)	92 (17, 11)	10 (1, 10)	8.1 (0.4, 11)	1.61 (0.12, 11)	21 (10, 9)
30	Irrigation Canal	NA	NA	Data not available	1.88 (0.16, 11)	103 (21, 11)	10 (1, 10)	9.5 (0.8, 11)	1.49 (0.19, 11)	31 (16, 8)
48	Hassayampa River bed	+0.27	12.1 (22.7) 12.5 (23.7) 8.4 (20.6)	39	1.99 (0.17, 11)	72 (8, 11)	11 (1, 10)	11.1 (1.2, 11)	1.32 (0.21, 10)	28 (12, 9)
59	Gila River bed	+0.35	1.6 (21.2) 5.1 (21.7) 9.1 (21.0)	54	2.89 (0.15. 9)	95 (15, 9)	11 (1, 8)	10.4 (0.9, 9)	0.99 (0.24, 8)	129 (62, 6)
67	Gila River bed	-0.18, +0.44	8.0 (20.3) 11.3 (16.0) 11.1 (16)	65	2.90 (0.15, 12)	70 (11, 11)	14 (1, 10)	9.7 (0.5, 11)	0.87 (0.22, 9)	41 (27, 7)

spatially patchy and arrived in short, but intense, rain bursts. Summer storms were unlikely to produce flooding in the system, whereas winter storms, with more protracted but less intense rains, covered a large spatial extent and created flooding along the flowpath.

Sample collection and analysis

We sampled surface water at roughly 10-km intervals along the flowpath three times (March, June, Oct) in 2000, approximately every 6 weeks during 2001, and immediately following two winter floods in 2001, to better explore the preliminary patterns found through the CAP LTER sampling. The sampling protocol followed one developed originally by the USGS and modified by the CAP LTER (http://caplter.asu.edu/datacatalog/dataresearch.asp). Samples for total inorganic carbon and pH were collected in the field with no headspace and transported to the laboratory for analysis. Conductivity and water temperature were measured at each site using an Orion field meter. A depth-integrated, channel-wide sample was collected at each site into a 3-L nalgene bottle, transported to the laboratory on ice, and then split into 10 subsamples. Three subsamples were filtered through a Whatman GF/F ashed filter, and the filtrate was used for DOC analysis using high-temperature combustion on a Shimadzu TOC-5000 carbon analyzer. Materials remaining on the GF/F filter were used for ash-free dry mass determination and elemental analysis using a Perkin-Elmer 2400 Series II CHNS/O analyzer. Three other subsamples were filtered through a membrane filter of porosity 0.45 μm, followed by cation (Ca, Mg, Na, K) analysis using a Varian SpectrAA 400 Flame atomic absorption spectrometer, dissolved nutrient analyses using colorimetric

methods on a LACHAT 'Quick Chem' 8000 flow-injection autoanalyzer, and sulfate analysis using a Dionex 4000i ion chromatograph. The remaining subsamples were filtered through a Whatman GF/F filter and a known volume of filtrate was placed in a pre-weighed glass beaker, dried at 100°C, and reweighed. The difference in mass between beakers before water addition and after evaporation was used to calculate total dissolved solids (TDS).

In addition to quantifying the concentration of DOC in the water, two measures of DOC chemical complexity were used. One was specific ultraviolet absorbance (SUVA), which is the absorbancy at 245 nm of a filtered, acidified water sample, divided by the concentration of DOC in the sample. SUVA is an indicator of the quantity of double-bonded C atoms (unsaturated sp^2-hybridized carbon atoms). An aromatic carbon ring has half of its carbon as C=C, and since most natural organic matter is aromatic, not aliphatic, SUVA is a good measure of the aromaticity of a DOC sample. The second measure used was the fluorometric index. Water samples are excited on a fluorometer at 370 nm and scanned from 400 to 600 nm. The intensity of the scan at 450 nm divided by the intensity at 500 nm is the fluorometric index (FI). McKnight et al. 2001 found that samples with a FI < 1.5 had high-complexity organic material, while a FI value closer to 2.0 came from aquatic systems with low-complexity, algae-dominated, organic matter pools. Interpretation of FI results is patterned after the McKnight et al. (2001) analysis.

Test of hydrologic inputs

To test Hypothesis 1 (Dilution Hypothesis), we intended to characterize the chemistry and quantity of all three major hydrologic inputs (H.I.) along the flowpath.

However, we were not able to sample H.I. #1 (Fig. 1) due to its inaccessibility on private land. For H.I. #2 we acquired information regarding inputs of groundwater from deep wells, as well as the quantity of drainage well water that is routed directly to the Gila River bed, from Buckeye Irrigation District Managers. Well-water chemistry was collected in conjunction with sampling by the Arizona Department of Environmental Quality (summer 2002) and analyzed using the methods described above. Depths of wells were taken from public records filed when the wells were initially installed. H.I. #3 was sampled at location A (Fig. 29).

Test of microbial utilization

To test Hypothesis 2 (Microbial Hypothesis), sediment respiration measurements were made where sediments could be collected. Respiration chambers were constructed from clear plastic pipe (32 cm long, 4.4 cm inside diameter) that was sealed on both ends with rubber stoppers. Fifty percent of the chamber volume was filled with channel hyporheic sediments that were collected from a depth of 2-7 cm below the sediment surface. Sediments to fill chambers were collected by scraping away benthic sediments and algae (top 2 cm of sediments) then coring the next 5 cm of sediments. Five cores were taken in this manner along a transect across the channel, then combined in the laboratory and redistributed to each chamber. The remainder of the chamber volume was then filled with water from the surface, gently inverted three times to allow any air trapped within sediments to escape, and sealed on the ends with rubber stoppers. Sealed chambers were incubated in the dark at 20°C for 4 hours. Sediment dry mass, ash-free dry mass, and particle size distribution were determined for every chamber. Respiration

rates were originally expressed as daily consumption of dissolved oxygen per gram of dry sediment or per m^2 (g O_2 g $sediment^{-1}$ or g O_2 m^{-2} d^{-1}), then converted to a rate per gram of sediment less than 2 mm. Particles over 2 mm in diameter (break between the classification of sand and coarse material) contribute very little to total respiration due to their low surface to volume ratio, but contribute significantly to total sample mass (Brady and Weil 1999). By expressing rates on a per gram of dry sediment less than 2 mm basis, we can eliminate bias due to the presence of large sediment particles when considering patterns in benthic respiration.

To estimate the direction of exchange of stream water with benthic and subsurface sediments, vertical hydrologic gradient between the surface and subsurface at these sites was measured once using mini-piezometers (Grimm 1996). Piezometers (tubes with lateral perforations near the tip) were inserted to a depth of 10-15 cm below the streambed and hydraulic head (cm) was measured on a simple manometer as the difference in water column heights between water columns drawn simultaneously from the piezometer and surface stream. VHG was calculated as the hydraulic head divided by piezometer depth (cm/cm). Positive VGH indicates surface waters upwelling into subsurface sediments, whereas negative VHG indicates surface waters downwelling into subsurface sediments.

Denitrification is a form of anaerobic respiration that might also account for some of the DOC utilization in this N-loaded flowpath. Therefore, denitrification enzyme assays (DEA) were performed in the laboratory in February and June of 2001 using sediment collected at 3-4 sites. Sediment samples were extruded as described above, and

then incubated for 4 hours in Wheaton bottles under anoxic conditions, with (amended) and without (unamended) additions of nitrate and acetate, using the acetylene block method to prevent conversion of N_2O to N_2. Nitrous oxides samples were collected into vacutainer tubes using a double-ended needle, and stored for several weeks for later analysis on a Shimadzu gas chromatograph. As with aerobic respiration rates, the amended DEA values are maximum potential rates, whereas unamended DEA assays more closely reflect ambient rates.

Test of adsorption kinetics

To test Hypothesis 3 (Adsorption Hypothesis), an isotherm was constructed to estimate the adsorptive capacity of the suspended sediment for DOC. Suspended material was collected in the field, concentrated by centrifugation, and washed using nanopure water and 0.01 N NaOH. The sediments were then sterilized by high-temperature drying or autoclaving. Water from the head of the flowpath (outflow from the WWTP) was filtered through a Whatman GF/F filter and 250 ml was added to 0.25 L plastic incubation containers. Triplicate incubations of this water plus varying concentrations of sediment (0, 25, 75, 125, and 175 mg/L) were shaken on a Eberbach 6010 shaker at 1140 rotations per minute for 24 hours in the dark. The water was then filtered and analyzed for DOC and SUVA using the methods described above. Adsorbed DOC was calculated as the difference between pre- and post-incubation concentrations. An additional test was completed to determine the temporal pattern of DOC adsorption, using only 0 and 10 mg/L TSS, and the bottles were sampled at 0, 4, 8, and 14 hours after incubation.

Test of UV transformation

Using literature values of the potential rates of UV transformation of DOC, we estimated the amount of DOC that could be lost and/or altered in complexity based on the residence time of water moving through the waterway. In addition, we approximated UV transmission through the water column at each site using DOC concentrations to calculate UV attenuation coefficients (K_d) from literature models. DOC is the primary factor controlling attenuation of UV-A and UV-B in freshwaters (Morris et al. 1995, Scully et al. 1995).

RESULTS

Changes in Water Chemistry

DOC concentrations decreased downstream along the 67-km flowpath on all sampling dates, but to varying degrees (mean DOC decrease = 64%, range 47-80%). The decline in DOC was gradual and approximately linear through Reach 1 and 2, while the pattern between the last three sites was not consistent through time (Fig. 31). SUVA patterns were less spatially variable than the original LTER dataset suggested, with no increase in SUVA through Reach 1 and part of Reach 2, a slight decline along the last 18 km of canal, and a considerable increase in SUVA through Reach 3 (Fig. 31). An increase in SUVA indicates an increase in the average chemical complexity of the DOC pool, since the measurement is standardized to account for differences in DOC quantity. DOC concentrations and SUVA values were uncorrelated, even though DOC concentration was used in calculating SUVA values ($p=0.643$). The fluorometric index

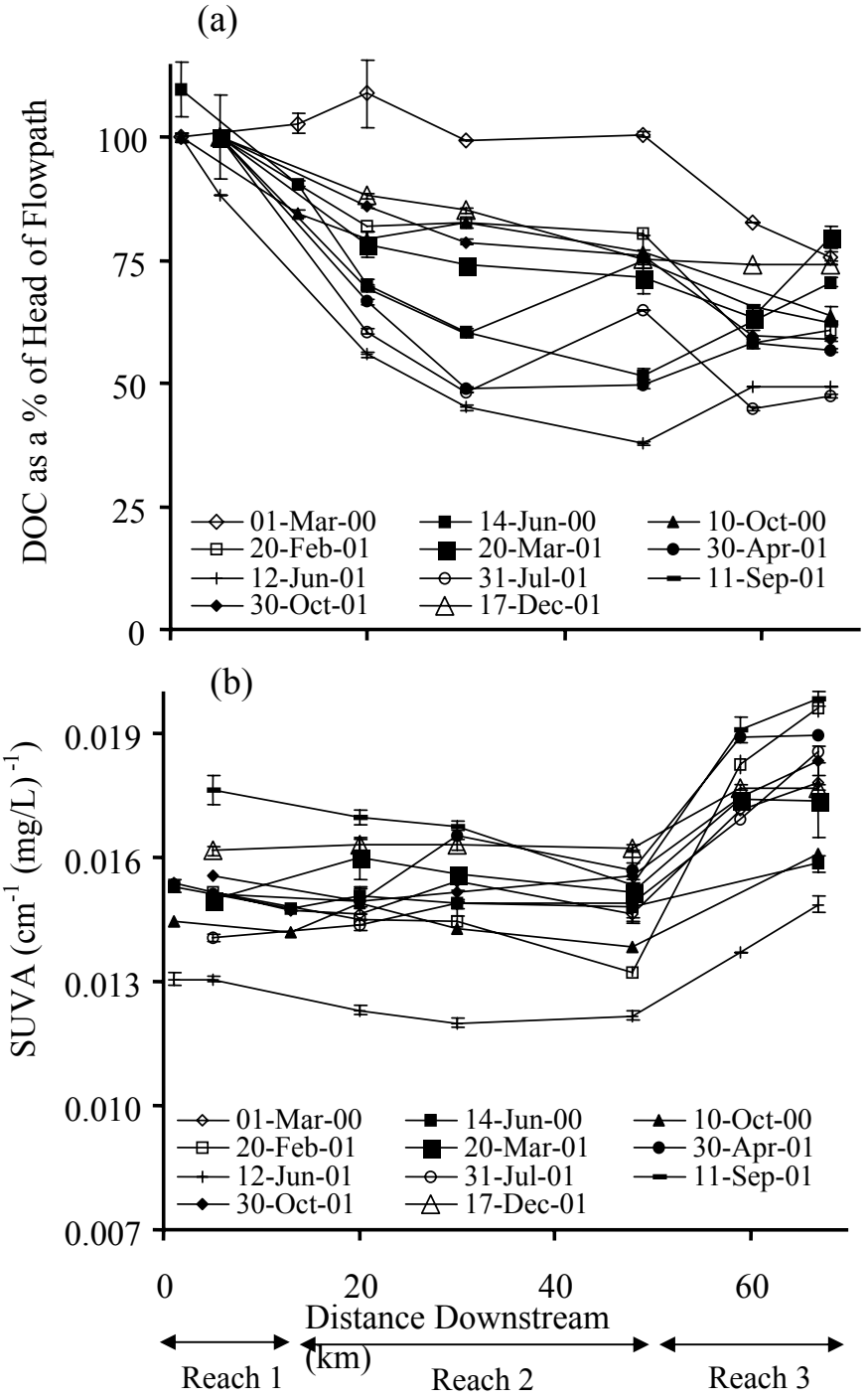

FIG 31. (a) DOC as a percentage of the DOC concentration at the head of the flowpath, and (b) SUVA for each sampling date versus distance downstream from the wastewater treatment plant. Higher SUVA values indicate higher average chemical complexity of the DOC pool. Error bars represent ± SE. Arrows below the x-axis indicate location of the three reaches defined in Fig 1.

(FI) for samples along the flowpath also indicated an increase in chemical complexity, with higher values upstream and lower values at the end of the flowpath (Fig. 32).

