ORGANIC CARBON SUPPLY AND METABOLISM IN A SHALLOW GROUNDWATER ECOSYSTEM

Michelle A. Baker,[1] H. Maurice Valett,[2] and Clifford N. Dahm

Department of Biology, University of New Mexico, Albuquerque, New Mexico 87131 USA

Abstract. In groundwater ecosystems, in situ primary production is low, and metabolism depends on organic matter inputs from other regions of the catchment. Heterotrophic metabolism and biogeochemistry in the floodplain groundwater of a headwater catchment (Rio Calaveras, New Mexico, USA) were examined to address the following questions: (1) How do groundwater metabolism and biogeochemistry vary spatially and temporally? (2) What factors influence groundwater metabolism? (3) What is the energy source for groundwater metabolism?

At Rio Calaveras, surface discharge and water table elevation increased at the onset of spring snowmelt. Groundwater biogeochemical changes in response to snowmelt included increases in dissolved oxygen and dissolved organic carbon (DOC) concentrations. Dissolved organic carbon concentration then decreased exponentially with time, suggesting that newly saturated floodplain sediments were a major source of DOC. Organic matter content in seasonally saturated sediments averaged 3% by mass, and ~0.05 mg C/g dry sediment was water soluble. Microorganisms from these sediments were able to consume an average of 45% of the leached DOC. These results show that snowmelt imports DOC to groundwater and that a substantial amount can be consumed by biota. These results may be important ecologically if the growth and abundance of groundwater organisms are limited by DOC availability.

The influence on groundwater heterotrophic metabolism of DOC availability, inorganic nitrogen (N), inorganic phosphorus (P), temperature, and season were assessed using laboratory manipulations of aquifer sediments and seasonal measurements in field microcosms. Augmentation with DOC (10 mgC/L above background) nearly doubled respiration rate during base flow but did not influence respiration during snowmelt. In contrast, addition of N and P did not influence respiration at any time. Respiration rate during snowmelt was significantly higher than at base flow and was not influenced by any combination of DOC, N, P, or temperature. The hypothesis that groundwater metabolism is limited by DOC availability during base flow was supported. Hydrologic linkage between soils and groundwater represents a critical flux of DOC that supports metabolism in unconfined alluvial aquifers.

Key words: aquatic–terrestrial interface; dissolved organic carbon (DOC); groundwater; hydrologic controls; limitation of metabolism by DOC availability; metabolism; organic carbon cycling; region of seasonal saturation (RoSS); seasonal variation; shallow groundwater ecosystem; snowmelt.

Introduction

Understanding energy flow has been a major focus of research in ecosystem ecology since Raymond Lindeman (1942) published his seminal work, "The Trophic-Dynamic Aspect of Ecology." Over the years, ecologists have developed an understanding of organic matter cycling in a variety of terrestrial and aquatic ecosystems. Working with a headwater stream, Fisher and Likens (1973) emphasized that many ecosystems are open to exchange of materials and energy across ecosystem boundaries and that import and export vectors should be considered in order to better understand organic matter dynamics.

Although 97% of global liquid freshwater resides underground (Gibert et al. 1994), the ecology of groundwater ecosystems is still poorly understood and ecological principles have only recently been applied to studies of subsurface aquatic environments (e.g., Vervier and Gibert 1991, Marmonier et al. 1993, Gibert et al. 1994). Because water and solutes can have residence times in groundwater on the order of centuries to millennia (Fetter 1988), a classic view of groundwater is that of a closed ecosystem, isolated from interaction with surface environments (e.g., Ghiorse and Wilson 1988, Chapelle and Lovley 1990). In shallow groundwater, or local flow systems (sensu Toth 1963), residence times are shorter, and the open-system perspective of organic matter dynamics embraced by Odum (1956) and extended by Fisher and Likens

[1] Current address: Department of Biology, Utah State University, Logan, Utah 84322-5305 USA.
E-mail: mbaker@biology.usu.edu

[2] Current address: Department of Biology, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0406 USA.
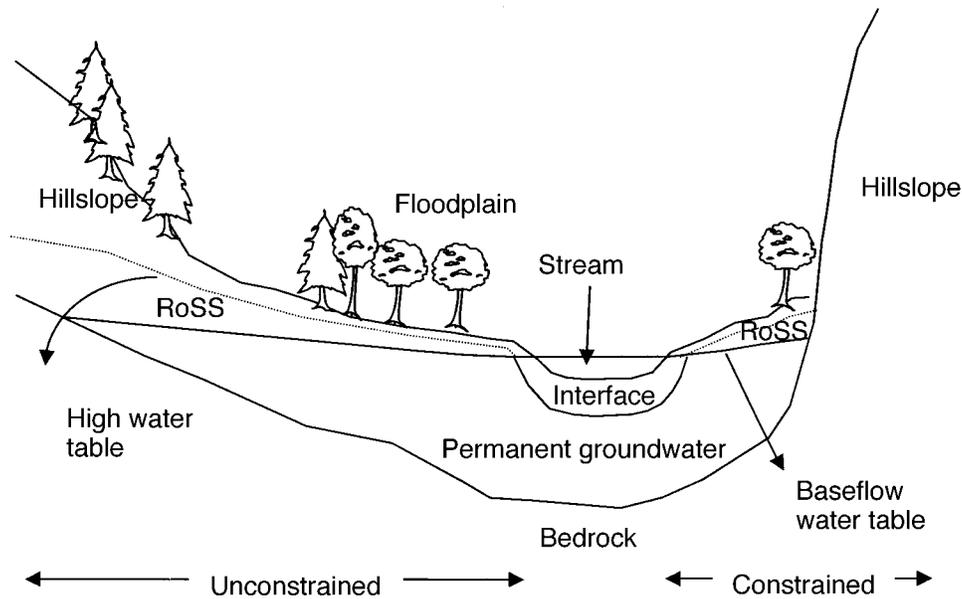
FIG. 1. Components of a hypothetical catchment. Ecosystem components include the surface stream, surface water/ groundwater interface, permanent alluvial groundwater, and the region of seasonal saturation (RoSS). The RoSS is defined as the portion of floodplain sediments that is seasonally saturated by a rising groundwater table (dashed line) during rainstorms and/or snowmelt. The left portion of the diagram represents the structure of an unconstrained reach where hillslope soils may contribute to the RoSS, and the right portion represents a constrained reach (sensu Gregory et al. 1991) where exposed bedrock outcrops restrict hillslope–floodplain interaction.

(1973) may hold great promise for understanding energy flow where metabolism may rely on material transport from the surface.

Groundwater ecosystems are constantly dark, thus photosynthesis does not occur in situ, organic matter standing stocks are low relative to surface ecosystems (Ghiorse and Wilson 1988, Chapelle and Lovley 1990), and biological productivity in the subsurface is often limited by organic matter availability (Jones 1995). Because subsurface rates of chemoautotrophic primary production are low (Chapelle and Lovley 1990, Jones et al. 1994), groundwater food webs are usually heterotrophic (sensu Odum 1956) and may rely on import of organic matter from surface environments (Jones et al. 1995). Therefore, hydrologic connectivity between the surface and subsurface is likely of great importance to energy flow in shallow groundwater ecosystems.

Recognition that surface water–groundwater exchange influences biological responses in both streams and shallow groundwater has led to a considerable body of research directed at understanding surface water–groundwater (SW/GW) interactions in recent years (see reviews by Jones and Holmes [1996], Brunke and Gonser [1997], Boulton et al. [1998]). In the context of organic matter cycling, many studies have addressed the influence of groundwater on streams (e.g., Wallis et al. 1981, Rutherford and Hynes 1987, Fiebig and Lock 1991, Fiebig 1995), and an increasing emphasis has been placed on understanding the functioning of the SW/GW interface or hyporheic zone (sensu Triska et al. 1989).

Stream ecologists have shown that SW/GW interactions can supply organic matter to subsurface organisms. For example, Jones et al. (1995) showed that respiration in the SW/GW interface of Sycamore Creek, Arizona, USA is fueled by stream algal production. In the Steina River, Germany, and in the Necker River, Switzerland, respiration in the SW/GW interface is primarily supported by particulate organic matter buried during floods (Pusch and Schwoerbel 1994, Nageli et al. 1995). These studies highlight the importance of SW/GW exchange to subsurface energy flow.

In many catchments, the SW/GW interface may account for only a small portion of the saturated subsurface (Morrice et al. 1997, Wroblicky et al. 1998), and in these systems it is unlikely that SW/GW interaction provides all of the organic matter required to support subsurface heterotrophic metabolism. Interactions between alluvial groundwater and overlying unsaturated sediments may be important to subsurface ecology, but these terrestrial–aquatic interactions are less well understood (Danielopol 1980).

The region of seasonal saturation (RoSS) is defined as the sediments overlying the unconfined alluvial groundwater ecosystem that are seasonally saturated during wet periods (Fig. 1). We hypothesize that the RoSS represents an interactive component of catchments that is located at a terrestrial–aquatic ecotone

and that the RoSS plays a unique and regulatory role in the structure and functioning of shallow groundwater ecosystems. We define the vertical boundaries of the RoSS to include the sediments of the vadose (unsaturated) zone, which is delimited by the lowest mean water table elevation during base flow and the highest mean water table elevation observed during periods of high flow, including rain storms and snowmelt. Laterally, the RoSS includes the entire extent of the floodplain defined as valley floor width (Gregory et al. 1991), and in many unconstrained systems may also include alluvium within hillslopes up to the watershed boundaries (Fig. 1). We propose that hydrologic integration of the RoSS and shallow groundwater supplies organic matter for heterotrophic metabolism.

Mountain catchment model

The hydrology of mountain catchments is often dominated by spring snowmelt (e.g., Bales and Harrington 1995). In these catchments, snowmelt results in an increase in water table elevation and surface water discharge. Previous research has shown that the RoSS contains high levels of dissolved organic carbon (DOC) that can be flushed into both surface and groundwater (Hornberger et al. 1994, Boyer et al. 1997, Mulholland and Hill 1997, Hinton et al. 1998). A characteristic of the flushing response is a peak in DOC concentration on the rising limb of the hydrograph, followed by a logarithmic decline in DOC with time (Hornberger et al. 1994, Boyer et al. 1996, 1997). These recent papers highlight the role of the RoSS in DOC export to streams. Our study relates the RoSS to DOC supply for groundwater metabolism, and provides insight on how aquatic–terrestrial interactions may influence energy flow and biogeochemistry in headwater catchments.

We investigated the shallow alluvial aquifer associated with the Rio Calaveras, a semiarid mountain catchment in New Mexico, as a model ecosystem for a study of the influence of the RoSS on groundwater organic carbon cycling. We hypothesized that hydrologic fluxes between the RoSS and saturated zone are critical to heterotrophic metabolism in near-stream groundwater.

