Application of alternative hydrograph separation models to detect changes in flow paths in a watershed undergoing urban development

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Abstract:

Runoff characteristics in a low-gradient central-Florida watershed were analysed using environmental δ^{18} O and a series of conservative-tracer mass-balance models applied to a storm event (109 mm over approximately 30 h) monitored in May and June 1993 on the Econlockhatchee River, Florida. The assumption of steady-state conditions implicit in the widely used two-component mixing model was tested by applying steady-state and non-steady-state models for a subcatchment (215 km²) of the river. Both models indicated that about 76% of the resulting river flow was composed of pre-storm water. A third mass-balance model (steady-state) was developed to separate pre-storm from storm-event runoff over a discrete reach of the river, which had a contributing area of 135 km². This model indicated that approximately 47% of the water entering the reach could be attributed to pre-storm water. The greater proportion of event water entering the reach was attributed to suburban development in the watershed and indicates that urbanization in watersheds not only affects the timing, peak and total runoff, but also may change flow-paths for runoff, and may significantly affect down-stream water quality. Copyright © 2000 John Wiley & Sons, Ltd.

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INTRODUCTION

Increased volume of runoff and higher peak flows are well-known hydrological responses to urban development. Stormwater management regulations in much of the USA are structured around attenuating postdevelopment hydrographs through several proven strategies, such as detention and retention ponds, pervious pavement and infiltration swales (Wanielista and Yousef, 1992; Wanielista *et al.*, 1997). Less attention, however, has been paid to changes in flow paths with urban development. For example, a commercial developer may demonstrate an adequate post-development hydrograph, but stormwater runoff may have been converted from primarily surficial aquifer recharge to channelized flow post-development.

The transition from subsurface flow to overland or channelized flow with urban development may bring about several fundamental changes in the function of the watershed, particularly the riparian zone. In the pre-development state, if a significant component of the storm hydrograph is composed of water already in the system prior to the onset of the storm event, then most of the flow in the river passed through the riparian zone as subsurface water upwelling through the sediments. Thus the sediment chemistry in the riparian zone and the water quality of river flow must be tightly coupled. The water quality significance of this relationship may include factors such as denitrification of nitrate-rich groundwater or mobilization of redox-sensitive metals passing through anoxic riparian sediments (Dahm *et al.*, 1998).

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Changes in flow paths may affect the general ecology of riparian zones as well. It has been demonstrated that some riparian vegetation relies primarily on near-stream groundwater rather than the river itself (Dawson and Ehleringer, 1991). In a watershed undergoing significant urban development, groundwater levels and quality may be altered significantly by the transition to channelized flow. Even though the riparian zone itself may be protected by wetland regulations, upland stormwater management practices may sufficiently alter the riparian hydroperiod to damage the health of these wetlands.

A geographical region that may be particularly sensitive to changes in flow paths is central Florida. Mild topographic gradients and well-drained sandy soils in uplands create excellent conditions for widespread recharge of the surficial aquifer (Brown *et al.*, 1991). Stream and river channels deeply incised in the surface sands provide groundwater discharge areas that support bottomland hardwood and conifer wetlands (Ewel, 1991). Extensive urban development in central Florida since the early 1970s has replaced massive areas of sandy mineral soil with impervious surfaces (Wanielista *et al.*, 1997). Many riparian wetlands have been preserved, however, the nature of changes in the hydrology of these systems is poorly understood. Whereas the long-term geochemical and ecological effects of changing hydrological pathways may be unclear, methods to characterize flow components have been thoroughly investigated.