In addition to changes in water quality, the DOC flux leaving the system (i.e. DOC concentration X discharge) was lower than the flux at the head of the flowpath, or in other words, there was net positive retention of DOC. The change in the DOC flux through the flowpath (i.e. DOC retention) ranged from an increase of 207 kg C day^{-1} to a decrease of 3,388 kg C day^{-1}. When changes in DOC flux were calculated for each of the three reaches, Reaches 1 and 3 were consistently a source (increase in flux) of DOC, and Reach 2 was where the majority of the DOC retention was occurring on sampling days when retention occurred. We felt it was important to consider both DOC concentrations and fluxes (or loads calculated as total mass lost along a reach), as concentrations are more important to communities associated with stream sediments than the flux, and change in flux (i.e. retention) is important when considering interactions on larger spatial scales and across subsystem boundaries.

Role of hydrologic inputs

The hydrology of this system is complex but requires close examination, because it determines the source of material inputs that may have contributed to the spatial pattern seen in the surface waters (Hypothesis #1). Three large sources of water entered the flowpath at different locations below the wastewater treatment plant (indicated in Fig. 29 and Fig. 33a). The first was shallow groundwater from the Gila River at the Salt-Gila confluence (H.I. #1 in Fig. 1). The second input (H.I #2 in Fig. 1) was from the pumping of 34 groundwater wells distributed along the Buckeye Canal. These wells run as

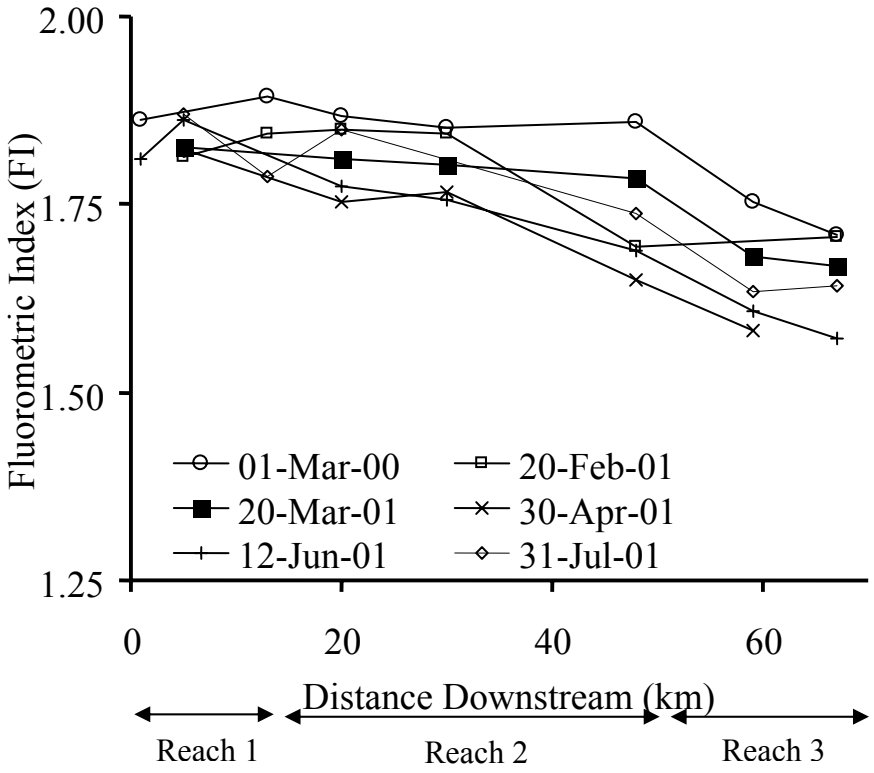

FIG 32**.** Fluorometric index (FI) for each sampling date versus distance downstream from the wastewater treatment plant. Higher FI values indicate lower average chemical complexity of the DOC pool. Error bars represent ± SE. Arrows below the x-axis indicate location of the three reaches defined in Fig 1.

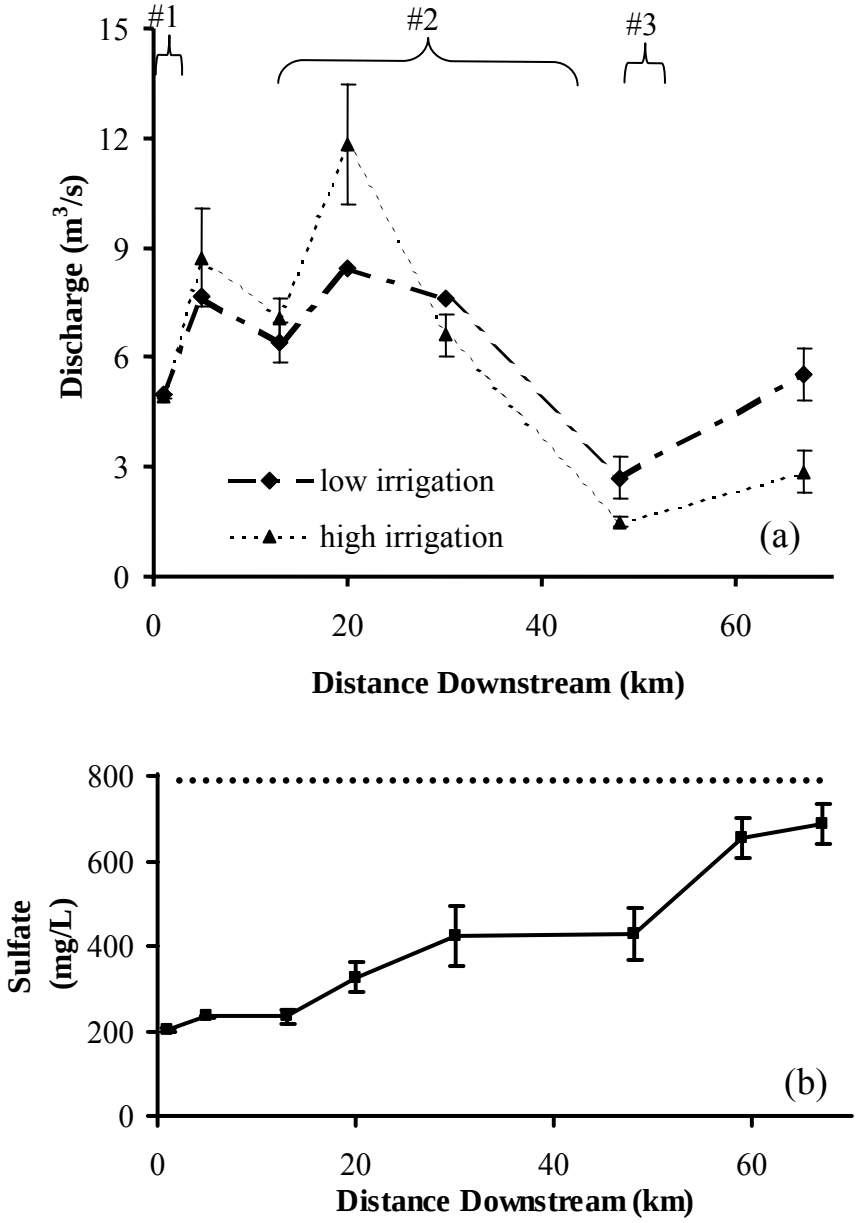

FIG 33**.** a) Average discharge for high water use days and low water use days, error bars represent ± 1 SE. The brackets indicate the location of hydrologic inputs. Input #1 is an input of shallow hyporheic water from the Gila River, #2 is the beginning of the addition of deeper (200-600 ft below surface) groundwater from the regional aquifer, and #3 is a mixture of groundwater and surface water (see text); b) average sulfate concentrations in the surface stream along the flowpath as compared to an average groundwater concentration for this area (dotted line).

needed, and they do not necessarily all run at the same time. The third input was a mixture of water from drainage wells that are pumped directly into the Gila River and natural groundwater discharge (H.I. #3, Fig. 29). Concentrations of SO_4^{2-}-S were very high in ground waters in the area as compared to the wastewater treatment plant outflow; therefore sulfate concentrations were a strong predictor of locations of groundwater addition to surface water (Fig. 33b), supporting P1a (Table 10).

DOC retention along the flowpath was different on days when fewer groundwater wells were pumping, supporting P1b (Table 10; Fig. 34). While there was still a decline in DOC concentrations when only 1-3 deep groundwater wells were pumping, the changes in concentrations along the canal (Reach 2) were insignificant, which is where most of the DOC decline occurred on high-water use days. Instead, the DOC decline was concentrated on low-pumping days in Reach 3, where groundwater from the Gila River surfaced and was joined by the Hassayampa River. Comparison of DOC declines in concentration between the days with and without groundwater pumping finds unregulated groundwater inputs lowered the DOC concentration by 20-35%. This decline was not evident on days with large inputs from deep groundwater well pumping, because the chemistry of these wells dominated the DOC pool.

As a first approximation at quantifying the relationship between DOC concentration and hydrologic inputs, we regressed the change in DOC with several parameters. For Hydrologic Input #1 in Reach 1, there was a consistent decrease in DOC, but no change in SUVA and FI. For Hydrologic Input #2 in Reach 2, there was a strong relationship between the DOC retention and the number of groundwater wells that

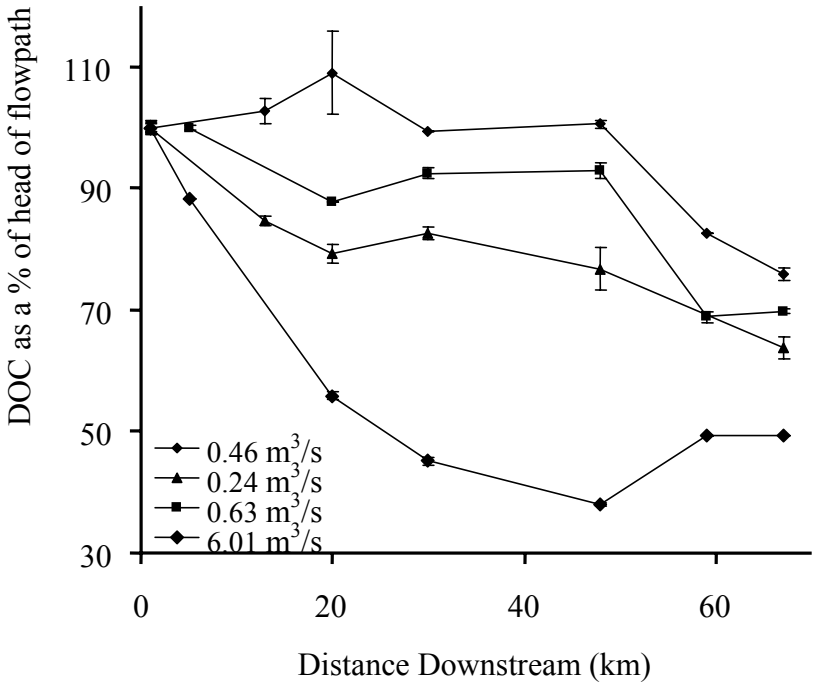

FIG. 34**.** Change in DOC along the flowpath as a percentage of the DOC concentration at the head of the flowpath. Four dates with varying discharge rates from groundwater wells along Reach 2 are shown, with discharge as cubic meters per second (cms) included in legend.

were pumping on any particular day (Fig. 35a). For the third hydrologic input, in Reach 3, an increase in discharge resulted in a proportional drop in DOC concentration (Fig. 35b, inset). At the same time, 60 percent of the increase in SUVA at this juncture was explained by increases in discharge (Fig. 35b).

Given what we know about groundwater DOC concentrations and the chemistry of the ground water that travels parallel to the canal in the Gila River bed, we tested P1c (Table 10) by calculating how much of a decrease in DOC and increase in SUVA was expected due solely to additions of groundwater through the pumping of wells. Unfortunately, we do not know enough about the shallow, unregulated groundwater inputs from the Gila River that enter at the confluence of the Salt and Gila River to use a mass balance approach to determine the predicted DOC concentrations along Reach 1. The percentage decrease along Reach 2 was predicted using mass balance calculations based on known groundwater inputs from the wells adjacent to the canal. The majority of the DOC retention was accounted for, with only 7-25% not explained by groundwater inputs on 8 of the 12 sampling dates (Fig. 36). The degree to which groundwater inputs did or did not explain retention was not correlated with water temperature ($p=0.347$) or the number of groundwater wells that were pumping ($p=0.093$). The expected decrease in DOC due to groundwater discharge alone through Reach 3 underestimated the actual DOC decline by 1-22% on all sampling dates except two. The increase in SUVA as water from the canal was joined by surface water in the Gila River (Hydrologic Input #3 in Reach 3) was underestimated by 4 to 43% for all but 1 of the 12 sampling dates using our known values for Gila River water chemistry and the change in discharge at the

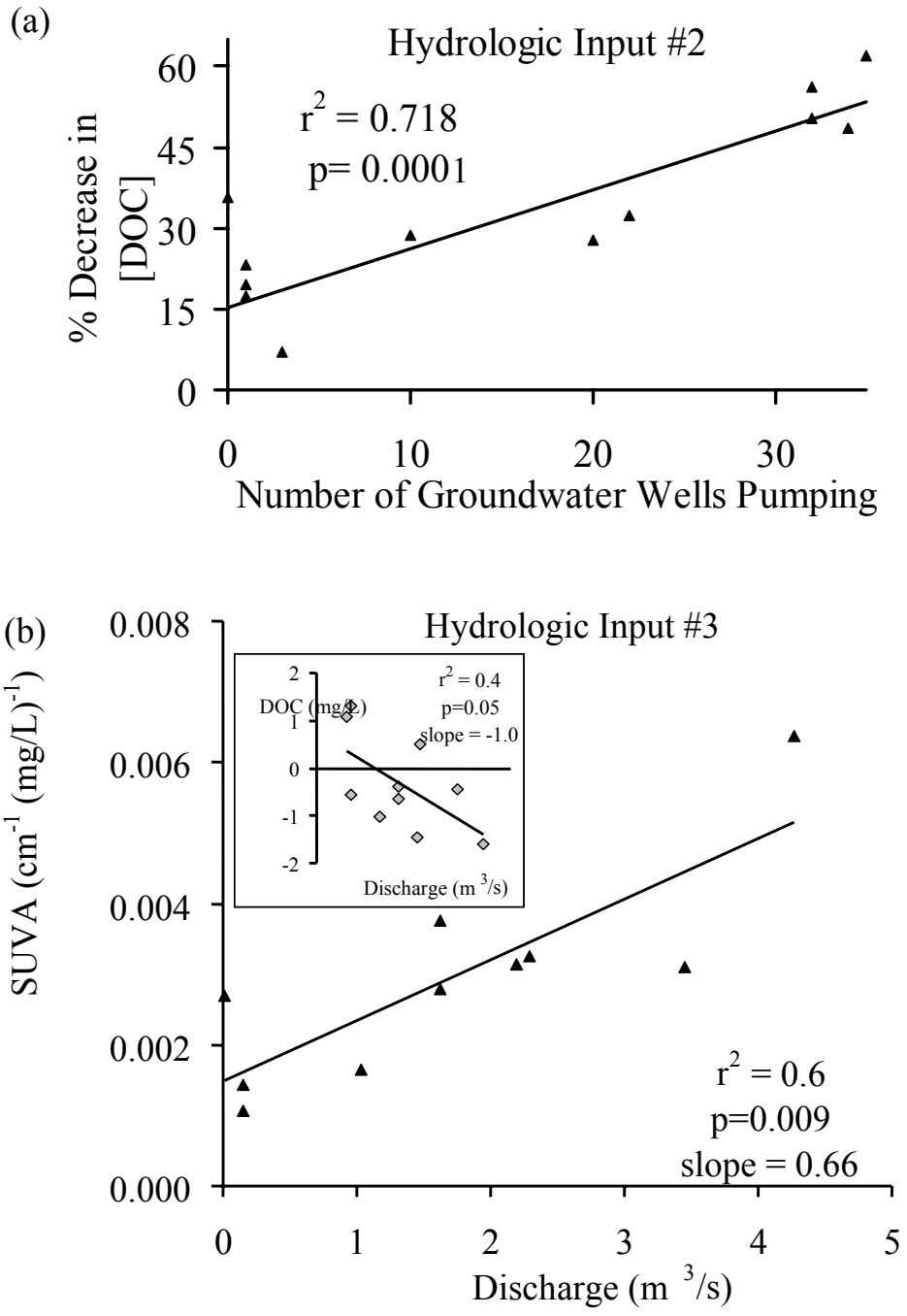

FIG. 35. a) Decrease in DOC through Reach 1 and 2, expressed as a percentage of DOC at head of flowpath vs. the number of groundwater wells that were pumping on the sampling date. b) change in SUVA due to input of water from Gila River below site 6 in Reach 3 vs. change in discharge for same section; inset graph is change in DOC concentration vs. change in discharge for same location along the flowpath.