Study Site

Rio Calaveras is a first order, spring-fed, perennial stream at 2475 m elevation in the Jemez Mountains, New Mexico (35°56′ N, 106°42′ W). Catchment area is 3760 ha, and mean stream gradient is 1.3%. Alluvium is a silty sand (Wroblicky et al. 1998) derived from welded Bandelier tuff formed after the eruption of the Valles Caldera 1.2 yr BP (Dane and Bachman 1965). Average grain size of alluvium is 1–2 mm and alluvial depth ranges from 1–3 m (Wroblicky 1995). Soils are frigid–mesic eutroboralfs and haploborolls. The catchment is in a mixed conifer forest; dominant tree species include Douglas fir (*Pseudotsuga menziesii*), white fir (*Abies concolor*), blue spruce (*Picea pungens*), and ponderosa pine (*Pinus ponderosa*). The stream canopy is mostly open, and there is limited overstory riparian vegetation. Climate at the study site is semiarid, with mean annual precipitation of 450 mm (National Weather Service, Los Alamos, New Mexico, USA). Most of the precipitation occurs as rain during monsoon thunderstorms during July–September and as snow during November–March. Stream discharge and groundwater table elevation respond to precipitation inputs from rain and snowmelt. Stream discharge ranges from ~1 L/s during autumn base flow to >100 L/s during spring snowmelt. Subsurface water during base flow is characterized by low dissolved inorganic nitrogen (0.137–0.167 mg N/L), soluble reactive phosphorus (mean = 0.008 mg P/L), and DOC ranging 1.27–1.58 mg C/L (Valett et al. 1996). In addition, baseflow groundwater is anoxic or hypoxic, with dissolved oxygen (DO) concentration ranging 0.0–0.95 mg DO/L (Valett et al. 1996). Because subsurface anoxia and hypoxia are common at Rio Calaveras (Baker et al. 1999, 2000, Valett et al. 1996, 1997), DO can be used as a tracer of surface–subsurface linkage, because it is transported to the saturated zone during snowmelt and storms.

Instrumentation

Rio Calaveras was instrumented with two Palmer–Bowlus (Plasti-Fab, Oregon, USA) plastic flumes (installed November 1995); one was located several meters below the perennial spring source, and the second one was located 120 m downstream (Fig. 2A). Twenty-four groundwater sampling wells were installed in five transects perpendicular to the stream (hereafter referred to as interface wells; Fig. 2A). An additional 24 wells were installed in the floodplain and near the hillslope edges (referred to as floodplain wells) at various distances (3–20 m) from the active stream channel (Fig. 2A). All wells were constructed of 5 cm inner diameter polyvinyl chloride (PVC) pipe with 50-cm screen lengths (25-μm slots), capped on the bottom. Wells were installed 30–50 cm below the baseflow water table or the stream bottom, using either a hand or gasoline-powered auger. Well holes were packed with silica sand to several cm above the well screen, backfilled with native fill, and capped with bentonite to prevent infiltration of water along the well casing (Valett et al. 1996). The interface wells were installed in 1991–1992. An additional 14 floodplain wells were installed in autumn 1993, and 10 floodplain wells were installed in autumn 1995.

Methods

Catchment hydrology, biogeochemistry, and hydrologic linkages among the RoSS, groundwater, and stream

The aerial extent of catchment subsystems, including the active stream channel, surface water–ground water (SW/GW) interface, and the region of seasonal satu-
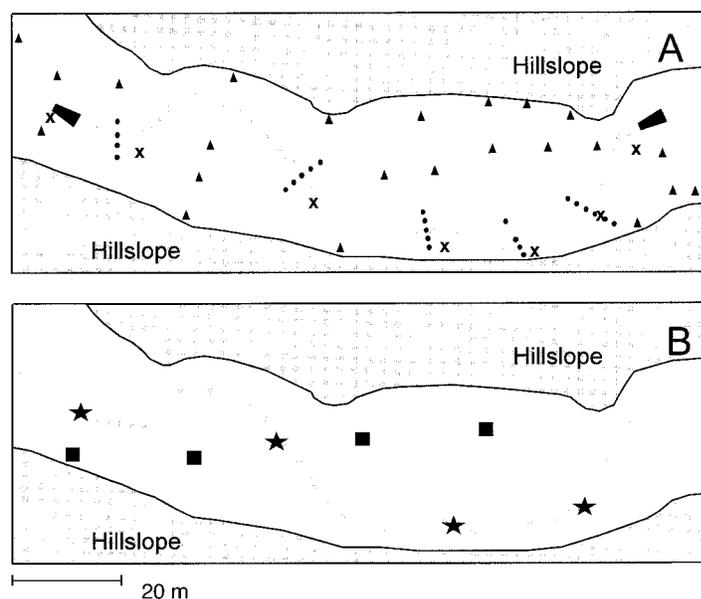
FIG. 2. (A) Map of Rio Calaveras study catchment showing locations of interface wells (circles), floodplain wells (triangles), flumes (trapezoids), surface stream (gray line), and stream sampling locations (×). Surface flow is from right to left. Hillslopes are represented by the shaded areas and the floodplain is represented by the white area. Well symbols are not drawn to scale. (B) Locations of field microcosms used for measuring heterotrophic metabolism in floodplain locations (squares) and interface locations (stars). Microcosms were buried 30–50 cm below the baseflow water table.

ration (RoSS) were determined for base flow and snowmelt conditions. The active stream channel was surveyed and its area calculated (Wroblicky 1995). Wroblicky et al. (1998) used a two-dimensional hydrologic model (MODFLOW) to define the SW/GW interface (i.e., lateral hyporheic area) at Rio Calaveras as the area bounded by water moving from the stream into the subsurface and returning to the stream in ≤10 d. At Rio Calaveras, the RoSS was defined as that part of the floodplain bounded by the hillslopes and not occupied by the active stream channel or SW/GW interface.

Field sampling of system hydrology and biogeochemistry occurred twice per month during February 1995–August 1996 and monthly during August 1996–October 1997. On each visit, surface water discharge at the downstream end of the reach was measured by using either a solute (chloride) injection (Stream Solute Workshop 1990) or stage measurements in the flumes (after November 1995). Water table elevation was measured in each well with an electric water level meter (Solinst, Georgetown, Ontario, Canada). Dissolved oxygen and temperature were measured at 5–7 stream sampling stations (Fig. 2A) and in each well using a YSI 55 DO meter equipped for low dissolved oxygen (DO) measurements (i.e., thin (0.013-mm) membranes [YSI, Yellow Springs, Ohio, USA]). Water samples were collected in acid-washed high-density polyethylene bottles from the surface stream stations as grab samples and from the wells with a bailer. Samples were stored on ice until returned to the lab where they were filtered using glass microfiber filters (Whatman Glass Fiber Filter, size F [GF/F], 0.7 μm pore size [Whatman, Cambridge, UK]). Samples were refrigerated or frozen until analysis. Dissolved organic carbon was deter-

mined by wet persulfate oxidation on an Oceanography International Model 700 Total Organic Carbon analyzer (College Station, Texas, USA; Menzel and Vacarro 1964).

Repeated-measures analysis of variance (ANOVA, Proc GLM, SAS Institute 1985) was used to indicate the influence of location (stream water, interface water, floodplain water) and season (repeated factor: premelt, snowmelt, and base flow) on the dependent variables DO, dissolved organic carbon (DOC), and water table elevation. Differences among levels of a factor were considered statistically significant at $P \leq 0.05$, and Tukey multiple-comparison tests were used to identify the differences among locations. Wilks' λ was used to identify differences among levels of the repeated factor (i.e., seasonal differences, SAS Institute 1985). System hydrology was used to define seasons as follows: premelt included days during which the water table elevation and stream discharge were rising (late February–early May); snowmelt was defined as days when discharge and water table elevation peaked (May–June); and base flow included days (June–February) during which the water table elevation and discharge were decreasing and then stabilizing at lower values than were observed during snowmelt.

If DOC is flushed from the RoSS at the onset of snowmelt, a semilogarithmic relationship should exist between DOC and time, as observed in other mountain catchments (Hornberger et al. 1994, Boyer et al. 1997). Furthermore, DO imported during snowmelt may be consumed by chemical processes and by biota during organic matter decomposition, producing a rapid decline in groundwater oxygen content. We used linear regression to assess the relationship between log DO or log DOC and time (SAS Institute 1995). The neg-

ative inverse of the slope of the line describing this relationship is the time constant (measured in no. days) of the flushing event (Boyer et al. 1997). The time constant represents the amount of time that hydrologic linkage between the RoSS and groundwater may influence biogeochemical and ecological processes. In this paper, we use the time constant as a proxy for DOC residence time.

Characterization of sediment organic matter content

Nine floodplain sediment cores were obtained from the Rio Calaveras catchment by hand-driving a split-spoon sampler to depths of 0–150 cm below the ground surface (to ~50 cm below the baseflow water table). Sediment organic matter (OM) content at ~2.5-cm intervals was determined by mass loss on combustion at 500°C for 2 h (ash-free dry mass, AFDM). Dissolved organic carbon was extracted from samples at 12.5-cm intervals (composited from homogenized 2.5-cm subsamples) by incubating 50 g (wet mass) sediment in 100 mL of deionized water with shaking for 15 min (Nelson et al. 1994). Subsamples (50 mL) were centrifuged at 3000 rpm for 15 minutes, and supernatant was filtered first through GF/F glass microfiber filters then through deionized water-rinsed 0.22 μm nitrocellulose membrane filters. The filtrate was split into two 20-mL subsamples used to determine the quantity and relative bioavailability of extracted DOC.

Dissolved organic carbon concentration was measured following procedures we have described. Relative bioavailability was assayed using a microbial inoculation technique (Marmonier et al. 1995). A microbial solution was prepared by backflushing membrane filters that were originally used to filter the 50-mL samples, with 40 mL of filter-sterilized deionized water. We inoculated each 20-mL subsample of filtered water with 0.2 mL of this microbial solution. Controls consisted of (1) uninoculated DOC samples, (2) inoculated deionized water, and (3) sterile deionized water. Samples were stored in sealed 50-mL Erlenmeyer flasks and incubated at 22°C in the dark for one month. Following incubation, samples were refiltered through rinsed membrane filters with pore size of 0.22 μm. Dissolved organic carbon content of the filtrate was measured, and bioavailable DOC was determined as the difference between pre- and postincubation DOC concentrations. Data for bioavailable DOC are presented as percentage of the preincubation DOC concentration. The inoculated deionized water served as blanks, and DOC resulting from inoculation was subtracted from the DOC concentration in samples. Changes in inoculated DOC and sterile water following incubation were within analytical error (±2%) of our measurements.