Hydrograph separation

The relative contributions of *old* and *new* water to river flow may be estimated through hydrograph separation techniques. Early hydrograph separation studies used hydrometric data to analyse the recession limb of hydrographs, with the principal objective of understanding the characteristics of baseflow, an important factor in such engineering applications as bridge and reservoir design and flood forecasting (Meyboom, 1961; Singh, 1968; Todd, 1980). More recently, researchers interested in interactions between surface and subsurface components of runoff have applied mass-balance models using conservative tracers (e.g. Fritz *et al.*, 1976; Sklash and Farvolden, 1979; Kennedy *et al.*, 1986; Hooper and Shoemaker, 1986; McDonnell *et al.*, 1991; Buttle and Sami, 1992; Maule *et al.*, 1994).

$$Q_{\rm R} = Q_{\rm O} + Q_{\rm N} \tag{1}$$

$$Q_{\rm R}C_{\rm R} = Q_{\rm O}C_{\rm O} + Q_{\rm N}C_{\rm N} \tag{2}$$

$$Q_{\rm O} = Q_{\rm R} \frac{C_{\rm N} - C_{\rm R}}{C_{\rm N} - C_{\rm O}} \tag{3}$$

where Q_R , Q_o and Q_N are the river, old and new discharges, respectively and C_R , C_o and C_N are their respective tracer concentrations (after Sklash *et al.*, 1976). C_N and C_o are known as *end members*, because they represent the extreme possible concentrations for C_R (Hooper *et al.*, 1990).

A variety of tracers has been proposed. The tracer must be either conservative, i.e. unchanging over time and space, or the behaviour of the tracer must be predictable, as in the decay of a radioisotope (Dinçer *et al.*, 1970; Kennedy *et al.*, 1986; Martinec, 1974). Among the naturally occurring constituents, solute and isotope tracers have been most widely used. Electrical (specific) conductivity (Noland and Hill, 1990; Tranter and Raiswell, 1991), dissolved silica (Kennedy, 1971; Wels *et al.*, 1991a, b), and various anions and cations (Pinder and Jones, 1969; Fritz *et al.*, 1976; Hirata and Muraoka, 1988; Caine, 1989; McDonnell *et al.*, 1991) have been used in hydrograph separation studies. Solute tracers are seldom truly conservative, as their concentrations in water may vary with residence time or some local geochemical or biological influence (Kennedy *et al.*, 1986). The stable isotopes of water, oxygen-18 (δ^{18} O) and deuterium (δ D), are considered excellent conservative tracers, because they are constituents of the water molecule itself, rather than a solute transported with water, and can form distinctive signatures in water masses. Bowen (1988) and Coplen (1993) provide introductions to stable isotope properties, measurement, and applications in the environmental sciences.

Equation (3) represents steady-state conditions, applied over an unspecified control surface, presumably

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the river channel. Spatially, the model is applied at the catchment scale, with Q_R and C_R measured at a single outflow from the catchment. Variables C_0 and C_N reflect average tracer concentrations over the watershed. Temporally, Equation (3) is solved for average conditions during a single storm hydrograph or is solved over discrete time steps that reflect the availability of field data (McDonnell *et al.*, 1991).

The expression of hydrological interactions at the watershed level in the form of a two-component model requires several simplifying assumptions. Many investigators (e.g. Buttle, 1994) have recognized at least some of the limitations in applying Equation (3). The major assumptions of the two-component model (after Kennedy *et al.*, 1986; Buttle, 1994) are described below.

- 1. Co remains constant during the storm event, or varies predictably.
- 2. $C_{\rm O}$ is significantly different from $C_{\rm N}$.
- 3. $C_{\rm N}$ undergoes no changes while being routed through the watershed, or changes predictably.
- 4. A steady-state model adequately represents watershed conditions.

Most researchers have estimated C_0 as the isotopic content of the near-stream groundwater or pre-storm river (Hooper and Shoemaker, 1986; DeWalle *et al.*, 1988), and assumed C_0 to remain constant through the storm event (Assumption 1). By analysing a period of hydrological recession in the Econlockhatchee River, Gremillion and Wanielista (2000) determined that C_0 varied, probably as a result of evaporative enrichment. The requirement for C_N to be significantly different than C_0 (Assumption 2) has been recognized, although McDonnell *et al.* (1991) are among the few that provide a quantitative expression of signal strength. Assumption 3 requires that C_N equal the isotopic content of precipitation. Hydrological processes such as throughfall and temporary surface storage (DeWalle and Swistock, 1994) may result in isotopic enrichment of C_N .