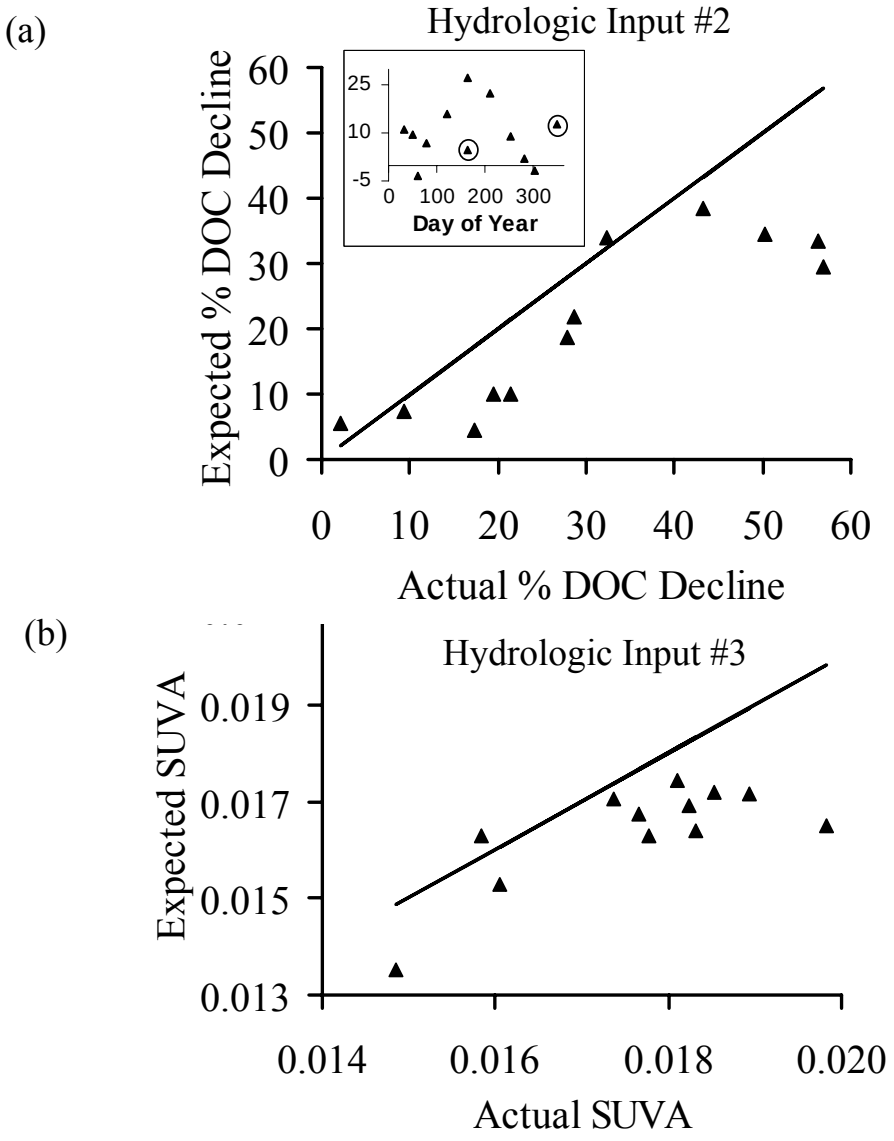

FIG 36**.** (a) The actual decrease in DOC concentration (as a percent of the DOC concentration at the head of the flowpath) along Reach 2 vs. the expected decline in DOC calculated using only known hydrologic inputs for each sampling date (groundwater well pumping). The line is the 1:1 expression of the actual DOC decline values, therefore any value that falls under the line is an underestimation of the change in DOC. On 75% of the dates, the decline in DOC was under-predicted by > 5% when using hydrologic inputs of groundwater into the canal to explain the DOC patterns. Inset graph shows the distance from the line of each triangle as a function of the day of the year the samples were taken. The circled values are discussed in the text. (b) Relationship between the expected change in SUVA at hydrologic input #3 (Reach 3), and the actual change that occurred. Any value that falls under the line (1:1 line of actual values) is an underestimation of the change in SUVA due solely to hydrologic inputs.

juncture (Fig. 36). This is not surprising given that measured SUVA values at site A (Fig. 29) never exceed 0.018, and yet the SUVA values downstream from the input were often higher than this value. These mass balance calculations do support P1c, but not without some additional unexplained variance that could be due to other proposed mechanisms.

Role of the microbial community

Estimates of the rate of aerobic sediment respiration at each site were made by monitoring changes in dissolved oxygen (DO) during chamber incubations. The goal was to understand the role of the heterotrophic microbes in explaining changes in water chemistry, particularly DOC (Hypothesis #2). Ranges in respiration rates are shown in Table 3, expressed both per g dry sediment < 2 mm diameter, and per meter squared using just the sediment size fraction < 2 mm diameter. Due to the large variation in sediment particle size from site to site (Fig. 37a), it was very important to consider sediment particle size when expressing respiration rates. Higher sediment respiration rates were associated with sites having, on average, smaller sediment particles (r^2 =0.522, $p<0.001$; Fig. 37b). The DOC retention (i.e., input flux – output flux) along the entire flowpath increased with increasing water temperatures (Fig. 38), supporting P2a (Table 10).

For P2b (Table 10), we calculated the percentage of the DOC retention along each reach that could be explained by benthic respiration rates. By dividing the DOC retention by the amount of DOC consumed in the sediments during the time water traveled down

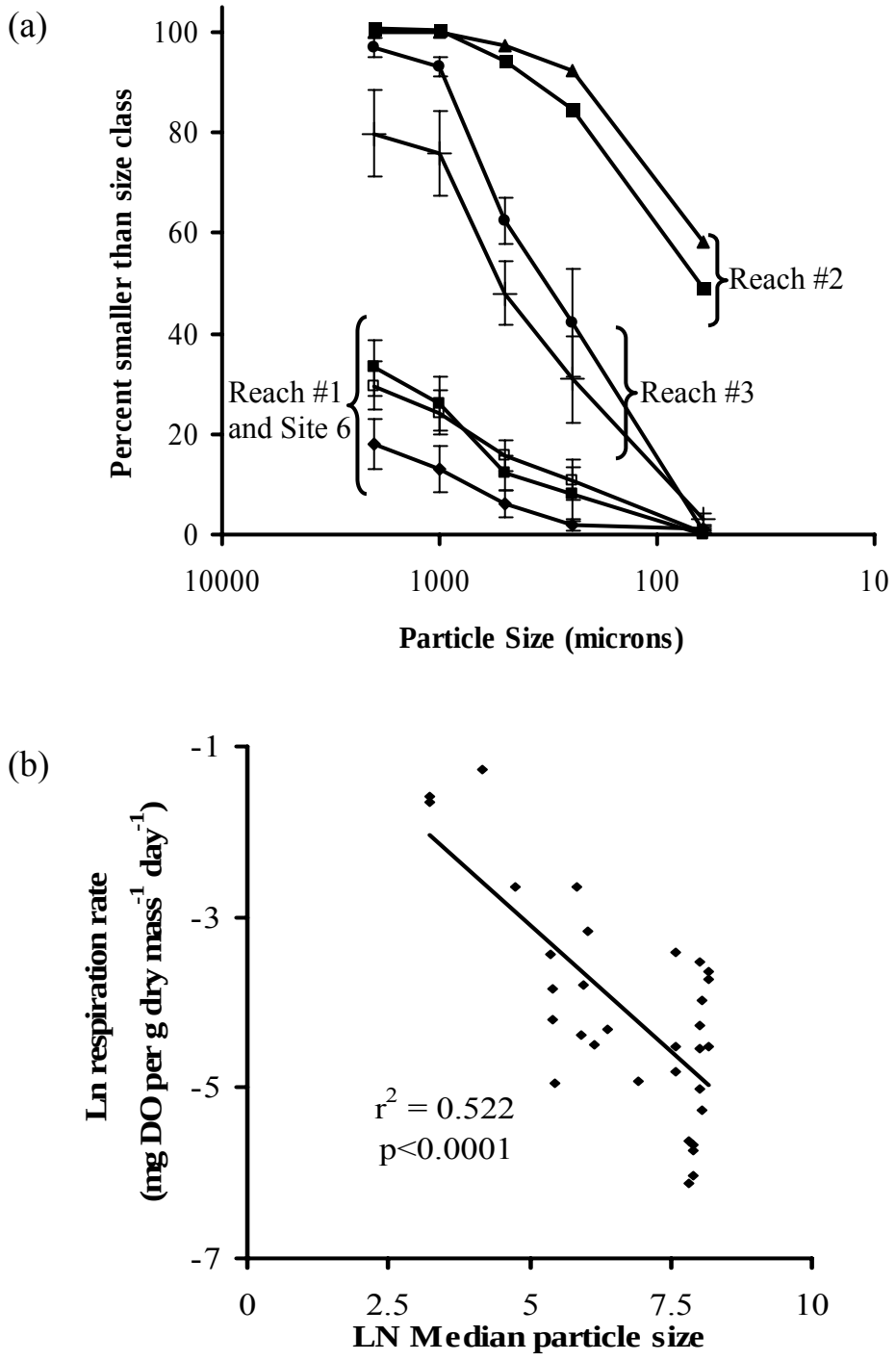

FIG 37. (a) Sediment particle size distributions at all sampling sites averaged over all dates, n= 1 to 7, depending on sampling site; error bars represent ± 1 SE (b) correlation between median particle size of the sediment sample taken and respiration rate for each site on each date (11 dates total).

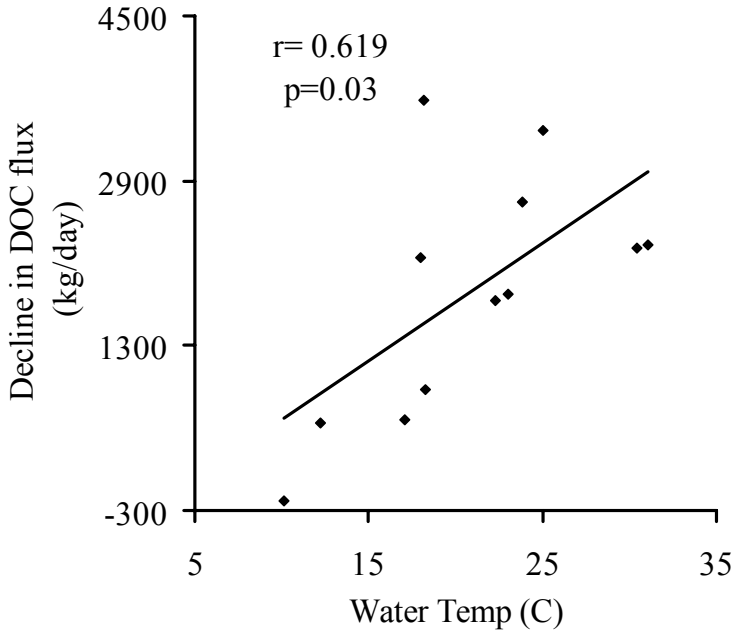

FIG 38**.** DOC retention (calculated as change in DOC flux) versus water temperature for 12 sampling dates.

each reach, we calculated the percentage of the water column that needed to exchange with the sediments (and was thereby subject to utilization by benthic microorganisms) to account for the DOC retention. Daily aerobic consumption of carbon in the sediments in Reach 1 ranged from 12-110 kg C, and from 4-45 kg C in Reach 3. Therefore, in Reach 1 and 3, < 1% of the water column would have needed to exchange with the sediments and fuel benthic respiration to explain the DOC retention found on one date. VHG measurements suggest there was a small amount of exchange with the surface at the four sites where measurements could be made (Table 11). Through Reach 2, the decline in DOC load ranged from 8-274 kg C (after taking losses to irrigation of crops into account). In comparison, the calculated DOC retention due to water column respiration associated with suspended solids was orders of magnitude lower, ranging from 1.6 to 25.4 g C. Obviously, water column respiration could not explain the decline in this reach, but for all but one of the days where a DOC decline occurred, the mass of DOC consumed was less than 7% of the load that was diverted due to irrigation. Imprecision in discharge alone could explain this difference, in which case we would assume that all of the DOC consumption was due to losses for irrigation.