Vertical structure of floodplain sediment organic matter was investigated by comparing each organic matter parameter (total organic matter content, DOC, and bioavailable DOC) in three defined layers: soil or-

ganic horizon (0–20 cm below surface), RoSS (21–100 cm below surface), and permanently saturated sediments as defined by the mean baseflow water table elevation (>100 cm below surface). One-way ANOVA and Tukey multiple comparison tests were used to test the influence of sediment depth on organic matter content, water soluble organic carbon and labile water-soluble organic carbon. Differences were considered statistically significant at $P \leq 0.05$.

Heterotrophic metabolism

Field microcosms for measuring heterotrophic metabolism were made from clear Plexiglas tubes (20 cm long, 7 cm diameter; Fig. 3A). Tube interior was roughened with 100-grit sandpaper to prevent preferential flow along the inner chamber walls. Tubes were filled with floodplain alluvium obtained from a single location 30–50 cm below the baseflow water table upstream of the study reach at Rio Calaveras. Alluvial material was sieved to 1–2 mm grain size, washed with deionized water, and dried prior to being packed into the microcosms. Alluvial organic matter content (as ash-free dry mass) was ~1% by mass, and porosity was $37 \pm 0.8\%$ ($n = 3$). Prepared alluvium was placed into each microcosm, and Plexiglas separators (drilled with 1.5-mm holes) were placed on each end to secure sediments within the microcosms (Fig. 3A). The remaining length of the tube (14 cm) was backfilled with prepared alluvium (Fig. 3A), and nylon window screen (1 mm diameter mesh) was attached to the tube ends to secure backfilled sediment and stabilize microcosm contents.

On 18 October 1996, microcosms were installed in subsurface locations at Rio Calaveras (Fig. 2B). Interface microcosms were placed 30–50 cm below the stream bottom in four locations, with microcosm openings oriented parallel to stream flow. Three microcosms were installed in one location, and the remaining three interface locations each contained one microcosm. Floodplain microcosms were installed in four locations several meters away from the stream, 30–50 cm below the baseflow water table (1–2 m below the ground surface), and oriented parallel to the direction of groundwater flow as determined from a water table map. As with interface locations, one floodplain location contained three microcosms, while three locations each contained one microcosm (Fig. 2B). Burial of multiple microcosms in a single location allowed us to determine within-location variability and assess the validity of the respirometry method. All measurements made on the three microcosms buried in single locations were averaged to avoid pseudoreplication (sensu Hurlbert 1984) when performing statistical analyses to test for location and time effects.

Microcosms were removed for measurement of heterotrophic metabolism on four dates: 8 March 1997 (winter), 24 April 1997 (spring), 17 July 1997 (summer), and 23 October 1997 (autumn). Microcosms were excavated and stored in sealed plastic bags on ice until
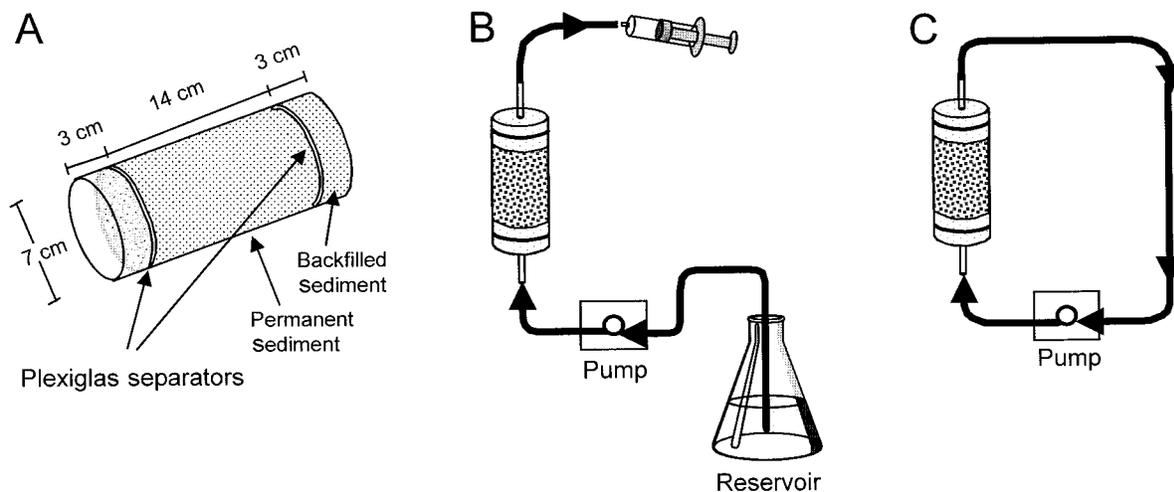
FIG. 3. (A) Schematic representation of microcosm used to measure subsurface heterotrophic metabolism. The figure also depicts the recirculation apparatus during (B) sampling mode, and (C) recirculation mode. Arrows indicate flow direction.

returned to the lab for analysis. Water for use in metabolism measurements was obtained from the surface stream (for interface microcosms) and from a groundwater well (for floodplain microcosms). Metabolism measurements were made within two to three days of excavation, and the microcosms were reburied within a week of excavation. Microcosms were stored at 4°C when not in use.

Metabolic rates were measured in the laboratory using a recirculation apparatus (adapted from Pusch and Schwoerbel 1994 and Jones 1995). All equipment was sterilized prior to measurements using a 15% bleach solution. Metabolism measurements were done at constant temperature reflecting the average subsurface temperature at the site on the day of excavation. Incubation temperatures were 5°C for microcosms collected in winter and spring, 14°C during summer, and 10°C during autumn. Water for recirculation was degassed by constant bubbling with N_2 to bring DO concentrations to values reflecting in situ conditions. Just prior to metabolism measurement, the sediment between the Plexiglas separators and microcosm ends was removed and stored in a sterile plastic bag. These sediments were subsampled for organic matter content, extractable DOC, and bioavailable DOC. The ends of the tubes were fitted with washed (deionized water) polyester quilt batting followed by ground plastic stoppers. Microcosms were attached vertically to the recirculation apparatus (Fig. 3B) and were connected to the water reservoir via Tygon R3603 beverage grade tubing (9 mm outer diameter, 5 mm inner diameter; Saint-Gobain Performance Plastics, Akron, Ohio USA).

Heterotrophic metabolic rates were determined by measuring carbon dioxide (CO_2) and methane (CH_4) generation and DO consumption during microcosm incubations. The general method entailed taking initial

dissolved gas samples following microcosm preparation and a series of samples taken over the course of the incubation during which water was continuously recycled through the microcosms.

Initially, water was pumped vertically through the microcosms at a rate of 1.5 mL/min using a peristaltic cartridge pump (Manostat, New York, New York, USA). Tubing inside the pump was Tygon R1000 peristaltic pump tubing (9 mm outer diameter, 5 mm inner diameter). All tubing types and connectors were selected to minimize gas exchange. We confirmed that no gas was exchanged across the tubing by running $CO_2 + CH_4$ saturated deionized water through the recirculation apparatus for 8 h, over which time we observed no significant change (determined using linear regression) in gas concentrations. Water used in metabolism incubations was allowed to purge through the microcosm outlet for 1.5 h to remove any resident interstitial water. After purging, water at the outlet was collected for initial samples of dissolved CO_2, DO, and CH_4 by attaching a 15-mL nylon syringe to the microcosm outlet (Fig. 3B). Circulating water was collected by allowing pump pressure to displace the syringe plunger. Free dissolved CO_2 was extracted from 5-mL samples using a syringe equilibration technique (Kling et al. 1992) and was measured using a gas chromatograph with a thermal conductivity detector (Buck Scientific, Pennsylvania, USA). Dissolved oxygen was measured on 5-mL samples using a modified microwinkler technique (Wetzel and Likens 1991). To prevent atmospheric O_2 contamination, fixed samples were acidified within 5 min of collection and transferred to cleaned 8-mL serum vials prior to titration. Dissolved CH_4 samples (1–2 mL) were transferred to cleaned, evacuated 3.5-mL Vacutainer vials. Methane was released into the vial headspace by shaking and was mea-

sured using a Shimadzu gas chromatograph with flame ionization detector (Dahm et al. 1991).

Following sampling, the water in the microcosms was allowed to recirculate by attaching the inlet tube to the outlet tube (Fig. 3C). During recirculation, dissolved gas concentrations should change as a result of respiration. The water was allowed to recirculate for 60–90 min, and then dissolved gases were sampled. Four or five samples were taken every 60–90 min during incubations that lasted 240–400 min. Gas concentrations in the water reservoir were also measured at each sampling time to account for changes in gas concentration within the microcosms as a result of water replacement during sampling. Total respiration was calculated as the change in CO_2-C + CH_4-C with time. Aerobic respiration was calculated as the change in DO with time. The respiratory quotient (RQ) was determined as the molar ratio of CO_2:O_2 (Wetzel 1983). A molar ratio close to one indicates that most of the metabolism is via aerobic respiration. A molar ratio much greater than one is indicative of anaerobic metabolism.

A repeated-measures ANOVA followed by Tukey's multiple comparisons tested for differences in metabolic rates between interface and floodplain locations. Seasonal differences (time was the repeated variable) were identified by Wilks' λ (SAS Institute 1985). Because two hydrologic regimes were studied, base flow and snowmelt, a paired t test tested the hypothesis that total heterotrophic metabolism differed between base flow (winter, summer, and autumn measurements, averaged by location, $n = 8$) and snowmelt (spring measurement, $n = 8$ locations) periods.

Repeated-measures ANOVA followed by Tukey's multiple comparison tests were used to determine the influence of location (interface or floodplain) and season (spring, summer, and autumn) on microcosm organic matter content, extractable DOC, and bioavailable DOC. Season was the repeated variable in this analysis, and seasonal differences were identified using Wilks' λ. Differences were considered statistically significant at $P \leq 0.05$. Finally, a two-way ANOVA and Tukey's multiple comparisons (proc GLM, SAS Institute 1985) were used to determine the influence of location (floodplain or interface) and season on respiratory quotient. Repeated-measures ANOVA was not used for this data set due to its unbalanced design.

Environmental parameters that best explain variation in metabolic rates measured in field microcosms were assessed with a multiple-regression analysis. The environmental variables we tested were water table elevation, DOC, DO, temperature in the nearest well on the day of excavation, incubation temperature, the percentage of organic matter, extracted DOC, and bioavailable extracted DOC in microcosms. Factors were entered into the model using stepwise linear regression (SAS Institute 1985) with an inclusion criterion of α ≤ 0.1.