The assumption that a steady-state model adequately represents watershed conditions (Assumption 4) is seldom stated explicitly in the literature. In fact, of the peer-reviewed journal articles reviewed for this study, none included derivations of hydrograph separation models from the differential forms of the mass-balance equations. This results in the tacit assumption that changes in the volume and isotopic content of channel storage over time are negligible.

This paper approaches two aspects of hydrograph separation: assessing the validity of the steady-state assumptions and applying the two-component hydrograph separation model to an urbanized central-Florida watershed.

STUDY DESIGN

Site description

The Econlockhatchee River basin occupies approximately 620 km² in and east of Orlando, Florida and consists of two major branches, the Big and Little Econlockhatchee Rivers (Figure 1). Data were collected for this study within the Big Econlockhatchee basin. The Big Econlockhatchee River is about 60 km long with a watershed of approximately 440 km². Approximately 150 km² are occupied by forested wetlands. The remaining area, occupied historically by pine flatwoods and sand-pine scrub, has been partially developed for citrus agricultural and range use with some suburban residential development (Abrahamson and Hartnett, 1991). At low flow, the Big Econlockhatchee River is contained within an incised channel, which meanders through a relatively undisturbed floodplain. The unconfined aquifer is composed of silica sand, with a water-table aquifer occurring at depths ranging from 0.3 to 1.5 m below land surface. The aquifer extends to a depth of approximately 20 m, where it meets the Hawthorne semi-confirming unit, which retards hydraulic communication with the upper Floridan aquifer (Tibbals, 1990).

Two subcatchments within the Big Econlockhatchee River were considered in this study: the watershed upstream from station HR (215 km²) and the subcatchment between stations HR and FR (135 km²). The watershed upstream from station HR is almost completely undeveloped and is comprised mainly of headwater and riparian wetlands (Gremillion and Wanielista, 2000), upland pine forest, range land and citrus



Figure 1. The Econlockhatchee River watershed in east-central Florida. The shaded area to the south drains to station HR and the smaller hatched area in the central portion of the watershed is the subcatchment between stations HR and FR. The northernmost gauging station is station SH

Land use	Upstream from station HR (%)	Subcatchment between HR and FR (%)	
Urban	5	23	
Agricultural	26	30	
Upland forest	36	21	
Wetlands and open water	33	26	

Table I. Land use in subcatchments of the Econlockhatchee River basin,	Florida
(Source: Wanielista et al., 1992)	

agriculture (Table I and Wanielista *et al.*, 1992). The only urban development within this catchment lies along the corridors of two highways, State Route 50 and the Bee Line Expressway, which cross through the watershed. The HR–FR subcatchment collects flow from an unnamed tributary stream and direct contributions into the Big Econlockhatchee River main channel between stations HR and FR (Figure 1). Land use within that basin was formerly upland pine forest, but now includes significant areas of single-family residences, range land and citrus agriculture (Table I and Wanielista *et al.*, 1992).

Sampling design

A field-sampling programme was conducted to monitor river water, groundwater and precipitation in the Econlockhatchee basin during the spring of 1993. The river was in an extended period of recession at the start of sampling. Thus antecedent conditions reflected low storage in both the surficial aquifer and the river channel and high potential for initial abstraction.

Samples were collected from the Big Econlockhatchee River at stations HR and FR (Figure 1). River and groundwater samples were collected daily from 1 May through to 18 May and on 26 May. In response to a storm event (29–31 May), samples were collected twice daily from 29 May until 7 June, then daily until 11 June, with follow-up sampling on 15 and 23 June. River samples were collected at the shore. Water samples collected for isotopic analysis were placed in 30-mL glass vials with Poly-SealTM inverted-cone closures. Samples were analysed for δ^{18} O at the University of Florida Geology Department (Hodell *et al.*, 1989) using the method of Socki *et al.* (1992). Monitoring wells (HR0, HR1, FR0, FR1) were installed at distances of approximately 10 m and 15 m in a line perpendicular to the river channel at stations HR and FR in order to sample the surficial aquifer. Gremillion and Wanielista (2000) provide construction details for the wells. Wells were purged by pumping at least five well-casing volumes to assure that formation water was sampled. Water samples for isotopic analysis were collected in a bailer and poured into 30-mL glass vials.