Depending on which measurement of aerobic respiration was used for a particular site (lowest or highest), estimates of residence time of organic carbon in sediments ranged from 1 to 25 years through Reach 1, and 0.7 to 12 years through Reach 3. The highest rates of denitrification we measured would result in an additional daily consumption of 7 g C in Reach 1 and 0.9 kg C in Reach 3. While it appears that benthic respiration was fueled primarily by benthic particulate organic matter, the organic carbon

content of sediments only explained 39% of the variation in sediment respiration across all dates ($p<0.0001$). More organic matter was associated with sites that had a lower average particle size when all sites were considered together ($p<0.0001$, $r^2= 0.496$).

While explaining the temporal and spatial patterns we found in respiration was not our intention, we did hope to use these patterns to infer microbial community response to the water chemistry changes along the flowpath. A one-way ANOVA found only the most upstream site in Reach 1 was higher in respiration than all other sites along the flowpath (df=4, F=11.506, p=0.0001). Using a 2-way ANOVA, we found a significant interaction between space and time in rates of microbial respiration, but no significant main effects (df=30, F=18.516, p=0.000). We also measured denitrification, a form of anaerobic respiration, at these sites on two dates. Rates from unamended samples were higher at the head of the flowpath in February as compared to other downstream sites. In June, the end of the flowpath had a comparable rate to the head of the flowpath (Table 12). Unamended rates were not consistently different between the two dates. Amended samples were consistently higher than unamended samples at all sites in June, but not in February (2-way ANOVA). Amended samples showed a seasonal effect, with higher rates in June.

Role of adsorption kinetics

Neither P3a nor P3b was supported by changes in TSS along the flowpath. Water leaving the wastewater treatment plant at the head of the flowpath was low in suspended solids (14 mg/L) compared to the other sampling sites. Once the water moved into the canal system, velocity increased and sediment deposited in the system during floods was

Table 12. Average sediment denitrification rate in amended and unamended treatments (n=3 for all sites) made on two dates in 2001. Average values are given with standard error (SE).Values are in units of ng N_2O g sediment^{-1} day^{-1}, with only the mass of sediment < 2mm included

Site	February 2001		June 2001	
	Unamended denitrification (SE, n)	**Amended denitrification (SE, n)**	**Unamended denitrification (SE, n)**	**Amended denitrification (SE, n)**
Gila/Salt River confluence (Site 2)	4,815 (570)	16,324 (5,158)	2,602 (600)	20,311 (5,990)
Hassayampa River (Site 6)	137 (137)	216 (98)	119 (87)	3,788 (1,165)
Gila below Hassayampa (Site 7)	456 (208)	1,166 (361)	3,084 (609)	28,232 (2,204)
Gila below Hassayampa (Site 8)	228 (201)	5,047 (1,896)	Not available	Not available

resuspended, resulting in higher concentrations of suspended solids (Table 11). However, TSS was invariant along Reach 2 on all but two dates, and one of these two dates saw no decline in DOC concentrations along the canal. The percentage organic matter associated with TSS also did not increase with distance downstream. Using the DOC adsorption curve created in the laboratory as a test for P3c, 9.2% (±0.4) of the DOC at the outflow of the wastewater treatment plant adsorbed to suspended sediments (Fig. 39a). Suspended sediment concentrations in our experiment ranged from 25-175 mg/L, which encompasses all the values of TSS recorded along the flowpath. SUVA values did not change as DOC adsorbed on the sediments (Fig. 39b). After this initial test, we incubated water and sediment from the same sites using only 10 mg/L of TSS and sampled the bottles 4 times over the course of 15 hours. The proportion of the DOC pool that adsorbed with the sediments was essentially the same as in the first test, and the majority of which occurred during the first 4 hours of incubation.

Role of UV Transformation

UVA and UVB attenuation with depth of water is mostly influenced by the DOC concentration in the water (Yan et al. 1996). Using a published model relating DOC concentration to UV attenuation, we approximated attenuation coefficients (K_d) of 10 and 5 at 320 nm and 380 nm UV wavelengths, respectively (Morris et al. 1995). While UV radiation has been shown to break down complex organic matter, it can also inhibit bacterial activity. The literature suggests that as much as 2.8 mg of DOC could be oxidized to CO_2 by UV photobleaching within the time it takes the water to travel through this urban flowpath, assuming the entire water column is receiving equal

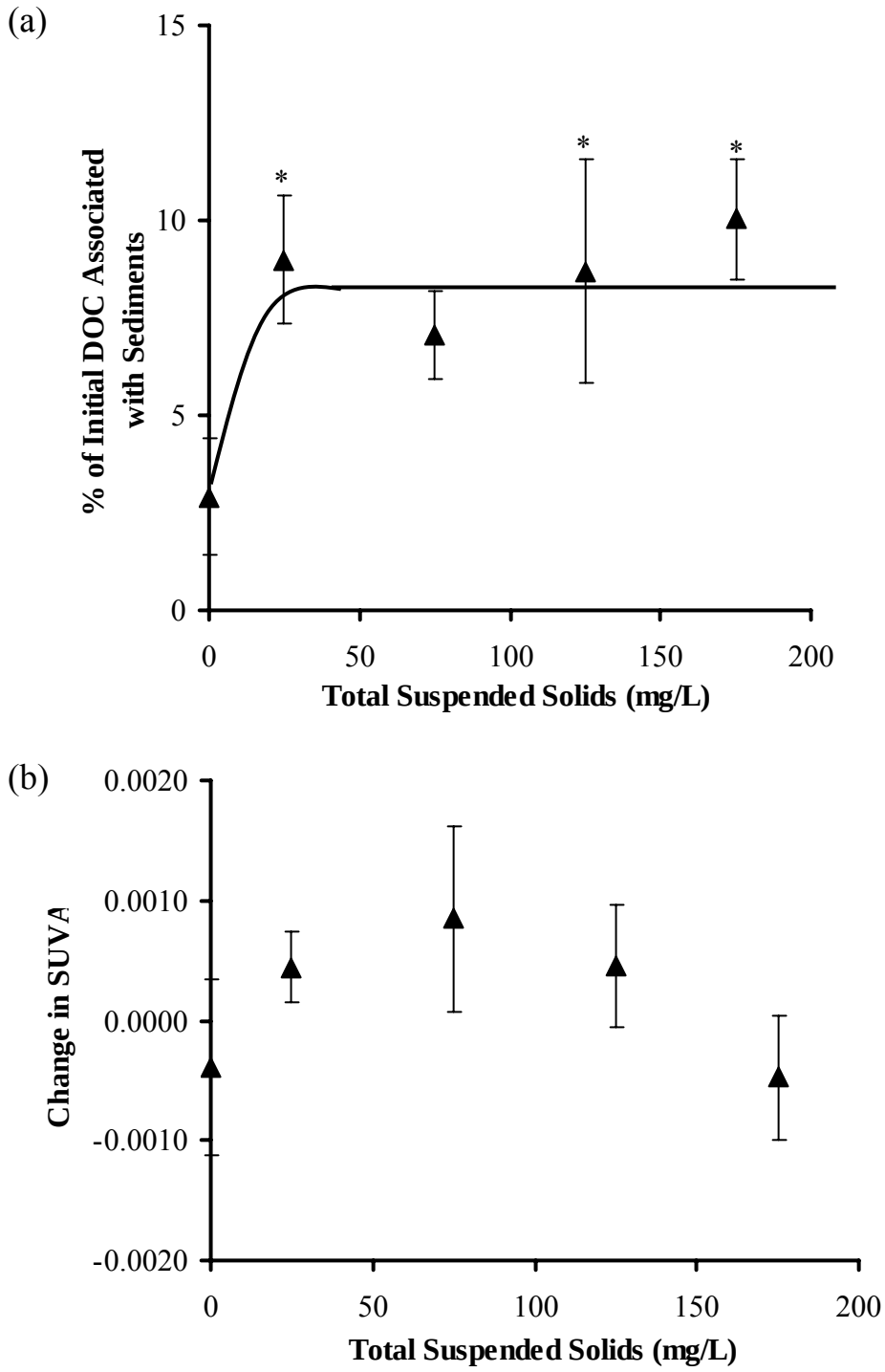

FIG. 39. Adsorption test to determine (a) DOC abiotic uptake capacity of washed suspended sediments and (b) change in chemical complexity (SUVA). Error bars represent ± 1 SE. Line drawn for illustrative purposes only. Values significantly different from zero (as determined by ANOVA) are indicated with an *.

amounts of UV radiation (Bertilsson and Tranvik 2000). UV oxidation, however, would also result in a decrease in SUVA, not an increase as was seen along the flowpath. Therefore, UV oxidation to CO_2 is not the mechanism to explain the patterns of increasing SUVA in the surface stream (Bertilsson and Tranvik 1998). Other researchers have shown that DOC with an initially low complexity may be transformed into larger, more complex compounds upon exposure to UV radiation (Tranvik and Kokalj 1998, Moran and Covert 2003). This would be a plausible mechanism to explain SUVA patterns we have documented.

Influence of flooding

Urban centers in arid lands are often engineered to retain the maximum amount of rainfall that can be captured, either through reservoirs, neighborhood retention basins, or groundwater recharge sites. Phoenix is no exception, and therefore much of the overland flow that occurred in the catchment of the lower Gila River never made it to the flowpath we studied. During 2001 two floods did occur, both during the winter rainy season. We wanted to know whether the floods would homogenize the chemistry along the flowpath and how long it would take to reestablish previous water chemistry patterns. DOC concentrations in floodwaters, while slightly higher than baseflow during the March flood, followed the same pattern of downstream decline seen at baseflow. SUVA was also higher than baseflow values during one of the two floods, but followed the same spatial pattern downstream that has been previously recorded (Fig. 40b). Dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) concentrations increased dramatically in the first flood (February 01), both in concentration and as a

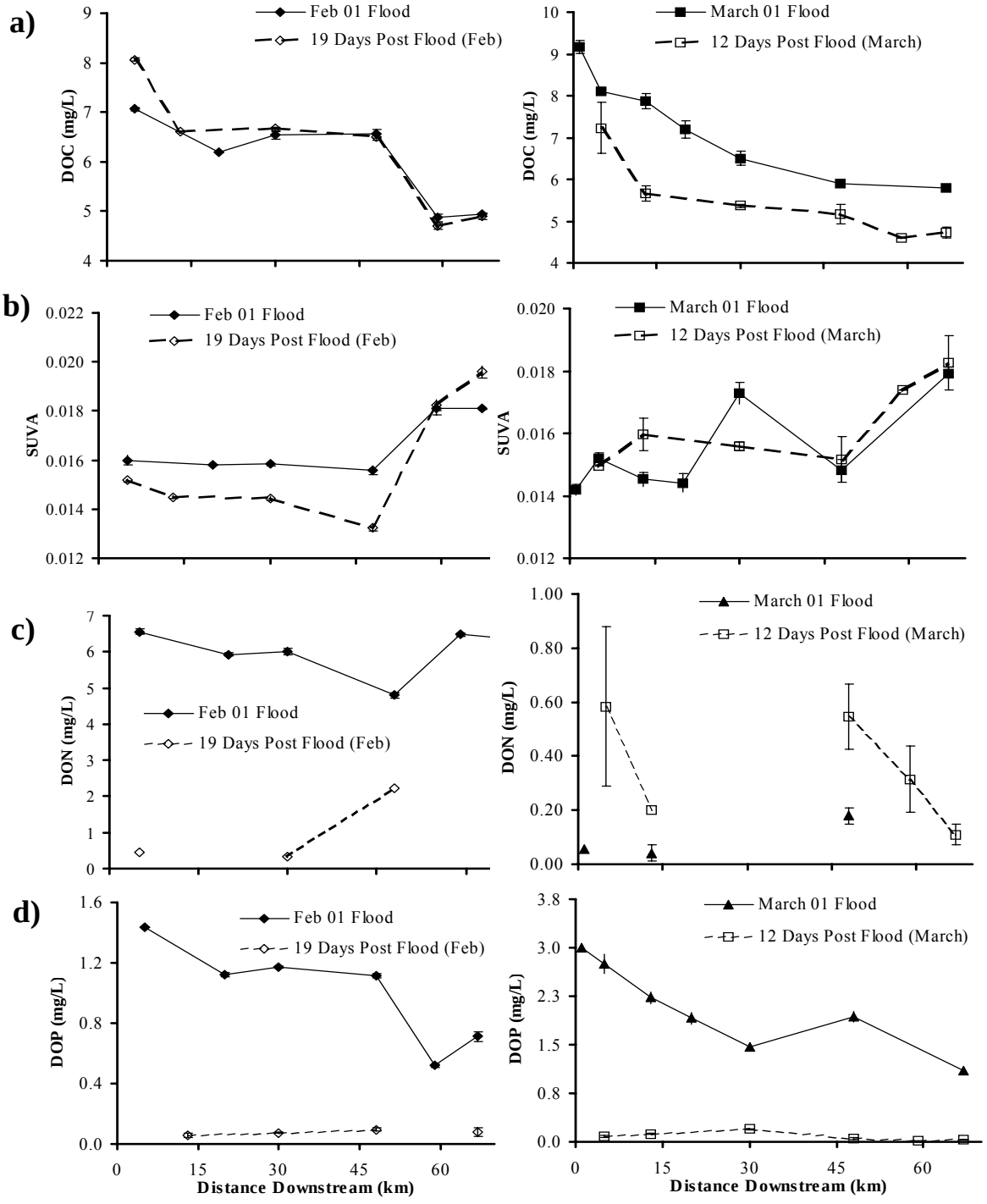

Fig. 40. a) DOC, b) SUVA, c) Dissolved organic nitrogen, and d) Dissolved organic phosphorus along the flowpath during and following two floods in Spring 2001. Missing DON values were negative when calculated as TDN minus TDIN, and TDP minus TDIP (error bars represent 1 SE).

percentage of total N and P (Fig. 40 c,d). However, the same increase in organic N was not found in the flood one month later (Fig. 40 c, d). Reestablishment of inorganic and organic concentrations to baseflow values took less than 19 days for both flood events.