Factors influencing heterotrophic metabolism

To experimentally assess the influence of DOC, dissolved inorganic nitrogen (DIN), soluble reactive phosphorus (SRP), season, and incubation temperature on total respiration, aquifer sediments were obtained from below the water table at a single location upstream of the study reach at Rio Calaveras. Mean porosity of the sediment was 35%, and organic matter content was ~1%. Water for incubations was obtained from a groundwater well using a peristaltic pump, and was degassed as we have described. Sediments were encased in a tube comparable to that used for field microcosms, topped with degassed water, and connected to the water source. Resident interstitial water was flushed out of the tubes, and five replicates were used in each experimental treatment. Experimental manipulation of baseflow sediments included (1) control (no additions), (2) added DOC, (3) added DIN, (4) added SRP, (5) added DOC and DIN, and (6) added DOC and SRP. Dissolved organic carbon (as equal parts dextrose and sodium acetate carbon) was added to inlet water to increase the total DOC concentration to 10 mg C/L above background. Dissolved inorganic nitrogen as NH_4-N was increased to 2 mg NH_4-N/L above background, and SRP was increased to 0.2 mg PO_4-P/L above background, and reflect the highest concentrations observed in our long-term data record. Baseflow incubation temperature was 22°C. The nutrient addition experiments were repeated using sediments obtained during spring snowmelt. Incubations were performed at 22°C and 5°C. In all experiments, total respiration was measured as the change in CO_2 concentration with time. No changes in dissolved CH_4 were observed during the experiments, so these data were not included in the calculation of total heterotrophic metabolism.

One-way ANOVA followed by Fisher's multiple comparisons (SAS Institute 1985) was used to compare among nutrient additions during baseflow experiments. Two-way ANOVA and Fisher's multiple comparison tests (SAS Institute 1985) were used to test for differences in rate of heterotrophic metabolism between seasons (base flow and snowmelt) and carbon addition (+DOC or no addition). The same statistical analysis was also used to determine the influence of carbon addition (+DOC or no addition) and temperature (5°C and 22°C) on heterotrophic metabolic rates during snowmelt. In all tests, differences were considered statistically significant at $P \leq 0.05$.

RESULTS

Catchment hydrology

During this study, snowmelt was the predominant hydrologic event in the surface stream (Fig. 4A). The highest discharge (102 L/s) was observed on 2 May 1995, and the stream did not return to base flow (~1.5 L/s) until October 1995 (Fig. 4A). A severe drought occurred from winter 1995–summer 1996, when only
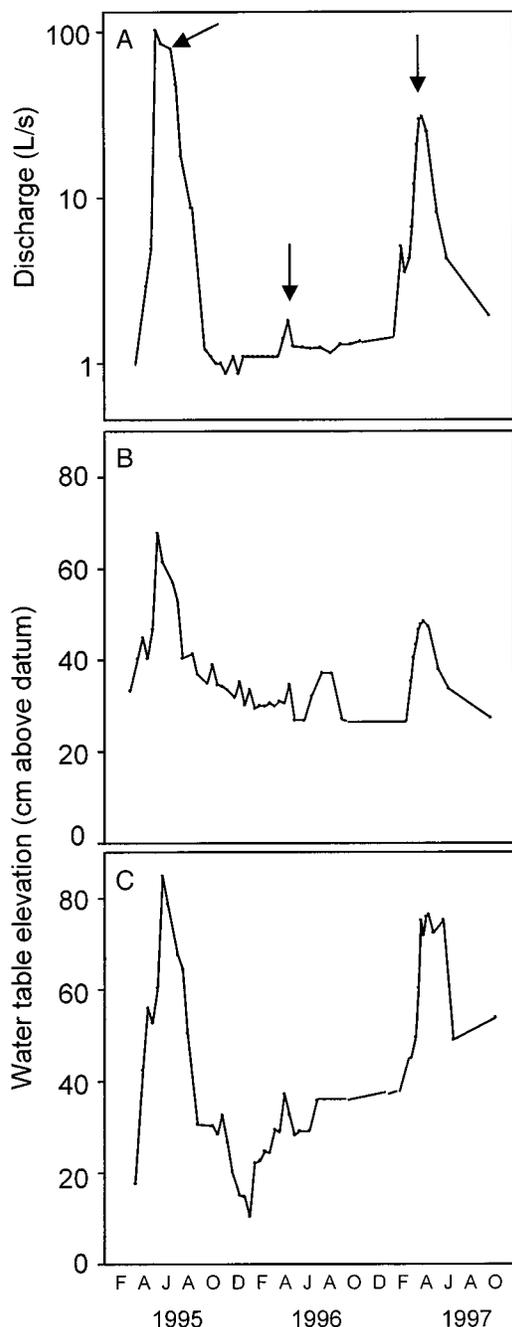
FIG. 4. Snowmelt influence on (A) surface water discharge, and water table elevation for (B) interface wells and (C) floodplain wells, during February 1995–October 1997. Snowmelt occurred with varying magnitudes in May of each year (arrows).

23 mm of precipitation was recorded during October 1995–May 1996 (National Weather Service, Los Alamos, New Mexico, USA, and on-site weather station). As a result of the lack of precipitation, peak discharge during water year 1996 was only 1.8 L/s on 7 May 1996 and the stream returned to base flow within two

weeks (Fig. 4A). During the 1997 water year, maximum discharge (30.8 L/s) occurred on 20 May 1997 (Fig. 4A).

Water table elevation in interface and floodplain wells significantly increased in response to spring snowmelt in all years (repeated measures ANOVA, Tukey, $P < 0.001$; Fig. 4B, C, Table 1). During 1995, the water level increased nearly 40 cm and 70 cm in interface and floodplain wells, respectively (Fig. 4B, C). In 1996, water table elevation peaked during the summer, and in spring 1997 the water table increased 20 and 30 cm for interface and floodplain wells, respectively (Fig. 4B, C). Differences in water table elevation between floodplain and interface locations were not statistically significant (ANOVA $P > 0.05$, Table 1).

On an areal basis, region of seasonal saturation (RoSS) sediments (2498 m^2) accounted for 94.9% of the study catchment area during snowmelt. In contrast, Wroblicky et al. (1998) showed that the surface water–ground water (SW/GW) interface accounted for only 0.066% (1.73 m^2) at this time. The RoSS remained partially linked to the saturated zone through most of the summer months; for example, the water table was elevated above baseflow conditions for 181 d in 1997 (Fig. 4B, C). During autumn base flow, the RoSS was not saturated, except only transiently during rainstorms, when the water table may rise several centimeters for a few days at a time (data not shown). Under baseflow conditions, the SW/GW interface had an area of 4.07 m^2 (Wroblicky et al. 1998), accounting for 0.15% of catchment area.

Biogeochemical dynamics

Dissolved organic carbon in the surface stream peaked prior to maximum discharge during snowmelt of each year (Fig. 5A). In water year 1995, the highest mean DOC concentration (7.4 mg C/L) was observed on 20 March, approximately six weeks prior to maximum discharge. In 1996, a high DOC concentration of 2.5 mg C/L occurred five weeks before maximum discharge, and in 1997 peak DOC (3.4 mg C/L) was observed six weeks before maximum runoff (Fig. 5A). Repeated-measures ANOVA indicated that season was a significant factor influencing stream DOC concentration (Table 1). In nondrought years (1995 and 1997), DOC concentration prior to and during snowmelt were significantly higher than the concentration observed during base flow (repeated measures ANOVA, Wilks' λ, $P < 0.05$, Tables 1 and 2).

DOC response in the surface stream during snowmelt exhibited a typical flushing response, as evidenced by logarithmic declines in mean DOC concentration with time (Fig. 5A, Table 3). The time constant for DOC flushing ([slope of the line relating log DOC vs. time]$^{-1}$) was 251, 163, and 680 d for 1995, 1996, and 1997, respectively (Fig. 5A, Table 3).

There was a significant increase in DOC concentration of 1–2 mg C/L above mean baseflow concentration

TABLE 1. Repeated-measures analysis of variance for biogeochemistry and water table elevation in three water years, 1995–1997.

	Mean square			F statistic		
Year	Location	Season	Interaction	Location	Season	Interaction
Dissolved organic carbon						
1995	0.511	15.745	1.506	0.43[NS]	38.75***	3.71*
1996	16.676	0.920	0.915	2.23[NS]	2.15[NS]	2.13[NS]
1997	0.218	0.729	0.242	0.51[NS]	6.74*	2.24[NS]
Dissolved oxygen						
1995	224.752	10.757	3.869	52.79***	11.00**	3.96*
1996	265.552	18.286	2.972	42.66***	23.04***	3.75*
1997	129.101	5.319	0.996	30.05***	3.91*	0.73[NS]
Water table elevation						
1995	0.174	1.048	0.118	1.713[NS]	154.14***	17.35***
1996	0.013	0.011	0.000	0.01[NS]	15.76***	0.60[NS]
1997	1.913	0.543	0.043	0.85[NS]	52.74***	4.2*

Note: Location (stream water, interface, or floodplain groundwater) is the independent variable; season (premelt, snowmelt, base flow) is the repeated variable.
* $P = 0.05$, ** $P \leq 0.001$, *** $P \leq 0.0001$; NS, $P \geq 0.05$.

in both well types during premelt of nondrought years (repeated measures ANOVA, $P < 0.05$; Fig. 5B, C, Tables 1 and 2). Similar to stream water responses, the DOC maximum generally occurred several weeks prior to highest water table elevation and peak surface water discharge (Fig. 5B, C). In many wells (42%), DOC response during snowmelt exhibited a typical flushing response, as evidenced by logarithmic declines in DOC concentration with time (Fig. 5B, C, Table 3). The time constants for DOC flushing ranged 56–550 d (Fig. 5B, C, Table 3).

Dissolved oxygen was always significantly higher in surface water compared to either groundwater type (Tables 1 and 2). During base flow 1995, interface groundwater had significantly lower DO levels than floodplain groundwater (Tables 1 and 2). Dissolved oxygen in interface and floodplain groundwater also increased significantly during snowmelt of all years (Tables 1 and 2). Dissolved oxygen concentration indicated a logarithmic decline following snowmelt import in 62% of wells (Fig. 6A, B, Table 3). Time constants for DO decline ranged 42–550 d (Table 3).

Characterization of organic matter content in the RoSS

Highest organic matter content, 25% by mass, was observed in the soil organic horizon, but organic matter content varied greatly with depth below the ground surface (Fig. 7A). Mean organic matter in the soil organic horizon (0–20 cm below the ground surface) was 7.8% and was 2.8% and 1% by mass in the RoSS and the permanently saturated zone, respectively (Fig. 7A). Differences among all three sediment layers were statistically significant (ANOVA, Tukey, $P = 0.001$).