Precipitation was collected through a NalgeneTM funnel (top diameter, 7.5 cm) into a 4 L Nalgene carboy at station FR. The precipitation monitoring station was placed in an open area with no aerial obstructions. The rain collected was checked twice daily during the storm event. Rain water was measured from the carboy into a graduated cylinder to compute the amount. Samples for isotopic analysis were sealed in 30-mL glass vials.

Hydrological gauging

Flow measurements were made at stations HR and FR to develop stage-discharge rating curves. Stream velocity and depth were measured at cross-sections within 20 m of staff-gauges at stations HR and FR using standard United States Geological Survey methods to assure a measurement quality of *good* or *excellent* (Rantz, 1983a, b). River elevation at staff-gauges was recorded before and after each flow measurement and rating curves were developed to relate area and flow as functions of river elevation. Least-squares analysis produced regression equations for the HR and FR (Figure 2) stations.



Figure 2. Hydrological gauging for stations HR (a) and FR (b) with least-squares linear regression lines and equations

RESULTS

Data collected immediately prior to, during and following a storm event, which occurred on 29 May through to 31 May, 1993 are plotted in Figure 3. Complete data listings are provided by Gremillion (1994). The river was in an extended period of recession prior to the storm event. Flow at both the HR and FR sampling stations was less than $0.03 \text{ m}^3 \text{ s}^{-1}$ at the onset of the event. The storm event placed approximately 109 mm of rainfall over the watershed with an amount-weighted δ^{18} O of -4.46%. This event resulted in peak flows of 1.09 and 1.36 m³ s⁻¹ at the HR and FR stations, respectively (Figure 3b).

Groundwater elevation and δ^{18} O were monitored during the storm event. The piezometric surface at all monitoring wells remained higher than that of the river throughout the storm event (Figure 3a), indicating no loss from the river channel to recharge bank storage (Meyboom, 1961) in the surficial aquifer. Surficial aquifer δ^{18} O was spatially and temporally homogeneous throughout the spring 1993 study period, with a mean δ^{18} O of $-3.05\pm0.14\%$ (n = 59). This was substantially more depleted than river δ^{18} O (Figure 3c), which averaged $-0.96\pm0.60\%$ (n = 74) and ranged from -2.26 to +0.02% during the spring 1993 study period. Enriched river water relative to groundwater δ^{18} O was consistent with autumn 1992 conditions in the Econlockhatchee River (Gremillion and Wanielista, 2000).

MODELLING STUDIES

Three mass-balance models were derived in order to examine the relative contribution of new water to a storm hydrograph in the Econlockhatchee River using hydrometric and oxygen isotope data. Catchment-scale steady-state (SS) and non-steady state (NSS) models were applied at two sites and an SS model was applied for a discrete reach of the river. Estimating the old-water fraction was the primary objective of the modelling exercise, but an essential aspect of the study was to analyse the adequacy of the models in representing the hydrology of the system. Specific areas of concern were the reliability of control over end-members and the assumptions of steady-state conditions.



Figure 3. Data collected at stations HR and FR during a storm event in spring 1993. River elevation (a), flow and precipitation (b) and δ^{18} O (c). Precipitation was monitored at station FRP (Figure 1) and δ^{18} O was monitored from the river (HR and FR) and monitoring wells (HR0, HR1, FR0 and FR1)

Catchment models

The differential equations for two-component hydrograph separation at the catchment scale are

$$\frac{\mathrm{d}V}{\mathrm{d}t} = Q_{\mathrm{N}} + Q_{\mathrm{G}} - Q_{\mathrm{E}} - Q_{\mathrm{R}} \tag{4}$$

$$\frac{\mathrm{d}CV}{\mathrm{d}t} = C_{\mathrm{N}}Q_{\mathrm{N}} + C_{\mathrm{G}}Q_{\mathrm{G}} - C_{\mathrm{E}}Q_{\mathrm{E}} - C_{\mathrm{R}}Q_{\mathrm{R}}$$
(5)

where V is channel volume (m³), Q is flow (m³ s⁻¹), C is tracer concentration (‰ for δ^{18} O), N is new water and subscripts G, E and R are groundwater, evaporation and river water.