DISCUSSION

Hypothesis Testing

Hypotheses 1-4 (Table 10) are proposed as the four most likely mechanisms explaining changes in DOC quantity and quality along the flowpath (Fig. 31). While these hypotheses are not mutually exclusive, the research was intended to identify the relative importance of each. Dilution (Hypothesis 1) was the dominant mechanism influencing patterns in DOC quantity throughout the flowpath. This mechanism of organic matter transformation through dilution was a more complete explanation for changes in DOC chemistry in Reach 2 as compared to the other two reaches. The significant alteration of channel geomorphology along the canal created an environment where primary production was low, surface-subsurface exchange was minimized, and heterotrophic community activity was too low to alter water chemistry patterns. The importance of these types of changes to in-stream biogeochemistry has been discussed in the literature, but our study is novel in its documentation of the effect of these geomorphic changes in an urban system (Graf 1975, Doyle et al. 2003). Although dilution was the principal explanatory mechanism for changes in water chemistry along Reach 2, some of the DOC retention was not accounted for by hydrologic additions. Also, increases in SUVA through Reach 3 were consistently under-predicted (in all but

one case) using simple groundwater additions as the explanatory mechanism. This unexplained variance suggests alternative mechanisms were acting as well.

The influence of microbial mineralization of DOC to CO_2 (Hypothesis 2) was dependent on quantifying the amount/duration of exchange between the surface water and the subsurface sediments so that benthic respiration could be related to water column chemistry changes. Given the high velocity of the surface water along the flowpath (0.1-0.8 m/s in Reach 1, 0.3-1.0 m/s in Reach 3), and the relatively gradual change in elevation, limited surface-subsurface exchange might be expected. If the exchange between shallow sub-surface water and the surface water was small, these two subsystems were in effect acting as separate systems, reducing the influence of benthic microbial activity on retention of nutrients and carbon as water flowed downstream. In fact, porewater concentrations of DOC made at site 2 were slightly elevated with respect to surface water. Therefore, any upwelling of subsurface water would result in input of DOC to the surface waters, ameliorating the decline in DOC along the surface water flowpath. Unfortunately, patterns in groundwater pumping mirrored seasonal patterns in temperature, which makes teasing apart biological transformations versus groundwater effects difficult (Fig. 41).

The microbial hypothesis was best supported in explaining the increase in SUVA values through Reach 3. Given that SUVA values were higher than expected after water entered the system at Hydrologic Input #3, we suspect that biological processing of DOC was responsible. Laboratory incubations in other systems have shown SUVA values to increase as microbial utilization of DOC occurs, presumably due to mineralization of less

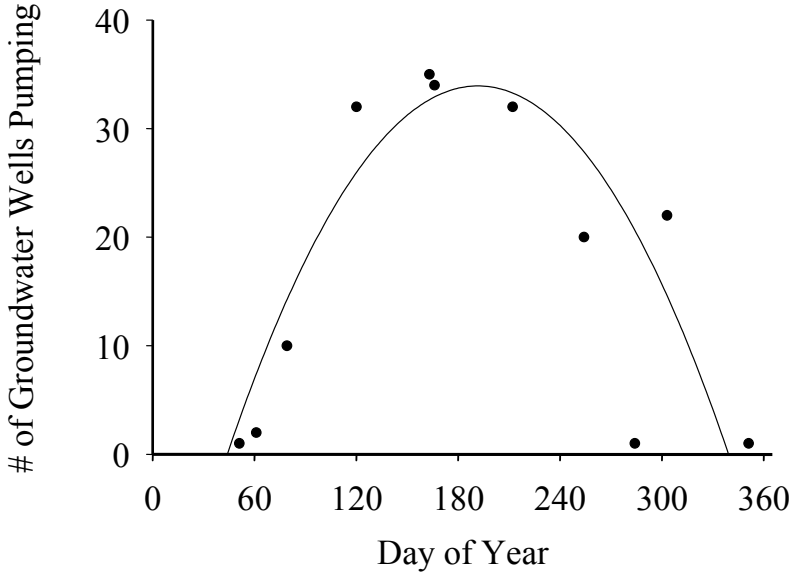

Fig 41. Timing of pumping of groundwater wells along the canal.

chemically complex DOC leaving more complex material behind (Edmonds and Grimm, in prep, (Pinney et al. 2000, Maurice et al. 2002). Reach 3 had the largest concentration of fine sediments in the benthos, with 80-96% of benthic substrate less than 2 mm, in comparison to 18-33% in Reach 1. This abundance of fine material to a sediment depth of 15-20 cm should support a high mass of microbial biofilm, which may have facilitated greater biological processing of DOC by the microbial community than in other reaches.

Rates of respiration not only were used to make mass balance calculations, but the spatial pattern can also be interpreted as a bioassay of the quality of carbon being utilized at a particular site. When average rates of benthic respiration over all sampling times were compared along the flowpath, expressed on a per g sediment <2 mm basis, only the site at the head of the path at the wastewater treatment plant outfall was higher than the other four locations along the flowpath. This is expected given the hypothesis that higher chemical complexity DOC (water towards the end of the flowpath) will be less accessible for microbial utilization (respiration) because of the additional energy needed to breakdown complex/strong chemical bonds. Thus, benthic respiration rates suggest that DOC quality was higher at the head of the flowpath, and that temporal variability in benthic community activity was low.

The lack of spatial variability in respiration, despite significant changes in water chemistry, could be due to the stability of water chemistry patterns seen along the flowpath through time. This stability may have allowed microbial communities to become well adjusted to their local environment. Another explanation for the lack of spatial variability is that subsurface respiration was not strongly connected to water

chemistry in the overlying water, instead utilizing buried organic matter. This second explanation does not fit well with longitudinal patterns of respiration, since the highest percentage (by mass) of organic matter was associated with sediments at the end of the flowpath, while rates of respiration were highest at the head of the flowpath. Potential denitrification enzyme activity data also suggested that there was a switch from high quality to low quality DOC along the flowpath. Most sites responded positively to amendments of acetate and nitrate-N (DEA increased a factor of 2.5 to 14 over unamended). Given that ambient concentrations of nitrate are probably above limiting levels (*in situ* values range from 2-8 mg/L NO_3^-N), this result suggests carbon limitation of denitrification.

For Hypothesis #3 (Adsorption Hypothesis), our DOC adsorption experiment suggested no discrimination between materials of different SUVA values. The importance of adsorption, therefore, is not inconsequential, but cannot be used to explain changes in SUVA or create a longitudinal pattern in DOC decline, given the short time period required for DOC to form a sediment association (less than 4 hours). Only the third prediction from this hypothesis was supported, and the association of DOC with particulates was less than 10% of the concentration at the head of the flowpath.

Our fourth hypothesis (Table 10) was that UV radiation changed DOC quantity and structure. A recent synthesis of the literature on UV photobleaching of DOC in aquatic systems found a widespread trend of low complexity DOC transformation to more complex compounds upon exposure to UV radiation. The pattern of increased SUVA along the flowpath would be congruent with this general model. However,

penetration of UV light through the water column is inhibited by high conductivity and pH, both of which were found along this flowpath (Bertilsson and Tranvik 2000). Second, rates of DOC transformation are unlikely to be sufficiently fast to cause significant changes in SUVA in the 11 hours water spent in Reach 3. Without further testing in the field, this hypothesis remains unsubstantiated.

Reinventing Streams in Urban Environments

This study has examined the importance of flooding, hydrologic flowpaths, and in-stream processing of materials in a river highly modified by humans. We return to our original goal to consider what mechanisms of DOC cycling were altered as the Gila River developed its current configuration by comparing its present status to that of non-urban stream ecosystems. Referring to the conceptual structure of Grimm et al. (2004), we found significant changes in flood disturbance, surface-groundwater interactions, and the location of hot spots of DOC retention. An important characteristic essentially lost from the urban flowpath was temporal variability of stream nutrient and DOC concentrations in response to disturbance by flooding (Fisher et al. 1982, Jones et al. 1996, Holmes et al. 1998). Resistance to disturbance events such as floods appears to be high in this system; there was little to no impact of flooding on DOC dynamics. In addition, N and P concentrations were only temporarily influenced by floodwaters. This resistance has important implications for biological communities of the water column and benthos, particularly as it relates to community development and stability in a relatively invariant environment.

Surface-subsurface exchange continued to be important along the urban flowpath, but at depths much greater than commonly considered in arid-stream ecosystems (Grimm and Fisher 1984, Valett et al. 1994, Stanley and Boulton 1995, Dent et al. 2001). In addition to shallow subsurface water, deep (35-275 meters) groundwater was pumped directly into the stream. Since groundwater chemistry was so distinct from that of surface water, the extent to which groundwater wells were being utilized controlled nutrient and carbon chemistry, particularly along the canalized portions of the flowpath. Whether or not the subsurface water was coming from depths < 30 m or > 30 m had a strong influence on DOC concentrations (Fig. 42), with the highest concentrations from groundwater near the surface. There was no relationship between well depth and SUVA values, but there was considerable variation in SUVA values from groundwater wells with a range of 0.01-0.023. Therefore, a switch from shallow to deep groundwater inputs, as occurred along this flowpath, influenced the quality of the water moving through the reach. Urbanization not only influenced surface water-groundwater interactions through well pumping, but also through changes to channel geomorphology. Canalization and the reduction or elimination of the complexity in stream geomorphic structure increased the velocity of the water. A consequence of these changes may be isolation of the surface water from subsurface processes (Haggard et al. 1999).

Predicting the location of hotpots of nutrient retention in ecosystems is often a matter of identifying where hydrological flowpaths containing complementary substrates or reactants converge, stimulating biological activity (McClain et al. 2003). In the urban flowpath studied here, abiotic mechanisms of DOC retention were more important than

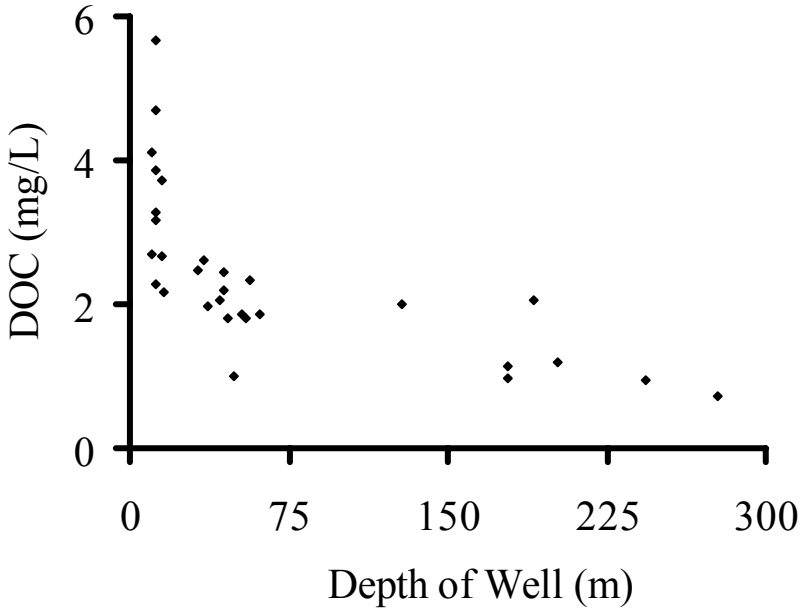

FIG 42. DOC concentration in water samples collected from groundwater wells (summer 2002) throughout the study area, graphed as a function of the depth of the well.

biotic, and they were responsible for the location and timing of hot spots. Work in non-urban desert streams has found hot spots of biological carbon utilization where surface water moves down into the subsurface sediments or laterally into the riparian zone (Jones et al. 1995, Holmes et al. 1996). In contrast, abiotic mechanisms influencing DOC retention in this urban stream were located in the water column (adsorption and hydrologic mixing).

The dominance of abiotic mechanisms of organic matter cycling in any ecosystem may dampen temporal variability in DOC patterns, as abiotic mechanisms are often not influenced by temperature or living biomass to the extent biotic mechanisms are. However, in urban ecosystems, abiotic mechanisms of retention may be just as temporally variable as biotic pathways due to variability in human decision-making. For example, the chemistry at the head of this urban flowpath was a function of the ability of the wastewater treatment plant to remove materials from incoming sewage. This large plant releases effluent with variable concentrations of organic carbon, which sets the baseline water chemistry of the stream (Fig. 43). Additional temporal variability was introduced by meeting the need for irrigation water in the area. Demand for groundwater pumping was highest during the warmest months of the year. Therefore, DOC retention was closely related to air temperatures. Understanding the biogeochemistry of an urban ecosystem requires understanding decisions being made by humans and traditional ecological theory falls short.

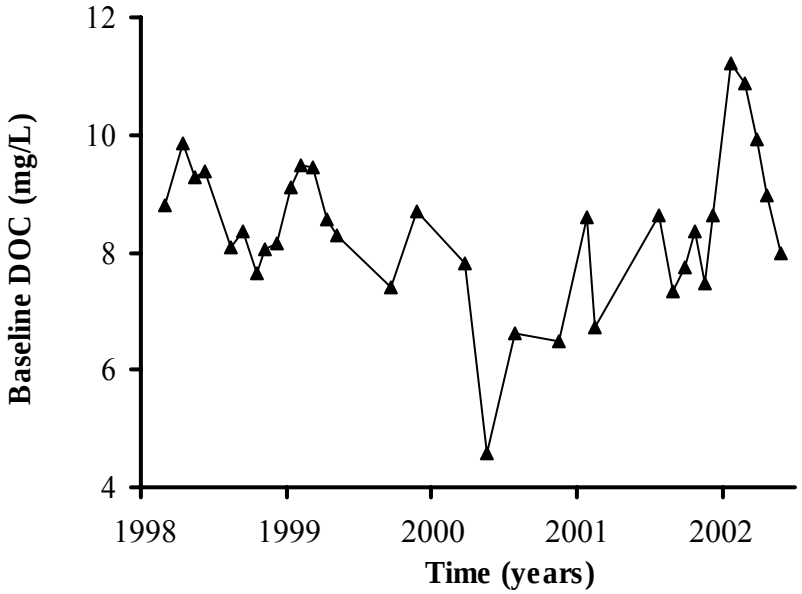

FIG 43. DOC concentrations at the outfall from the 91st Avenue wastewater treatment at the head of the urban flowpath. Data from CAP LTER.

Conclusions

Human alteration of geomorphology and hydrologic flowpaths of a large desert river have substantively altered stream-water chemistry of DOC in comparison to less-disturbed streams in the Sonoran Desert. Mechanisms of nutrient retention and transformation have shifted from dominance by biotic to abiotic pathways, severely dampening the influence of climate regime and substituting the maintenance of human food production and waste management as dominant large-scale controlling factors. Both the surface stream and sediment-subsurface exhibited little variation over time in organic matter chemistry. Urban ecosystems, therefore, provide an opportunity for ecologists to test theory concerning microbial community structure and stability under an environmental regime that is extremely stable.