Extractable DOC was present at all sediment depths and there were no significant differences in the amount of DOC leached from each depth (Fig. 7B). A mean value of 0.04 mg C/g dry sediment was leached from RoSS sediments, and 0.07 mg C/g dry sediment was leached from the entire unsaturated zone (RoSS + organic horizon; Fig. 7B). The extracted DOC was consumed by resident microbiota in laboratory assays (Fig. 7C). The mean value of bioavailable DOC was 45% of the initial DOC concentration, and there were no significant differences among sediment depths (Fig. 7C).

Metabolic consequences of hydrologic linkages among the RoSS, groundwater, and stream

Total heterotrophic metabolism did not differ significantly between interface and floodplain locations (repeated measures ANOVA $P = 0.54$; Table 4). In addition, the repeated measures ANOVA did not detect seasonal differences in total heterotrophic metabolic rates ($P = 0.14$; Table 4). When the data were grouped by hydrologic regime, total heterotrophic metabolism was significantly higher during snowmelt compared to base flow (paired t test $P = 0.002$; Fig. 8). Total heterotrophic metabolism ranged from 0.084 mg C·(L sediment)$^{-1}$·h^{-1} during winter to 0.470 ± 0.094 mg C·(L sediment)$^{-1}$·h^{-1} during spring in interface microcosms, and ranged from 0.212 ± 0.124 mg C·(L sediment)$^{-1}$·h^{-1} during autumn to 0.513 ± 0.115 mg C·(L sediment)$^{-1}$·h^{-1} in summer in floodplain microcosms (Table 4). Aerobic respiration rates did not differ significantly between locations or flow regimes (repeated measures ANOVA $P > 0.05$; Table 4). Methanogenesis did not occur in either location during winter, and the rate of change in CH_4 during incubations in other seasons was $\leq 1\%$ of the rate of change in CO_2 in the microcosms in which it was observed. In all cases, the respiratory quotient (RQ, CO_2:O_2 molar ratio) was ≥ 1 (Table 4). The RQ was lowest during winter and highest during summer in both groundwater locations (Table 4).

Organic matter content in microcosms did not differ significantly between locations or among seasons (repeated measures ANOVA $P > 0.05$; Table 5). Mean organic matter content in microcosms was 1% (Table 5). Extractable DOC in microcosms ranged 0.011–
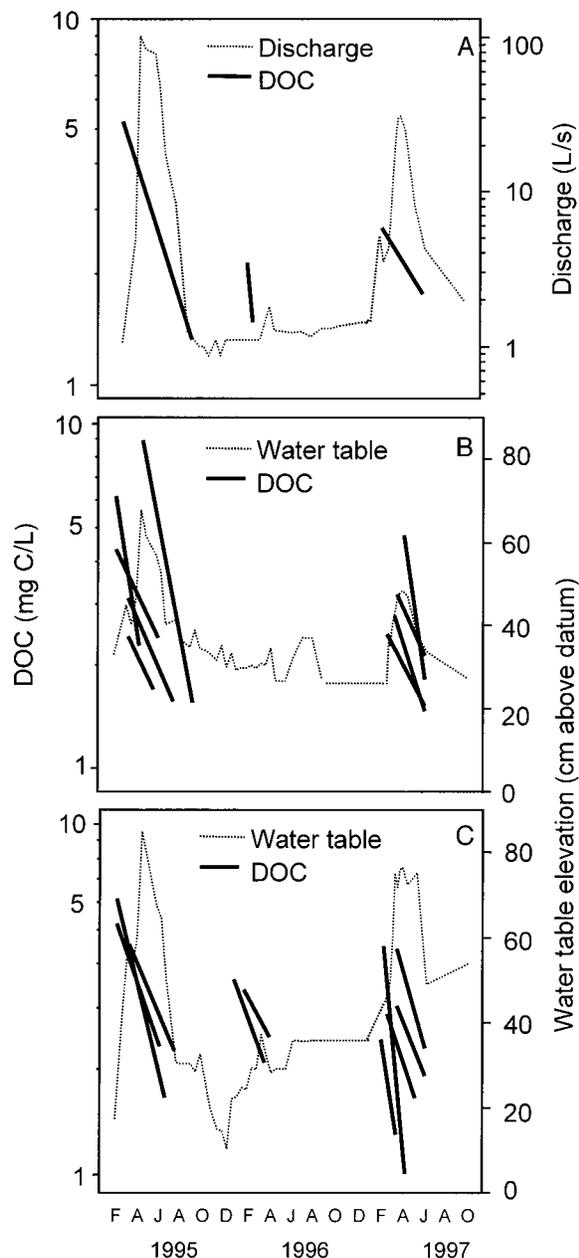
FIG. 5. Dissolved organic carbon flushing responses (bold lines) during the study period (February 1995–October 1997) for (A) surface water, (B) interface wells, and (C) floodplain wells. Dashed lines in each panel represent hydrologic data shown in Fig. 4. Bold lines are best-fit regression lines ($P <$ 0.05) describing the relationship between individual measures of log(DOC) and time. For groundwater [panels (B) and (C)], bold lines represent the regression lines for a single well, and individual sample points are not shown for clarity. Regression statistics are given in Table 3.

0.019 mg C/g dry sediment, and 50–60% of the DOC leached from microcosm sediments was bioavailable (Table 5).

According to multiple regression analysis, the best predictors of total respiration were DO concentration in the nearest well (parameter estimate = -0.180), percentage of bioavailable DOC measured in the microcosm sediment (parameter estimate = 1.783), and water table elevation in the nearest well (parameter estimate = 0.185; $r^2 = 0.67$; $P = 0.0578$; Table 6).

Factors influencing heterotrophic metabolism

Experimental addition of DOC to floodplain sediments obtained during base flow significantly increased heterotrophic metabolic rate, from a minimum of 0.25 mg–0.9 mg $CO_2 \cdot$[L sediment]$^{-1} \cdot h^{-1}$ (ANOVA, Fisher's LSD, $P = 0.0286$; Fig. 9). Addition of DIN or SRP did not influence heterotrophic metabolism during base flow (Fig. 9). Furthermore, addition of these nutrients in combination with DOC did not further stimulate respiration beyond that observed from DOC additions alone (Fig. 9).

This experiment was repeated using floodplain sediments obtained during snowmelt, at which time addition of DOC, DIN, or SRP failed to significantly influence heterotrophic metabolism (ANOVA $P = 0.52$). Metabolic rates during snowmelt, with and without DOC addition, were similar to metabolic rates observed during base flow when DOC was added to sediments (two-way ANOVA, Tukey, $P < 0.01$; Fig. 10). Repeating the DOC addition experiment at 5°C showed that neither DOC or temperature (5°C vs. 22°C) influenced heterotrophic metabolism during snowmelt (two-way ANOVA, $P = 0.9$).

DISCUSSION

Catchment hydrology, biogeochemistry, and hydrologic linkages among the RoSS, groundwater and stream

Our results show that snowmelt imported dissolved organic carbon (DOC) into the saturated zone, and that the region of seasonal saturation (RoSS) sediments were the likely DOC source. In years with sufficient snow accumulation, DOC concentration significantly increased before and during snowmelt in both surface water and groundwater. The DOC peak generally occurred before maximum discharge and water table elevation, and exhibited logarithmic declines in concentration with time; all of which are characteristics of DOC flushing from the RoSS (Hornberger et al. 1994, Boyer et al. 1996, 1997).

Hydrologic connection between the RoSS and groundwater dominated surface–subsurface interaction during snowmelt. The RoSS remained partially linked to the saturated zone through most of the summer months. As the aquifer drained during summer, hydrological connectivity between the RoSS and groundwater declined. During autumn base flow, the RoSS and saturated zone were generally disconnected; therefore, during base flow, the magnitude of surface water–ground water (SW/GW) interactions increased in importance (Morrice et al. 1997, Wroblicky et al. 1998).

TABLE 2. Mean $\pm$ 1 SE for dissolved oxygen (DO) and dissolved organic carbon (DOC) in stream surface water, interface, and floodplain groundwater; and water table elevations for three seasons (premelt, snowmelt, and base flow) in three water years (1995–1997).

Measurement	Premelt	Snowmelt	Base flow
1995			
Stream			
DO (mg/L)	5.99 $\pm$ 0.19[a]	8.22 $\pm$ 0.17[a]	7.87 $\pm$ 0.21[a]
DOC (mg/L)	4.02 $\pm$ 0.44[a]	3.14 $\pm$ 0.15[a]	1.67 $\pm$ 0.12[a]
Interface			
DO (mg/L)	1.38 $\pm$ 0.13[b]	1.65 $\pm$ 0.14[b]	1.17 $\pm$ 0.11[b]
DOC (mg/L)	3.31 $\pm$ 0.25[a]	3.28 $\pm$ 0.14[a]	3.11 $\pm$ 0.21[b]
Water table (cm)	61.2 $\pm$ 5.4[a]	75.3 $\pm$ 4.9[a]	45.9 $\pm$ 5.1[a]
Floodplain			
DO (mg/L)	1.84 $\pm$ 0.22[b]	3.00 $\pm$ 0.26[b]	3.12 $\pm$ 0.21[c]
DOC (mg/L)	3.74 $\pm$ 0.32[a]	3.30 $\pm$ 0.18[a]	3.11 $\pm$ 0.21[b]
Water table (cm)	69.3 $\pm$ 8.3[a]	87.3 $\pm$ 12.0[a]	45.9 $\pm$ 5.1[a]
1996			
Stream			
DO (mg/L)	8.21 $\pm$ 0.18[a]	6.71 $\pm$ 0.13[a]	8.92 $\pm$ 0.41[a]
DOC (mg/L)	1.68 $\pm$ 0.051[a]	2.18 $\pm$ 0.19[a]	1.75 $\pm$ 0.092[a]
Interface			
DO (mg/L)	1.95 $\pm$ 0.19[b]	1.30 $\pm$ 0.20[b]	2.29 $\pm$ 0.23[b]
DOC (mg/L)	2.06 $\pm$ 0.06[a]	2.45 $\pm$ 0.42[a]	1.87 $\pm$ 0.10[a]
Water table (cm)	50.4 $\pm$ 4.5	52.0 $\pm$ 6.90[a]	50.2 $\pm$ 4.52[a]
Floodplain			
DO (mg/L)	3.12 $\pm$ 0.21[a]	1.62 $\pm$ 0.18[a]	3.12 $\pm$ 0.21[b]
DOC (mg/L)	3.11 $\pm$ 0.21[a]	3.01 $\pm$ 0.22[a]	2.41 $\pm$ 0.14[a]
Water table (cm)	45.9 $\pm$ 5.1[a]	52.8 $\pm$ 9.0[a]	59.9 $\pm$ 6.2[a]
1997			
Stream			
DO (mg/L)	6.45 $\pm$ 0.15[a]	7.31 $\pm$ 0.087[a]	6.67 $\pm$ 0.16[a]
DOC (mg/L)	2.43 $\pm$ 0.69[a]	2.22 $\pm$ 0.028[a]	1.75 $\pm$ 0.09[a]
Interface			
DO (mg/L)	2.29 $\pm$ 0.25[b]	1.82 $\pm$ 0.23[b]	1.17 $\pm$ 0.15[b]
DOC (mg/L)	2.14 $\pm$ 0.12[a]	2.15 $\pm$ 0.07[a]	1.8 $\pm$ 0.05[a]
Water table (cm)	56.0 $\pm$ 5.4[a]	67.5 $\pm$ 6.6[a]	53.8 $\pm$ 7.0[a]
Floodplain			
DO (mg/L)	3.03 $\pm$ 0.32[b]	2.74 $\pm$ 0.21[b]	1.85 $\pm$ 0.20[b]
DOC (mg/L)	2.31 $\pm$ 0.13[a]	2.12 $\pm$ 0.13[a]	1.98 $\pm$ 0.077[a]
Water table (cm)	79.0 $\pm$ 8.5[a]	94.2 $\pm$ 9.0[a]	78.3 $\pm$ 10.0[a]

Note: Within each water-year and season, significant differences (ANOVA, Tukey $P < 0.05$) among locations are indicated if superscripts differ.

Throughout the year, SW/GW interaction via the hyporheic zone was continuous; however, the magnitude of this interaction during snowmelt was small compared to the terrestrial–aquatic interaction between the RoSS and saturated zone.

Geomorphological constraints may influence the extent of RoSS–groundwater interactions. Constrained and unconstrained stream reaches differ in the degree of alluvial deposition and floodplain development (Gregory et al. 1991, Stanford and Ward 1993). Surface water/groundwater interactions are more extensive in unconstrained reaches, relative to reaches constrained by hillslopes or valley "nick points" (Lamberti et al. 1989). In a similar way, RoSS–groundwater interactions may be more important in broad valleys with considerable alluvial deposits, while in other catchments the RoSS may be constrained to alluvium within the valley floor.

Geomorphology may interact with climate to structure RoSS–groundwater interactions. In mesic systems (e.g., Hornberger et al. 1994, Boyer et al. 1997, Mulholland and Hill 1997), the water table in hillslopes as

well as floodplains may rise during wet periods, extending the lateral boundaries of the RoSS beyond the floodplain and valley floor. In arid systems where there is exposed bedrock or hydrophobic soils, terrestrial–aquatic linkages may be more largely impacted by overland flow (Grimm and Fisher 1992).

Temporal variation in regional climate is likely to strongly influence terrestrial–aquatic linkages like RoSS–groundwater interactions. Catchments in the southwestern United States region are influenced by large-scale climatic phenomena like the El Niño–Southern Oscillation (Molles and Dahm 1991). The semiarid system we studied differs from previously studied mesic and alpine streams (e.g., Hornberger et al. 1994, Boyer et al. 1997, Mulholland and Hill 1997, Hinton et al. 1998) in that large temporal variation in snow accumulation alters the degree of interaction between the RoSS and groundwater. For example, in 1996, a severe drought resulted in little hydrologic change and subsequently little biogeochemical change at Rio Calaveras. Changes in hydrological connectivity between the RoSS and groundwater due to climate var-

TABLE 3. Linear regression statistics relating log DOC and log DO with time and time constants ([slope of line]$^{-1}$, in days) in surface water, interface, and floodplain wells during snowmelt of three water years (1995–1997).

Year	DOC r^2	DOC Time constant (d)	DO r^2	DO Time constant (d)
Stream				
1995	0.9835	251	†	†
1996	0.9911	163	†	†
1997	0.5337	680	†	†
Interface				
1995	0.8757	200	0.8386	110
	0.8398	99	0.9118	79
	0.5037	289	0.9034	115
	0.7282	56	0.7412	98
	0.5074	289	0.9052	73
	…	…	0.8963	52
	…	…	0.7798	68
1996	‡	‡	0.7383	42
	‡	‡	0.8408	72
1997	0.8467	202	0.6843	84
	0.982	346	0.8742	550
	0.6687	482	0.8779	114
	0.5147	342	0.6937	66
	0.4399	550	0.7321	84
	…	…	0.8671	67
Floodplain				
1995	0.9873	224	0.8453	88
	0.5733	445	0.8132	45
	0.6913	253	0.8071	123
1996	0.9627	169	0.6282	146
	0.6174	334	…	…
1997	0.7645	362	0.8525	441
	0.9414	262	0.8917	503
	0.7272	188	0.7495	147
	0.9627	169	0.8577	205
	0.8399	89	0.6453	267
			0.7411	87
			0.4529	235
			0.3671	144
			0.6441	100
			0.6582	99
			0.8079	173

† Stream does not exhibit DO flush due to atmospheric saturation.

‡ No wells exhibited flush.

iability can have important ecological ramifications in groundwater ecosystems, especially when subsurface heterotrophic metabolism is limited by organic matter availability.

Ecological consequences of hydrologic linkages among the RoSS, groundwater, and the stream

The hypothesis that snowmelt-derived DOC imported from the RoSS fuels heterotrophic metabolism in the alluvial aquifer was supported. First, the analysis of organic matter in seasonally saturated floodplain sediments showed that a substantial amount of organic carbon could be liberated from unsaturated sediments and transported to the saturated zone by meltwater. Soil-derived DOC is generally comprised of fulvic and humic acids (e.g., Thurman 1985, McDowell and Lik-

ens 1988) that are believed to be recalcitrant to decomposition by biota. However, a mean value of 45% of the RoSS-leached DOC was consumed by subsurface microorganisms, suggesting that much of RoSS-derived DOC is relatively labile.

Snowmelt resulted in higher rates of heterotrophic metabolism in field microcosms, presumably because of the supply of labile DOC via hydrologic connections between the RoSS and groundwater. Multiple-regression analysis further supported this conclusion. Features of the groundwater (dissolved oxygen [DO], and water table elevation) and alluvial sediments (extracted bioavailable DOC) were important predictors of heterotrophic metabolic rates. While there were no seasonal differences in extracted bioavailable DOC, both DO and water table elevation were highest during snowmelt. The negative correlation between DO and heterotrophic metabolism suggests that high rates of respiration during snowmelt rapidly consume available DO. In addition, it implies that higher rates of total respiration may occur under hypoxic or anoxic con-
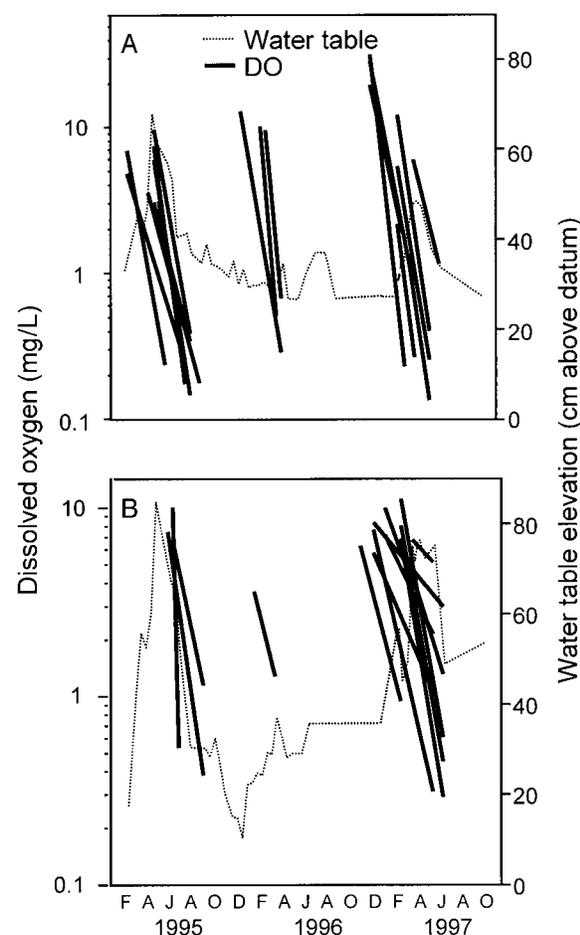

FIG. 6. Relationship between log(DO) and time for (A) interface and (B) floodplain groundwater (bold lines). Water table elevation is shown with dashed lines. Regression statistics are given in Table 3.
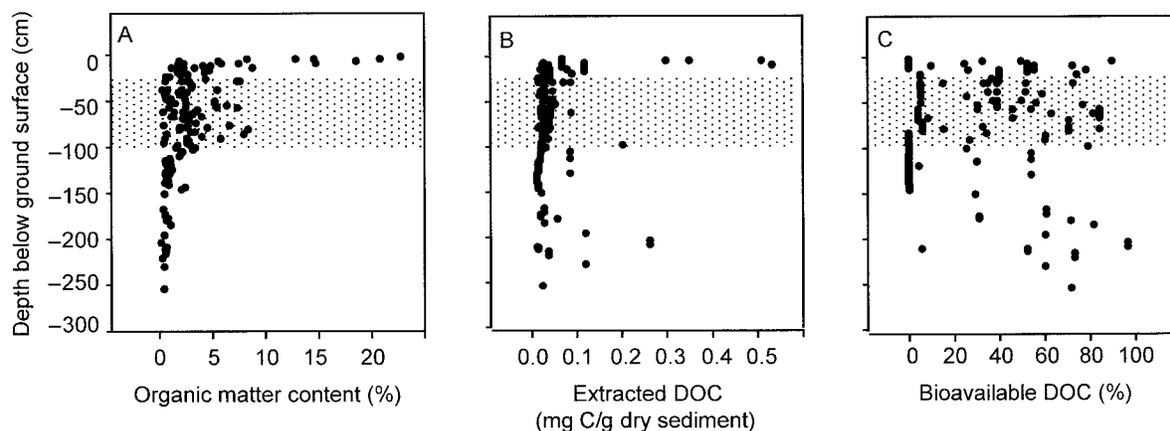
FIG. 7. Organic matter distribution in nine floodplain sediment cores: (A) percentage organic matter (as ash-free dry mass), (B) extractable DOC, and (C) bioavailable DOC. RoSS sediments are highlighted by the shaded area. Mean baseflow water table was 100 cm below the ground surface.

ditions, undoubtedly using a greater diversity of anaerobic metabolic processes (Baker et al. 1999, 2000). Conversely, low rates of total respiration may occur during base flow because of DOC limitation. The potential for DOC limitation is reflected by the fact that extracted bioavailable DOC also was a good predictor of heterotrophic metabolism. Under conditions of low DOC concentrations, labile DOC may dictate respiration rates. Finally, a positive correlation between heterotrophic metabolism and water table elevation indicates that hydrologic connection between the RoSS and groundwater is an important determinant of interstitial microbial activity.