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CHAPTER 4: DIFFERENTIAL RESPONSE OF BACTERIAL COMMUNITY ENZYME ACTIVITY AND RESPIRATION TO CHANGES IN ORGANIC MATTER QUALITY ALONG AN AGRO-URBAN FLOWPATH

ABSTRACT

Linking the physiological activity of microbes with ecosystem functions may help ecologists explain variation in carbon and nutrient cycling. In this study, microbial community respiration and enzyme production were monitored along a 67-km, effluent-dominated, urban flowpath in Phoenix, AZ. Throughout 2001, artificial substrates made of 2-mm glass beads were incubated in the surface stream at six sites along the flowpath to provide a uniform material upon which microbial communities could develop. Respiration rates associated with these artificial substrates were measured and found to be temporally and spatially variable. A 2-way ANOVA confirmed that heterotrophic microbial respiration rates (averaged over all sampling dates) were highest at the head of the flowpath. When averaged across all sample sites for a particular date, respiration rates were higher in the spring. There was also an interaction effect, indicating inconsistencies in the spatial pattern just described, through time. Extracellular enzyme production in the microbial community was monitored using Biolog® plates on two of the six dates for which respiration was measured (February and April 2001). The number of compounds utilized, of the 31 provided on the Biolog plates, was highest at the head of the flowpath and decreased downstream on both dates. This suggests that higher enzyme diversity created higher rates of respiration, linking diversity and ecosystem function. However, when comparing the two dates for which enzyme data were collected, a larger

number of substrates were utilized on the date with a lower average rate of respiration. Results from the Biolog plates were converted to binary data that were then used to generate a cluster analysis. One cluster contained all the samples taken in April 2001, and within this group, samples that were closer to each other on the urban flowpath were closer on the tree. For the other sampling date, site location was a stronger predictor of where the samples grouped. The cluster analysis demonstrated downstream changes in microbial enzyme production. These changes may explain variation in respiration rates. While each site appears to produce a unique suite of enzymes, variation in DOC composition through time constrains which enzymes will be present along the entire flowpath.

INTRODUCTION

Microbial ecologists have long been interested in how bacterial physiology integrates with carbon and nutrient cycling in aquatic systems (Sinsabaugh et al. 1993, Jones et al. 1995a, Mulholland et al. 1997). There is a bi-directional relationship between the activity of a microbial community and the aqueous environment in which it lives. Whether an ecosystem's patterns in water chemistry are significantly altered by microbial activity or whether they provide a template to which microbes respond is a function of the residence time of the water and the size of the dissolved load (Findlay 2003). Microbial transformation of dissolved organic carbon (DOC) will become measurably apparent in water with a long residence time and low DOC concentrations, but the same activity will have little influence on chemistry if the water moves quickly through the ecosystem or carries a large load. In the later case, measuring the activity of the

microbial community in response to changes in water chemistry may provide valuable insight into the variability of physiological diversity as it relates to community functioning.

The response of microbial communities to changes in inorganic and organic chemistry may be manifest as a change in respiration rates, extracellular enzyme production, fluctuations in the community's genetic diversity, or some combination of the above (Foreman et al. 1998, Baker et al. 1999, Bernhardt and Likens 2002, Findlay et al. 2002). Spatial or temporal uniformity in a more general community parameter such as rates of aerobic microbial respiration can often belie the complexity of the community's response if only this one measurement is used to assess microbial activity (Findlay et al. 1998). Additional measures of community response to a changing environment listed above can provide important information regarding cellular physiological diversity, which influences community-level respiration (Carreiro et al. 2000, Waldrop et al. 2000, Sinsabaugh et al. 2002). Understanding mechanisms by which microbial communities respond to a changing environment is key to understanding changes in microbially mediated carbon and nutrient cycling.

One of the most commonly measured response variables is heterotrophic bacterial respiration. These measurements are often used to quantify conversion of organic matter to CO_2 and CH_4 and to explain increases in nutrient availability due to mineralization during respiration. Recent research has found that the quality (defined here as the ability of the microbial community to utilize a carbon source for growth), not quantity, of organic matter is a strong determinant of respiration rates in a variety of ecosystems

(Hopkinson et al. 1998, Baker et al. 1999, Vitousek and Hobbie 2000, Craft et al. 2002, Dahm et al. 2003). Organic matter quality can be quantified as either the chemical complexity of the organic compounds, or their nutritional content, and it is often difficult to measure because compounds in the organic matter pool are diverse. In aquatic ecosystems, DOC sources change as a function of the interaction of water with soils and sediments, or the dominance of in-system primary production, all of which create fluctuations in DOC composition (Jones et al. 1995b, Boyer et al. 1996, Mulholland and Hill 1997). These fluctuations may change rates of in-stream decomposition and nutrient release depending on their magnitude and duration. Microbially mediated nutrient release stimulates primary production when that process is nutrient limited, and that which is not taken up by primary producers is exported to downstream recipient systems.

The first step in linking microbial diversity (either physiological or genetic) to ecosystem functioning is to identify patterns. Once variability in diversity has been correlated with changes in community activity (such as respiration) in a variety of environments under a variety of conditions, a mechanistic understanding of the relationship will develop. Some work has been done to link the two, but to date, reported patterns have been inconsistent (Martin et al. 1999, Broughton and Gross 2000, Collins and Cavigelli 2003, Freitag et al. 2003). For now, we can correlate microbial diversity with differences in community activity, with the expectation that higher diversity creates higher rates of activity.

For this study we tested whether patterns in water chemistry along an urban flowpath within the Phoenix metropolitan area of central Arizona created a template for variation

in microbial community dynamics. The waterway, or flowpath, originates as outflow from a tertiary wastewater treatment plant (Fig. 44) and terminates 67 km downstream at the hydrologic output for the lower Gila River in Maricopa County, AZ. Sampling in association with the Central Arizona- Phoenix Long Term Ecological Research Project (CAP LTER) revealed that concentrations of DOC decreased by an average of 64% as water flowed downstream, while the DOC-normalized chemical complexity of the DOC pool increased (reflected as an increase in specific UV absorbance (SUVA); Fig. 45). Four hypotheses as to the cause of the patterns in DOC chemistry along the flowpath were tested, and results showed that the majority of the changes were due to hydrologic mixing of shallow and deep ground water (Edmonds and Grimm, in prep).

This system was ideal for testing the effect of changes in DOC quantity and quality on multiple response variables of the microbial community. The spatial water chemistry pattern was temporally very consistent, increasing the likelihood that microbial communities had modified their physiology in response to changes along the flowpath. The specific objective of this study was to compare the response of microbial community respiration and extracellular enzyme production (measured as substrate-induced respiration on Biolog ® plates) to the gradient in DOC quantity and chemical complexity found on the urban flowpath.

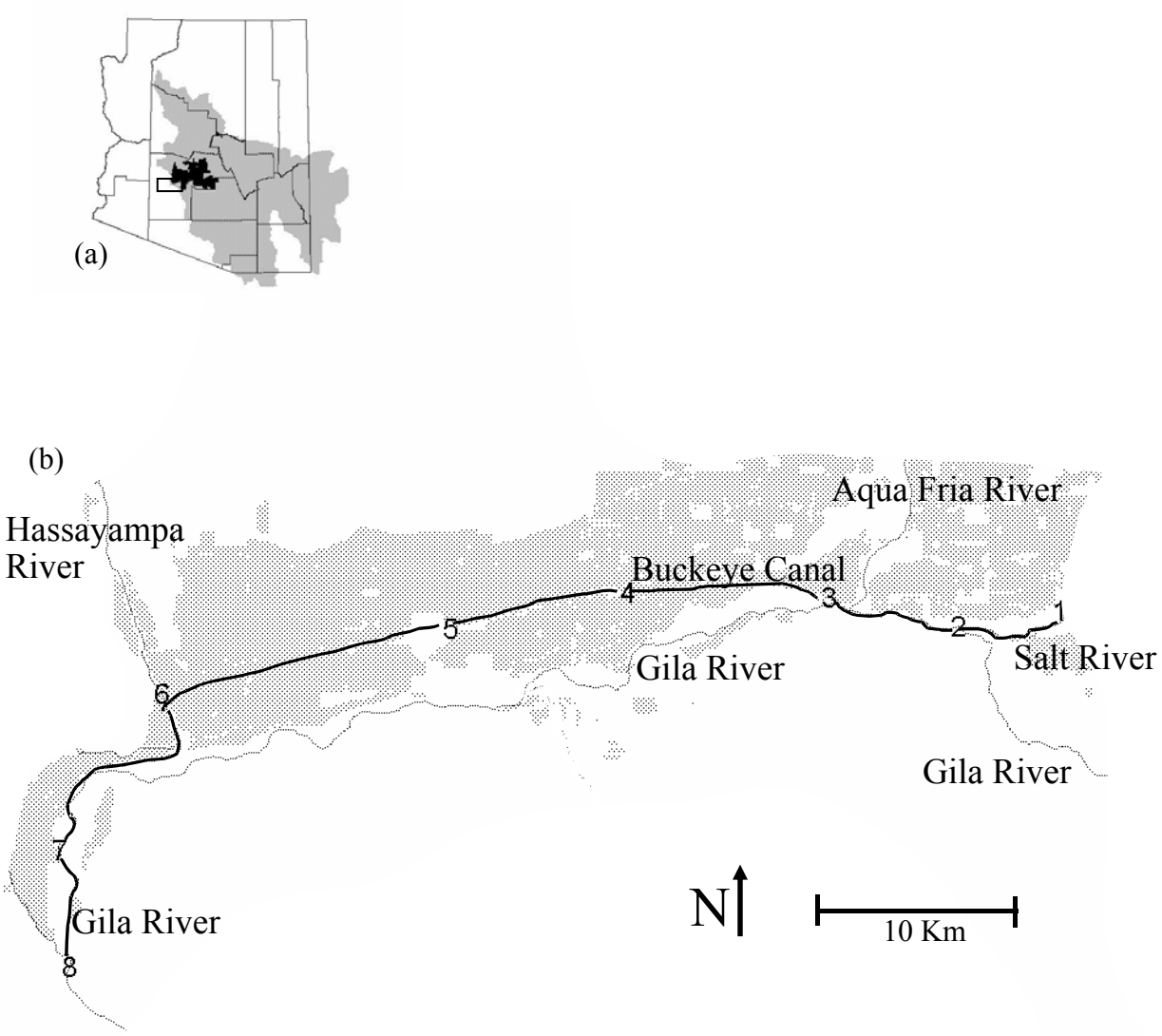

FIG. 44. (a) State map of Arizona indicating relative position of Phoenix (black shape), the Gila River watershed above the city (gray shape) and the study site within Maricopa County (box). (b) Larger map shows details of the study area. On the lower map, numbers mark locations of sampling points, the dark line indicates the flowpath (water flows from east to west), gray areas are agricultural fields. River section from sampling sites 1 to 3 will be referred to as Reach 1, from sampling sites 3 to 6 is Reach 2, and sampling sites 6 to 8 is Reach 3.

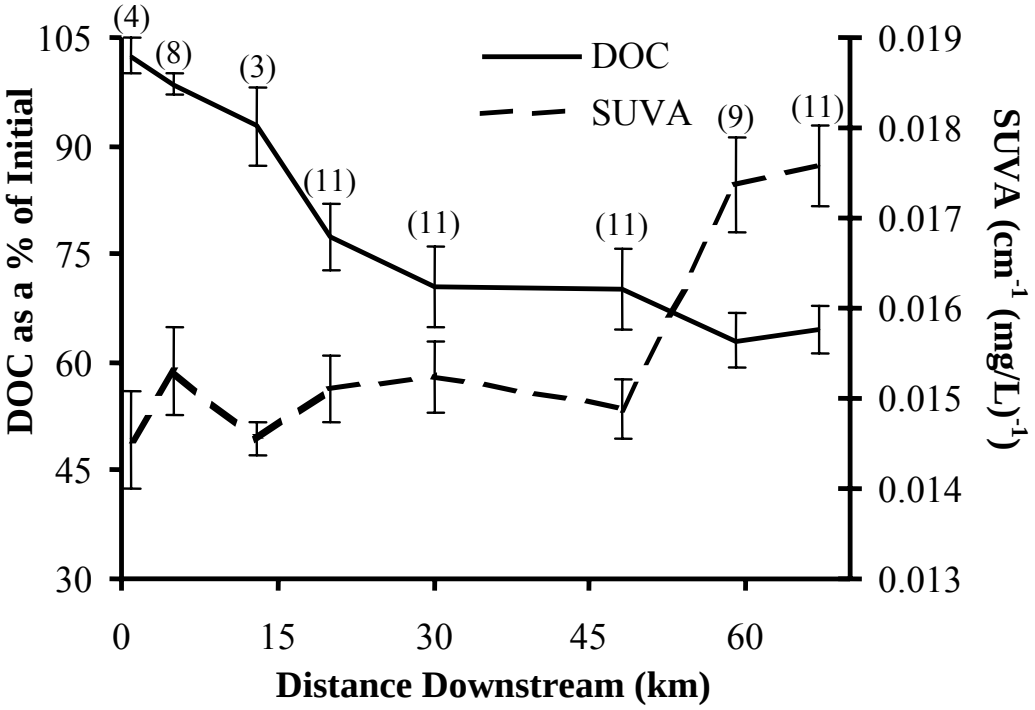

FIG. 45 Average dissolved organic carbon (DOC) concentrations and specific ultraviolet absorbancy (SUVA) values for sites along an urban flowpath downstream of the outfall from a wastewater treatment plant. Higher SUVA values indicate more complex DOC. Numbers in parentheses indicate number of sampling dates at each site for both DOC concentrations and SUVA. Error bars represent ± 1 SE

METHODS

Study site

This study was completed in the Sonoran Desert, Arizona, USA. The urban/agricultural waterway begins approximately 30 miles due west of Phoenix, AZ, in an agricultural community that is experiencing rapid urbanization. For ease of discussion, the 67-km flowpath has been divided into three reaches (Fig. 44). Reach 1 is the first 13 km of the flowpath (sites 1-3), before the canal begins. Reach 2 is the 35 km of the canal ending where it empties into the Hassayampa River (sites 3-6), and Reach 3 is the last 19 km of flow in the Hassayampa and Gila River (sites 6-8). Nutrient concentrations in the ecosystem were very high. Average nitrate concentrations in the surface waters were consistently above 2 mg/L NO_3^--N and reached as high as 8 mg/L by the end of the flowpath. Phosphate concentrations ranged from 0.5-2.5 mg/L soluble reactive phosphorus (SRP).