Experimental analysis of factors that influence heterotrophic metabolism during base flow and snowmelt

further supports our hypothesis that RoSS-imported DOC supplies energy for subsurface heterotrophic metabolism. During base flow, heterotrophy in floodplain groundwater was limited by labile DOC availability, but respiration was not DOC limited during snowmelt. Furthermore, experimental addition of bioavailable DOC to the SW/GW interface at Rio Calaveras during summer base flow increased both aerobic and anaerobic respiration (Baker et al. 1999). Together, these studies support the hypothesis that metabolic activity of both floodplain and interface locations are DOC limited during base flow. Our experiments did not show nutrient (N and P) limitation of respiration during these short-term incubations. Microbial respiration could be nutrient limited over the longer term (e.g., Christensen et al. 1996), however.

Import of RoSS-derived DOC clearly plays an important role in determining respiration rates during

TABLE 4. Total ($CO_2 + CH_4$) and aerobic respiration rates (mean of four sites $\pm$ 1 SE) and respiratory quotient (CO_2:O_2 molar ratio) for microcosms submerged in interface and floodplain locations at Rio Calaveras.

Season	Total respiration	Aerobic respiration	Respiratory quotient (CO_2:O_2)
Interface			
Winter†	0.084	0.212	1.0
Spring	0.470 $\pm$ 0.094	0.370 $\pm$ 0.106	6.6 $\pm$ 3.3
Summer	0.00 $\pm$ 0.055	0.00 $\pm$ 0.00	999 $\pm$ 0‡
Autumn	0.352 $\pm$ 0.178	0.465 $\pm$ 0.06	2.7 $\pm$ 0.88
Floodplain			
Winter†	0.286	0.455	1.7
Spring	0.334 $\pm$ 0.118	0.275 $\pm$ 0.106	2.66 $\pm$ 1.8
Summer	0.513 $\pm$ 0.115	0.148 $\pm$ 0.085	501 $\pm$ 287
Autumn	0.212 $\pm$ 0.124	0.233 $\pm$ 0.106	33.2 $\pm$ 17

Note: Total respiration is measured in units of milligrams C per liter of sediment per hour; aerobic respiration is measured in units of milligrams O_2 per liter of sediment per hour.
† $n = 1$ site.
‡ Mean respiratory quotient is significantly higher during summer relative to other seasons; ANOVA, Tukey test, $P = 0.003$. (Differences between floodplain and interface locations were not significantly different; ANOVA, Tukey test, $P > 0.05$.)
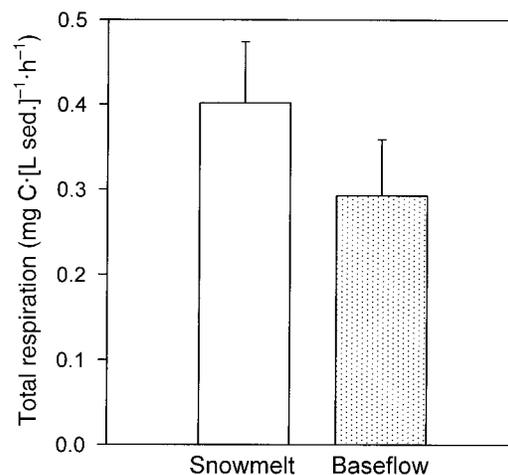

FIG. 8. Total heterotrophic metabolic rate during snowmelt and base flow. Mean rates (+ 1 SE) are significantly different at $P < 0.01$ (paired t test, $n = 8$ locations).

TABLE 5. Organic matter content, extracted DOC (exDOC), and bioavailable DOC (bioDOC), from interface and floodplain microcosms.

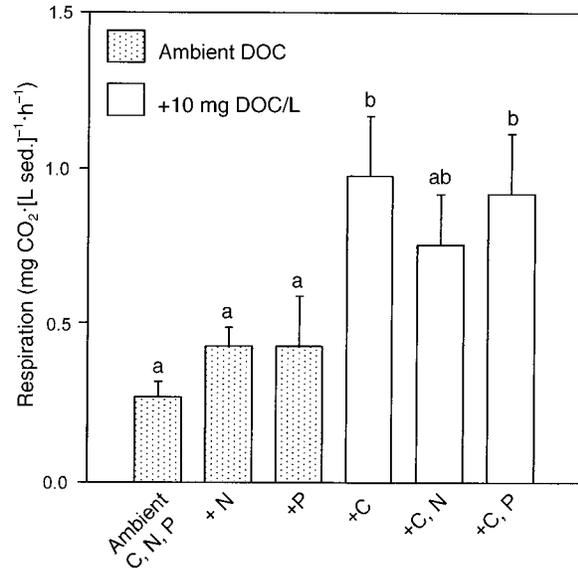| Season	Interface	Floodplain
Percentage organic matter		
Spring	1.25 ± 0.15	0.86 ± 0.09
Summer	1.10 ± 0.32	0.81 ± 0.08
Fall	0.78 ± 0.21	1.13 ± 0.12
exDOC (mg C/[g dry sediment])		
Spring	0.012 ± 0.003	0.011 ± 0.001
Summer	0.012 ± 0.002	0.013 ± 0.001
Fall	0.011 ± 0.001	0.019 ± 0.019
bioDOC (percentage of exDOC)		
Spring	63 ± 6.0	55 ± 6.9
Summer	61 ± 5.3	65 ± 1.4
Fall	52 ± 2.2	61 ± 2.5

Note: Values are mean of four sites ± 1 SE.

FIG. 9. Factors influencing total heterotrophic metabolism (mean + 1 SE) during base flow. Bars with the same letter are not significantly different (ANOVA, $P = 0.0293$; Fisher's LSD, $P > 0.05$). Metabolic rates for treatments with added DOC (open bars) are significantly higher than treatments with ambient DOC (shaded bars).

snowmelt, and it may also determine ambient rates for the majority of the saturated zone later, during baseflow conditions. Using the time constants determined from the regression analysis as a proxy for DOC residence time within the subsurface, RoSS-derived DOC supported groundwater respiration for most of the year (mean time constant over entire study period = 268 d).

Total respiration rate did not differ between interface and floodplain microcosms, indicating that both environments have similar metabolic capacities. Respiration rates measured in this study are within the same order of magnitude of those published for the hyporheic zone (e.g., Pusch and Schwoerbel 1994, Jones et al. 1995, Nageli et al. 1995) and are much higher than those reported for deep oligotrophic groundwaters (e.g., Chapelle and Lovley 1990). Within a catchment, heterotrophic metabolism in both floodplain and interface locations can strongly influence organic carbon availability and biogeochemistry in surface and groundwater. While several studies have documented the importance of the SW/GW interface in channel structure and function (e.g., Triska et al. 1989, Valett et al. 1994, 1996, Jones et al. 1995), expanding boundaries to include floodplain and hillslope environments may enhance our understanding of catchment ecosystems and mechanisms of terrestrial–aquatic interactions.

The hydrologic linkage between the RoSS and shallow groundwater clearly fuels subsurface heterotrophic metabolism. While surface water–groundwater interactions certainly influence the biogeochemistry and ecology of groundwater, the RoSS comprises a large area of catchments that can greatly influence groundwater ecosystems during periods of hydrologic connection. Thus, the RoSS represents a critical interface between aquatic and terrestrial ecosystems, and this region affects the organic carbon dynamics of the catchment as a whole. Aboveground primary production, soil organic matter, subsurface metabolism, and in-stream retention of organic matter are linked via this aquatic–terrestrial interface. The terrestrial–aquatic linkage represented by the RoSS shows how processes in hillslopes (Webster et al. 1983) and floodplains (Bayley 1995) impact the functioning of alluvial groundwater ecosystems. This aquatic–terrestrial linkage, moderated through alluvial groundwater (sensu Stan-

TABLE 6. Multiple regression model to predict rate of total heterotrophic metabolism from independent variables.

Variable	Parameter estimate	Partial r^2	Model r^2	F	P
DO (mg/L)	−0.180	0.3465	0.3465	4.2423	0.0734
bioDOC (%)	1.783	0.267	0.6135	4.8363	0.0638
Water table elevation (m)	0.185	0.0751	0.6886	1.4472	0.2743
Full model	…	…	0.6886	4.423	0.0578

Note: Of the six variables entered into the model (water table elevation, DOC in nearest well, DO in nearest well, percentage organic matter in microcosm, DOC extracted from microcosm, and bioavailable DOC [bioDOC] extracted from microcosm), only data from the three variables used to fit the model are shown (inclusion criterion, $\alpha \leq 0.100$).
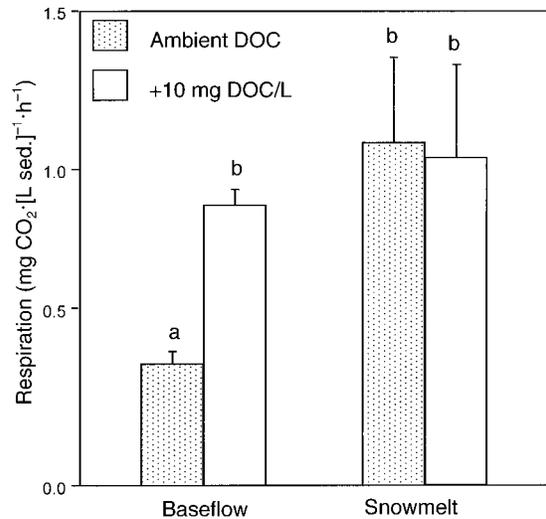
FIG. 10. Influence of experimental DOC addition on total heterotrophic metabolism during base flow and snowmelt (mean + SE). Bars with the same letter are not significantly different (two-way ANOVA, Fisher's LSD, $P < 0.01$).

ford and Ward 1993), likely influences energy and nutrient dynamics of streams, floodplains, and aquifers, and may impact the quantity and quality of water resources in stream–riparian corridors (Dahm et al. 1998).

LITERATURE CITED

Baker, M. A., C. N. Dahm, and H. M. Valett. 1999. Acetate retention and metabolism in the hyporheic zone of a mountain stream. Limnology and Oceanography **44**:1530–1539.

Baker, M. A., C. N. Dahm, and H. M. Valett. 2000. Anoxia, anaerobic metabolism and the biogeochemistry structure of the stream water–groundwater interface. Pages 259–284 *in* J. B. Jones, Jr. and P. J. Mulholland, editors. Streams and ground waters. Academic Press, San Diego, California, USA.

Bales, R. C., and R. F. Harrington. 1995. Recent progress in snow hydrology. Reviews of Geophysics **33**:1011–1020.

Bayley, P. B. 1995. Understanding large river–floodplain ecosystems. Bioscience **45**:153–158.

Boulton, A. J., S. Findlay, P. Marmonier, E. H. Stanley, and H. M. Valett. 1998. The functional significance of the hyporheic zone. Annual Review of Ecology and Systematics **29**:59–81.

Boyer, E. W., G. M. Hornberger, K. E. Bencala, and D. M. McKnight. 1996. Overview of a simple model describing variation of DOC in an upland catchment. Ecological Modelling **86**:183–188.

Boyer, E. W., G. M. Hornberger, K. E. Bencala, and D. M.

McKnight. 1997. Response characteristics of DOC flushing in an alpine catchment. Hydrological Processes **11**:1635–1647.

Brunke, M., and T. Gonser. 1997. The ecological significance of exchange processes between rivers and groundwater. Freshwater Biology **377**:1–33.

Chapelle, F. H., and D. R. Lovley. 1990. Rates of microbial metabolism in deep coastal plain aquifers. Applied and Environmental Microbiology **56**:1865–1874.

Christensen, S., et al. 1996. Soil respiration profiles and protozoan enumeration agree as microbial growth indicators. Soil Biology and Biochemistry **28**:865–868.

Dahm, C. N., D. L. Carr, and R. L. Coleman. 1991. Anaerobic carbon cycling in stream ecosystems. Verhhandlungen—Internationale Vereingung für theoretische und angewandte. Limnologie **24**:1600–1604.

Dahm, C. N., N. B. Grimm, P. Marmonier, H. M. Valett, and P. Vervier. 1998. Nutrient dynamics at the interface between surface waters and groundwaters. Freshwater Biology **40**:1–25.

Dane, C. H., and G. O. Bachman. 1965. Geological map of New Mexico. U.S. Geological Survey. Scale 1:500,000.

Danielopol, D. L. 1980. The role of the limnologist in groundwater studies. Internationale Revue der gesamten Hydrobiologie **65**:777–791.

Fetter, C. W. 1988. Applied hydrogeology. Second edition. Macmillan, New York, New York, USA.

Fiebig, D. M. 1995. Groundwater discharge and its contribution of dissolved organic matter to an upland stream. Archiv für Hydrobiologie **134**:129–155.

Fiebig, D. M. and M. A. Lock. 1991. Immobilization of dissolved organic matter from groundwater discharging through the stream bed. Freshwater Biology **26**:45–55.

Fisher, S. G., and G. E. Likens. 1973. Energy flow in Bear Brook, New Hampshire: an integrative approach to stream ecosystem metabolism. Ecological Monographs **43**:421–439.

Ghiorse, W. C., and J. T. Wilson. 1988. Microbial ecology of the terrestrial subsurface. Advances in Applied Microbiology **33**:107–172.

Gibert, J., J. A. Stanford, M.-J. Dole Olivier, and J. V. Ward. 1994. Basic attributes of groundwater ecosystems and prospects for research. Pages 7–40 *in* J. Gibert, D. L. Danielopol, and J. A. Stanford, editors. Groundwater ecology. Academic Press, San Diego, California, USA.

Gregory, S. V., F. J. Swanson, W. A. McKee, and K. W. Cummins. 1991. An ecosystem perspective of riparian zones. BioScience **41**:540–551.

Grimm, N. B., and S. G. Fisher. 1992. Response of arid land streams to changing climate. Pages 211–233 *in* P. Firth and S. Fisher, editors. Global climate change and freshwater ecosystems. Springer-Verlag, New York, New York, USA.

Hinton, M. J., S. L. Schiff, and M. C. English. 1998. Sources and flowpaths of dissolved organic carbon during storms in two forested watersheds of the Precambrian Shield. Biogeochemistry **41**:175–197.

Hornberger, G. M., K. E. Bencala, and D. M. McKnight. 1994. Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. Biogeochemistry **25**:147–165.

Hurlbert, S. H. 1984. Pseudoreplication in the design of ecological field experiments. Ecological Monographs **54**:187–211.

Jones, J. B., Jr. 1995. Factors controlling hyporheic respiration in a desert stream. Freshwater Biology **34**:91–99.

Jones, J. B., Jr., S. G. Fisher, and N. B. Grimm. 1995. Vertical hydrologic exchange and ecosystem metabolism in a Sonoran Desert stream. Ecology **76**:942–952.

Jones, J. B., Jr., and R. M. Holmes. 1996. Surface–subsurface

interactions in stream ecosystems. Trends in Ecology and Evolution **11**:239–242.

Jones, J. B., Jr., R. M. Holmes, S. G. Fisher, and N. B. Grimm. 1994. Chemoautotrophic production and respiration in the hyporheic zone of a Sonoran Desert stream. Pages 329–338 *in* J. A. Stanford and H. M. Valett, editors. Proceedings of the second international conference on ground water ecology. American Water Resources Association, Herndon, Virginia, USA.

Kling, G. W., G. W. Kipphut, and M. C. Miller. 1992. The flux of CO_2 and CH_4 from lakes and rivers in arctic Alaska. Hydrobiologia **240**:23–36.

Lamberti, G. A., S. V. Gregory, L. R. Ashkenas, A. D. Steinman, and C. D. McIntire. 1989. Productive capacity of periphyton as a determinant of plant–herbivore interactions in streams. Ecology **70**:1840–1856.

Lindeman, R. L. 1942. The trophic–dynamic aspect of ecology. Ecology **23**:399–418.

Marmonier, P., D. Fontvielle, J. Gibert, and V. Vanek. 1995. Distribution of DOC and bacteria at the interface between the Rhone river and its alluvial aquifer. Journal of the North American Benthological Society **14**:382–392.

Marmonier, P., P. Vervier, J. Gibert, and M.-J. Dole-Olivier. 1993. Biodiversity in groundwaters: a research field in progress. Trends in Ecology and Evolution **8**:392–395.

McDowell, W. H., and G. E. Likens. 1988. Origin, composition, and flux of DOC in the Hubbard Brook Valley. Ecological Monographs **58**:177–195.

Menzel, D. W., and R. F. Vacarro. 1964. The measurement of dissolved and particulate organic carbon in seawater. Limnology and Oceanography **9**:138–142.

Molles, M. C., Jr., and C. N. Dahm 1991. A perspective on El Niño and La Niña: global implications for stream ecology. Journal of the North American Benthological Society **9**:68–76.

Morrice, J. A., H. M. Valett, C. N. Dahm, and M. E. Campana. 1997. Alluvial characteristics, groundwater–surface water exchange, and hydrologic retention in headwater streams. Hydrological Processes **11**:253–267.

Mulholland, P. J., and W. R. Hill. 1997. Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: separating catchment flow path and in-stream effects. Water Resources Research **33**:1297–1306.

Nageli, M. W., U. Hartmann, E. I. Meyer, and U. Uehlinger. 1995. POM dynamics and community respiration in the sediments of a flood prone prealpine river (Necker, Switzerland). Archiv für Hydrobiologie **133**:339–347.

Nelson, P. N., M. C. Dictor, and G. Soulas. 1994. Availability of organic carbon in soluble and particle-size fractions from a soil profile. Soil Biology and Biochemistry **26**:1549–1555.

Odum, H. T. 1956. Primary production in flowing waters. Limnology and Oceanography **1**:102–117.

Pusch, M., and J. Schwoerbel. 1994. Community respiration in hyporheic sediments of a mountain stream (Steina, Black Forest). Archiv für Hydrobiologie **130**:35–52.

Rutherford, J. E., and H. B. N. Hynes. 1987. Dissolved organic carbon in streams and groundwater. Hydrobiologia **251**:239–248.

SAS Institute. 1985. SAS user's guide: statistics. Fifth edition. SAS Institute, Cary, North Carolina, USA.

Stanford, J. A., and J. V. Ward. 1993. An ecosystem perspective of alluvial rivers: connectivity and the hyporheic corridor. Journal of the North American Benthological Society **12**:48–60.

Stream Solute Workshop. 1990. Concepts and methods for assessing solute dynamics in stream ecosystems. Journal of the North American Benthological Society **9**:95–119.

Thurman, E. M. 1985. Organic geochemistry of natural waters. Nijhoff/Junk, Dordrecht, The Netherlands.

Toth, J. 1963. A theoretical analysis of groundwater flow in small drainage basins. Journal of Geophysical Research **68**:4795–4812.

Triska, F. J., V. C. Kennedy, R. J. Avanzino, G. W. Zellweger, and K. E. Bencala. 1989. Retention and transport of nutrients in a third-order stream in northwestern California: hyporheic processes. Ecology **70**:1893–1903.

Valett, H. M., C. N. Dahm, M. E. Campana, J. A. Morrice, M. A. Baker, and C. S. Fellows. 1997. Hydrologic influences on groundwater–surface water ecotones: heterogeneity in nutrient composition and retention. Journal of the North American Benthological Society **16**:239–247.

Valett, H. M., S. G. Fisher, N. B. Grimm, and P. Camill. 1994. Vertical hydrologic exchange and ecological stability of a desert stream ecosystem. Ecology **75**:548–560.

Valett, H. M., J. A. Morrice, C. N. Dahm, and M. E. Campana. 1996. Parent lithology, surface–groundwater exchange, and nitrate retention in headwater streams. Limnology and Oceanography **41**:333–345.

Vervier, P., and J. Gibert. 1991. Dynamics of surface water/ground water ecotones in a karstic aquifer. Freshwater Biology **26**:241–250.

Wallis, P. M., H. B. N. Hynes, and S. A. Telang. 1981. The importance of groundwater in the transportation of allochthonous organic matter to streams in a small mountain basin. Hydrobiologia **79**:77–90.

Webster, J. R., M. E. Gurtz, J. J. Hains, J. L. Meyer, W. T. Swank, J. B. Waide, and J. B. Wallace. 1983. Stability of stream ecosystems. Pages 335–395 *in* J. R. Barnes and G. W. Minshall, editors. Stream ecology. Plenum, New York, New York, USA.

Wetzel, R. G. 1983. Limnology. Second edition. Saunders College Publishing, San Diego, California, USA.

Wetzel, R. G., and G. E. Likens. 1991. Limnological analyses. Springer-Verlag, New York, New York, USA.

Wroblicky, G. J. 1995. Numerical modeling of stream–groundwater interactions, near-stream flowpaths, and hyporheic zone hydrodynamics of two first-order mountain stream–aquifer systems. Thesis. University of New Mexico, Albuquerque, New Mexico, USA.

Wroblicky, G. J., M. E. Campana, H. M. Valett, and C. N. Dahm. 1998. Seasonal variation in surface–subsurface water exchange and lateral hyporheic area of two stream–aquifer systems. Water Resources Research **34**:317–328.