Benthic sediments varied considerably from site to site, ranging from heterogeneous, coarse stones to very fine, homogenous sediment (Fig. 46). The proportion of the top 5 cm of benthic material that was smaller than 2 mm in diameter ranged from 20-100%. Sediment organic matter content was negatively correlated with sediment size ($p<0.0001$, $r^2=0.496$), and variation in the permeability of benthic substrates and the surface water velocity probably created differences in exchange between surface and subsurface water from site to site.

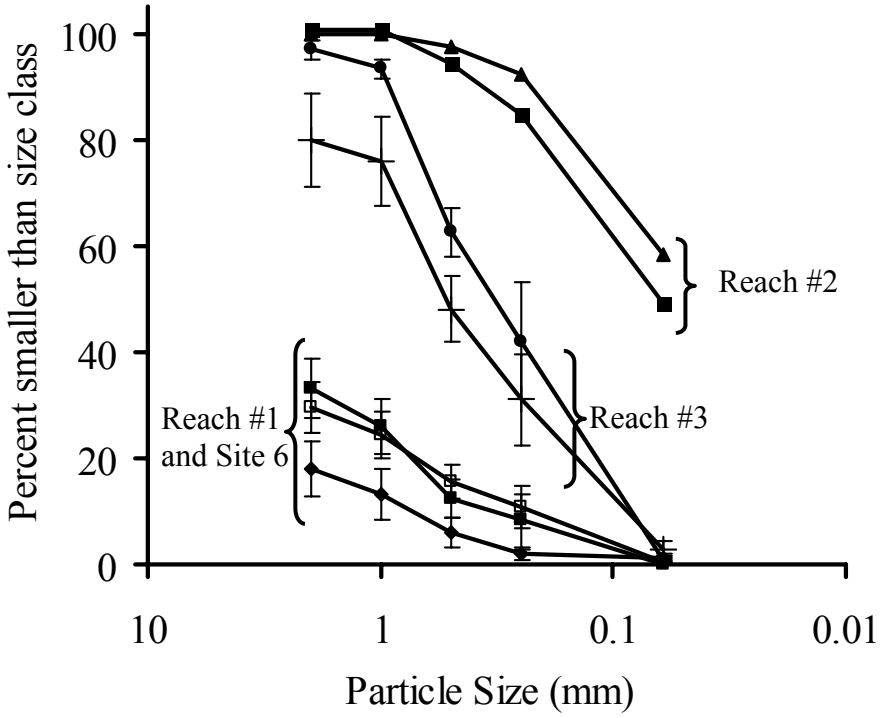

Fig. 46 Sediment particle size distributions at all sampling sites averaged over all dates, n= 1 to 7, depending on sampling site. Error bars represent ± 1 SE, x-axis graphed using a log scale.

Sample collection and analysis

Water samples were taken at all sites along the flowpath (Fig. 44) and processed as described by Edmonds and Grimm (in prep). In addition to quantifying the concentration of DOC in the water, a simple measure of DOC chemical complexity was used, specific ultraviolet absorbance (SUVA), which is the absorbance (λ= 254nm) of a Whatman GF/F filtered, acidified water sample, divided by the concentration of DOC in the sample. SUVA is an indicator of the quantity of double-bonded C atoms (unsaturated sp^2-hybridized carbon atoms). An aromatic carbon ring has half of its carbon as C=C, and since most natural organic matter is aromatic, not aliphatic, SUVA is a good measure of the aromaticity of a DOC sample.

Substrata were collected from sites 2 and 4-8 (Fig. 44) on 7 different sampling dates from February to December in 2001. Because of the differences in benthic sediment size, organic matter content, and hydrologic exchange with the surface, we placed artificial substrata in the water column at each site to serve as a source of bacteria for the measured response variables, eliminating variability due to these other factors. The artificial substratum consisted of 2-mm diameter glass beads packed in 7-cm PVC tubing (I.D. = 40 mm) with 1-mm Nitex mesh secured on each end. The beads were washed in 10% HCl and then combusted at 550 ºC before being packed in the tubes. Substrata were secured to rebar as close to the main channel flow as possible without risking losing them. They were incubated in the stream for 12 weeks before removal for laboratory assays. Once a substratum was used in the laboratory, it was repacked in the same tube (after washing and ashing) and returned to the same site.

Artificial substrata were removed in triplicate from the stream at each site on every sampling date. The substrata were washed in the stream to remove loosely attached material and sediment particles trapped in the interstices of the beads. Once in the laboratory, the substrata were removed from the PVC tubing and placed in respiration chambers constructed from clear plastic pipe (15 cm long, 4.4 cm inside diameter) that was sealed on both ends with rubber stoppers. Fifty per cent of the chamber volume was filled with the glass beads, and the remainder of the chamber volume was then filled with water from the surface stream at the site where the beads were incubated, gently inverted three times to allow any air trapped within the beads to escape, and sealed on the ends with rubber stoppers. Sealed chambers were incubated in the dark at room temperature to maintain consistency between sampling dates. Incubation times were approximately 4 hours, which was sufficiently long for a decrease in dissolved oxygen (DO) of >1 mg/L. DO was measured with a YSI 85 DO Meter.

On two dates in 2001 (20 February and 30 April), artificial substrata were used to measure substrate-induced respiration as a surrogate for extracellular enzyme activity. Following respiration measurements, a subsample of the glass beads was homogenized and a known aliquot was placed in a 60-ml nalgene bottle. Twenty ml of Ringer's solution was added, and the bottles were shaken on an Eberbach 6010 shaker at 1140 rotations per minute for 1 hour to detach the biofilm from the surface of the beads. Bottle contents were then homogenized, sonicated for one minute in a water bath, and homogenized again. The liquid was continuously stirred in a Petri dish and distributed into the 96 wells of the ECO Biolog plates using an 8-channel pipetter. ECO plates are a

product of Biolog®, and they consist of multiple carbon substrates, each contained in a separate well to which a minimal growth medium and tetrazolium violet also are added. The redox dye turns purple in the presence of electron transfer, indicating that the inoculated microbes have utilized the substrate. Biolog® plates are based on growth or activity under cultured conditions, that may or may not be similar to the sampling environment (Konopka et al. 1998).

Biolog's ECO plates have 31 carbon sources provided in triplicate within each plate. The blank is also in triplicate and is a well containing only the inoculum water. After the plates were inoculated, they were incubated for 24 hours at room temperature in the dark. Optical density (λ= 590 nm) of each well was determined immediately (0 hours) and at 12 and 24 hours using a spectrophotometric microplate reader. This same process was completed using benthic sediments at each site on 10 October 2000, and these data were included in the analyses. Statistical analyses included a 2-way ANOVA testing differences between respiration rates at each site and between dates, and a cluster analysis to determine relationship between samples using presence/absence data for each Biolog substrate.

RESULTS

We focused on relative values of the downstream patterns of respiration over time, as absolute values of respiration rates derived from biofilms growing on uniform glass beads do not reflect *in situ* conditions. A two-way ANOVA of respiration rates found date, site, and the interaction between the two to be significant ($p<0.0001$). Post-

hoc pair-wise comparisons (Tukey HSD) identified differences in the groups when aggregated in space or through time (Fig. 47). Average respiration rates decreased downstream, with a slight increase at the last site (Fig. 47a). Rates also decreased through 2001 until the last sampling date in December (Fig. 47b). The differences between sites were not consistent through time, as indicated by the significant interaction effect. However, the first site on the flowpath was always higher than the next to last site on the flowpath, which is important given that the SUVA values were almost always higher at this downstream site. The inconsistencies in spatial patterns along the entire flowpath could not be attributed to just one or two dates. Therefore, we looked for additional factors that might explain variation in respiration.

We had expected changes in DOC chemistry to influence community respiration in this nutrient-rich environment, as carbon often limits activity when N and P are in excess of physiological needs. In fact, we did find a weak but significant positive relationship between respiration rates and DOC concentration and between respiration and ultraviolet absorbance (UVA) at 254 nm (Fig. 5a, b). The UVA result is counter to expectations since higher UVA indicates more complex DOC, but whether the DOC or UVA was the controlling factor is hard to determine given the high co-variance between the two parameters (Fig. 5c). In either case, < 27% of the variation in respiration rates was explained by either DOC concentration or UVA. The relationship between respiration and UVA could be indirect if UVA co-varies with another chemical constituent that is actually responsible for changes in respiration. UVA and total

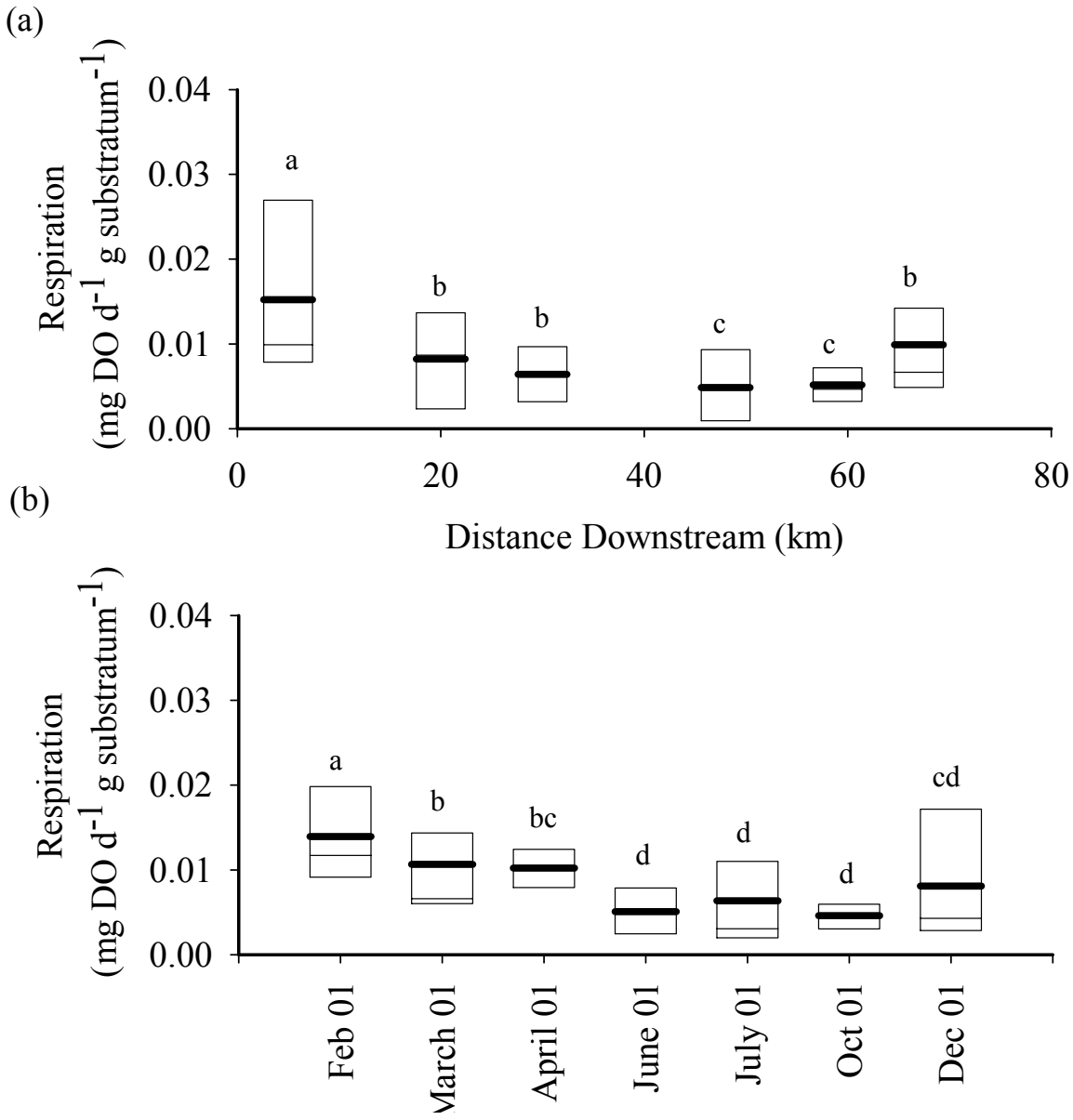

FIG 47. Respiration rates on artificial substrate incubated at six sites along the urban flowpath. For each graph, the boundary of the box closest to zero indicates the 25th percentile, and the boundary of the box farthest from zero indicates the 75th percentile. The mean is the dark line. (a) Data from all dates arranged by site, and (b) data organized by date sampled. Bars with the same letters are not significantly different from one another (Tukey post-hoc tests following 2-way ANOVA).

dissolved phosphorus (TDP) are correlated (Fig.48d), but given the very high levels of P in the system, it is unlikely that variation in TDP created variation in microbial respiration.

To better understand the response of the microbial community to changes in water quality, we also characterized patterns in enzymatic capabilities using prefabricated Biolog plates. To insure that differences in the intensity of the color development in the wells on the plates between dates did not skew statistical calculations, we used binary data in a cluster analysis. We subtracted the absorbency of the blank from each well, averaged the absorbency of the three wells on each plate, then averaged the three plates for each site for each source. Substrates with an absorbency of >0.5 were assigned a 1, substrates <0.5 were assigned a zero. This created binary data, which were used to generate a similarity matrix. The similarity matrix was used in an additive tree cluster analysis to look for groupings in the data, yielding two main clusters (Fig. 49). The first cluster contained all the samples taken in April 2001, and samples that were closer to each other on the urban flowpath were closer on the tree within this group. For the other two sampling dates, site location was a stronger predictor of where the samples grouped. Sites downstream of the Hassayampa on the lower Gila River (7, 8 on Fig. 44) clustered on the other end of the tree from the sites on the canal (4, 5 on Fig. 44) and the sites directly microbial communities on the substrata were similar, in carbon utilization to those on ambient sediments.

In general, the number of substrates utilized on the plates was lower at the downstream end of the flowpath compared with the upstream end with the exception of

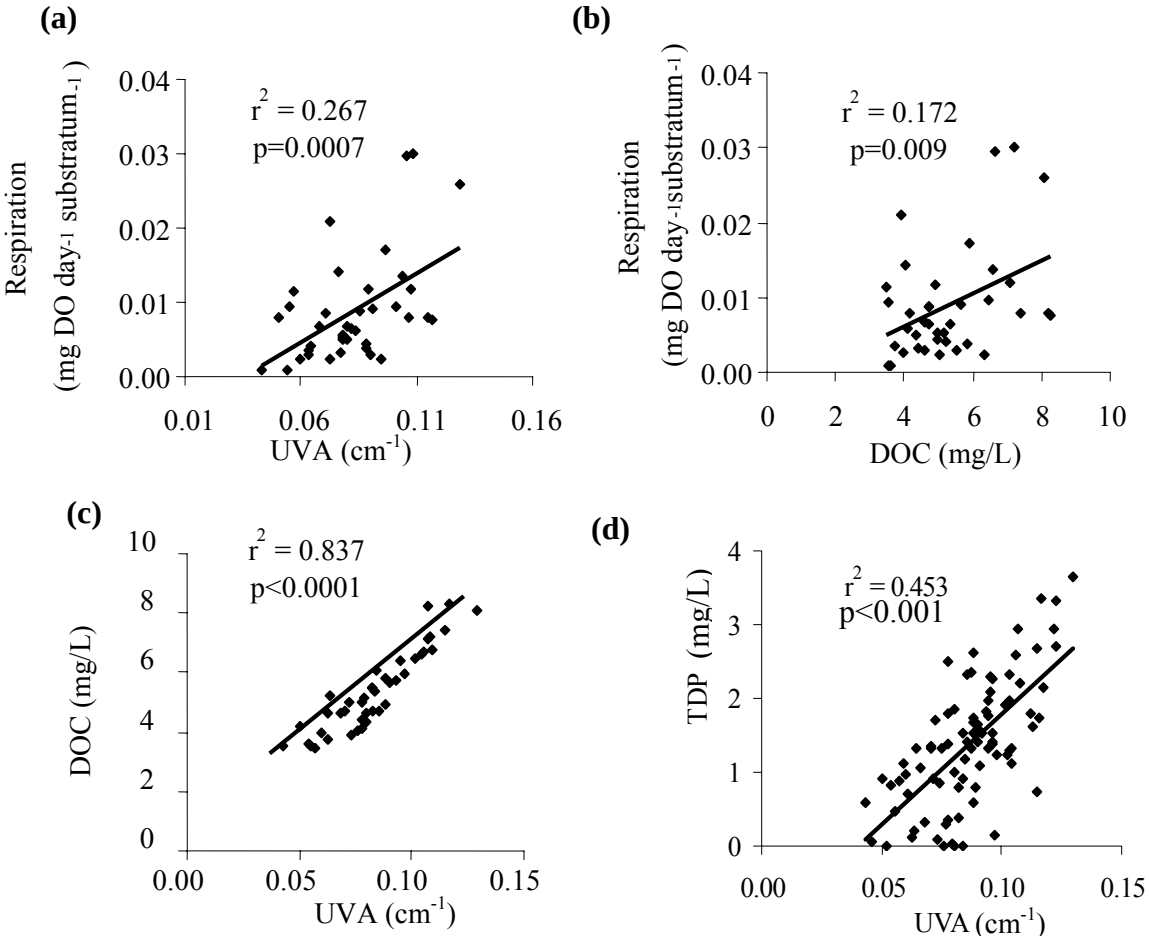

FIG 48. Respiration rates versus (a) UVA and (b) DOC concentrations for seven sampling dates along the urban flowpath. (c) DOC concentration vs. UVA for all sites and dates. (d) Total dissolved phosphorus (TDP) versus UVA for all sites and dates.

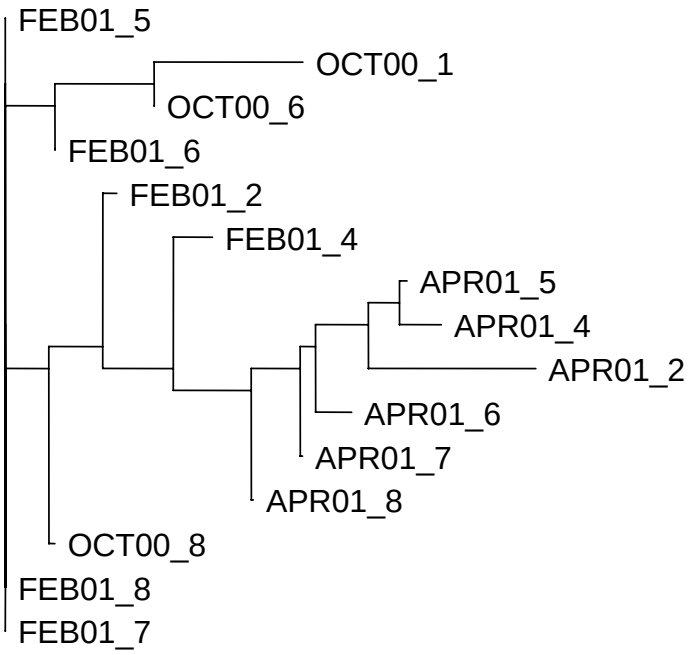

FIG. 49. Date and site (see Fig. 44) grouping in a cluster analysis using a similarity matrix generated from binary Biolog data.

the natural sediments collected in October 2000 (Table 1). Samples collected in April 2001 utilized more substrates. Most of the variability in substrate usage between dates and sites was found in the carbohydrate and carboxylic acid carbon classes. Note that for the date where naturally occurring sediment was used instead of artificial glass beads (October 2000), the samples grouped with other samples from the same site on different dates, confirming that sites on the flowpath (7 & 8), in particular, utilized three fewer carbohydrate compounds and two fewer carboxylic acid compounds than sites upstream. In April, several compounds were unique to the samples collected. The phenolic compound 4-hydroxybenzoic acid, carboxylic acids, D-malic and pyruvatic acid methyl ester; and phenyl ethylamine were utilized in all April 2001 samples collected, but not utilized by samples from any other sampling dates with one exception at one site on February 2001. In addition, the following four compounds were utilized by microbes from all samples on all dates except L-serine at site 1 in Oct 2000. The compounds utilized were 3 amino acids (L-arginine, L-serine, L-threonine) and the polymer, glycogen. Three carbohydrates, three carboxylic acids, two amino acids, one amine, and one phenolic compound on the Biolog plates were not used by any samples on any dates.

DISCUSSION

Microbial communities can perform the same ecosystem function using a variety of different physiological pathways. Determining when, and to what degree, different aspects of cell functioning are utilized to maintain growth is a relatively new frontier for microbial ecologists (Garland 1997, Sinsabaugh and Foreman 2001). We chose to focus

TABLE 13. Number of substrates utilized at locations along the urban flowpath for three sampling dates.

	October 2000 Sampling Date	February 2001 Sampling Date	April 2001 Sampling Date
Site 1	3		
Site 2		11	20
Site 3			
Site 4		13	18
Site 5		9	17
Site 6	6	8	16
Site 7		9	15
Site 8	10	9	14

on extracellular enzyme production as it relates to community respiration along a gradient in stream DOC concentrations and chemical complexity. In our work, the expectation was that respiration rates would decrease as DOC complexity increased, and that this variability in respiration would be reflected in the enzymatic capabilities of the microbial community. Enzyme production should change as new carbon sources are encountered (Arnosti 2003). Whether these changes take place as a replacement of one enzyme for another or if a larger suite of enzymes necessarily results in higher community respiration is largely unknown.

Very little of the variability in respiration was explained by DOC chemistry, possibly because community activity was limited by something other than C, N or P availability. However, spatial variation in respiration rates and enzyme production appeared to follow similar trends. Biolog data showed location along the flowpath to have a logical progression, with communities closer together being more similar in their extracellular enzyme production than communities farther apart. Changes in respiration rates along the flowpath also grouped according to location, with the exception of the last site. These patterns suggested that the composition of the DOC pool was changing as water moved downstream, and that the microbial community responded by changing the extracellular enzymes produced to match substrate composition. The number of enzymes produced, as measured by substrate-induced respiration, declined downstream, as did the respiration rates when averaged over time. This may indicate a link between enzyme diversity and ecosystem function. For example, greater enzyme diversity may be associated with higher respiration rates.

In contrast to the positive relationship between respiration and enzyme diversity, average respiration of samples taken in April 2001 was lower than February 2001, while enzyme diversity was higher on the April date. One explanation is that additional enzymes unique to April samples were not responsible for significant rates of respiration, but were a response to rare compounds in the environment. The new enzymes were those responsible for the breakdown of polymers, phenolic compounds, and carboxylic acids. These organic compounds could be relatively chemically complex. Therefore, their presence may be an indication that the microbial community was utilizing higher complexity DOC. The high energy expenditure required for breaking down complex DOC compounds might have prevented respiration from increasing significantly despite the addition of new enzymes. Resolving these differences in relationships between respiration and enzyme capabilities will require experimental work using controlled systems.

Measures of heterotrophic microbial activity in aquatic ecosystems range over orders of magnitude, whereas DOC concentrations vary little. A partial explanation for this mismatch is that DOC varies in complexity, but variation is not captured by measures of concentrations. Microbial communities adjust to these changes in DOC complexity by producing new extracellular enzymes. The interaction between physiological diversity and general community activity may be key to a better understanding of how microbial respiration and DOC chemistry are linked across ecosystem types. Models of ecosystem carbon cycling would be better constrained if physiological diversity were incorporated, particularly in lakes and oceans, where feedbacks between microbes and DOC are strong.

The next step in the state of the science is to relate changes in enzyme production to changes in genetic diversity, as some studies have begun (Baudoin et al. 2003, Girvan et al. 2003, Miethling et al. 2003).

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SYNTHESIS

Arid and semi-arid lands cover almost 30% of the world's landmass. Streams in these regions are characterized by well-lit surface waters that support some of the highest algal production ratesever measured (Grimm and Fisher 1989). Algal material produces leachate consisting of low complexity DOC that generates spatially distributed hot spots of microbial activity (Jones et al. 1995). In contrast, variation in DOC chemical complexity in runoff delivered to streams during floods may generate temporal hot spots of in-stream microbial respiration. Once urban activity moves into the watershed, modification of existing flowpaths may dampen temporal variability of DOC delivery. Higher C and nutrient loadings in urban ecosystems make it more likely that complexity of organic matter will control microbial activity and not quantity.

This research contributes to the body of scientific knowledge in three ways. First, we establish patterns in flood-related DOC quantity and quality under variable rainfall conditions along an upland to mainstem flowpath, and provide hypotheses to explain these patterns. Spatially explicit approaches to watershed studies are still relatively rare (Fisher et al. 2001). Second, we extend our work into an urban ecosystem, a new arena for testing riparian-stream concepts (Collins et al. 2000). Third, we couple measurements of microbial enzymatic capabilities with community respiration along a gradient in DOC chemical complexity to begin to assess the relationship between microbial functional diversity and ecosystem function (Chapin et al. 2000).

We found contrasting relationships between DOC concentrations, chemical complexity, and discharge in Sycamore Creek compared to the urban stream (Figure 50).

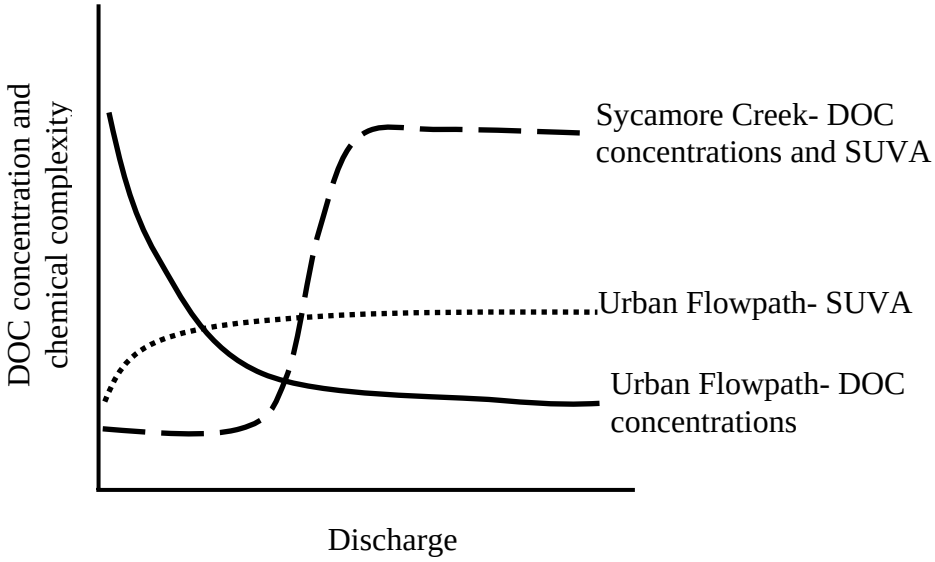

FIG. 50. Conceptual model linking urban and native desert stream ecosystems.

Increases in discharge in Sycamore Creek resulted from flooding, a period when terrestrial-aquatic linkages are strongest in the catchment. This increase in discharge elevated DOC quantity and complexity above baseflow values, and the trajectory of this relationship was a function of storm characteristics and long-term rainfall conditions, both of which are highly variable. In contrast, significant increases in discharge in the urban ecosystem were created by additions of ground water. Floods did occur, but were rare and relatively insignificant in controlling water chemistry. In the urban stream, DOC concentrations decreased as discharge increased along the flowpath, and chemical complexity was relatively unrelated, showing only a slight increase with discharge.

Underlying mechanisms driving these relationships between DOC chemistry and discharge have very different characteristics in the two systems, which have important implications for microbial communities living within them. In Sycamore Creek, variability in DOC chemistry in runoff was created by the climate regime, which also influences algal communities (another DOC source) persistence in the surface stream between flood events. High variability in DOC sources may create a sediment-associated microbial consortium that is genetically diverse and slow-growing (except where labile DOC is abundant), and yields spatially patchy community respiration rates. In contrast, patterns in DOC chemistry in the urban stream are created by shallow and deep groundwater additions that are chemically, spatially, and temporally consistent. We found average respiration rates were relatively consistent along the urban flowpath with the exception of the first site. At the same time, extracellular enzymes varied depending on sampling location and date. The consistency of this pattern in DOC concentrations

and chemical complexity may allow the microbial community to adjust or respond to changes in water quality to the point where community activity is maximized.

Finally, this work has shown the diversity of applications of a simple method for measuring chemical complexity. Although specific ultraviolet absorbancy (SUVA) is a measurement technique that has been used for many years, its application in ecological studies is relatively new. SUVA proved to be a useful tool for assessing DOC chemical complexity in our work, as it was variable enough to distinguish between samples from different sources and consistent enough that the numbers were meaningful. Microbial ecologists are always looking for the "silver bullet" for assessing organic matter quality. A simple measurement that can be used in many types of ecosystems to determine the relative quality of material in relation to microbial utilization is highly desirable. While we may never find one ideal measurement of DOC quality, SUVA is an easy, inexpensive measure of chemical complexity that appears to be ecologically relevant.

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