Lumping groundwater and evaporative terms with an empirical function represented by the subscript O, to indicate *old* water and solving for a discrete time interval Δt (s)

$$V_2 - V_1 = V_N + V_O - V_R \tag{6}$$

$$C_2 V_2 - C_1 V_1 = C_N V_N + C_0 V_0 - C_R V_R$$
(7)

where the subscript 2 indicates values at time t and the subscript 1 indicates values at time $(t - \Delta t)$. Variables V_1 and V_2 are channel volumes and C_1 and C_2 are the tracer concentrations in the channel, assuming completely mixed conditions. Assuming all values except V_0 and V_N can be measured or estimated, Equations (6) and (7) can be reduced to

$$V_{\rm O} = \frac{V_2(C_{\rm N} - C_2) - V_1(C_{\rm N} - C_1) + V_{\rm R}(C_{\rm N} - C_{\rm R})}{(C_{\rm N} - C_{\rm O})}$$
(8)

$$V_{\rm N} = V_2 + V_{\rm R} - V_1 - V_0 \tag{9}$$

Under steady-state conditions

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{\mathrm{d}CV}{\mathrm{d}t} = 0 \tag{10}$$

and Equations (8) and (9) reduce to the familiar two-component hydrograph-separation model

$$V_{\rm O} = V_{\rm R} \frac{(C_{\rm N} - C_{\rm R})}{(C_{\rm N} - C_{\rm O})}$$
(11)

$$V_{\rm N} = V_{\rm R} - V_{\rm O} \tag{12}$$

New water. The isotopic composition of precipitation C_P was taken to be C_N . This is the common assumption and neglects possible evaporative effects during surface runoff or in translation through the tree canopy (throughfall effects, e.g. Pearce *et al.*, 1986; DeWalle and Swistock, 1994). The value C_N at any time *t* was taken to be the amount-weighted average of all precipitation applied over the catchment up to time *t* (McDonnell *et al.*, 1990):

$$C_{\rm N} = \frac{\Sigma(PC_{\rm P})}{\Sigma P} \tag{13}$$

where *P* is rainfall amount. As a result, C_N was updated after every time-step during which rain was recorded, otherwise remained constant. Reapplying C_N over time steps subsequent to the end of rainfall event leads to the interesting question of how long *new* water remains new. Alternative approaches in hydrograph separation using time-series analysis and convolution integrals (Pearce *et al.*, 1986; Stewart and McDonnell, 1991; Turner and Macpherson, 1990) have applied, in effect, decay functions to diminish the weight of a precipitation event over time. Variable C_N was assumed there to be constant over time following the end of

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the event because the event was isolated and the resulting hydrograph occurred over a short duration. Analysis of an extended period of record with numerous events, such as presented by Gremillion and Wanielista (2000), may require a time-variable function for C_N .

Old water. The isotopic character of old water was given significant attention by Gremillion and Wanielista (2000), who concluded that δ^{18} O measurement of near-stream groundwater or pre-storm river water were inadequate to describe C_0 during a storm hydrograph. Hooper and Shoemaker (1986) observed that C_0 appeared to vary over time in the Hubbard Brook Experimental Forest, New Hampshire and attributed a systematic depletion in river isotopic content (δ D) to seasonal trends. They accounted for the change by linear interpolation of baseflow river δ D before and after storm events.

Because of the difficulty in directly measuring the old-water component of flow, the old-water tracer concentration, many researchers have assumed C_0 to equal either pre-storm baseflow concentration (e.g. DeWalle *et al.*, 1988) or the concentration of tracer in near-system groundwater. Buttle *et al.* (1995) discuss the relative merits of these assumptions. Gremillion and Wanielista (2000) attributed variable baseflow δ^{18} O to evaporative enrichment. A rigorous hydrograph-separation model would then require the two traditional end members, new water and old water, with a third end-member representing evaporation. Three-component mixing models have been applied previously (e.g. DeWalle *et al.*, 1988) in hydrograph separation studies. Rather than introduce a third end-member, however, we applied a variable function for the old-water tracer component. At stations HR and FR, the δ^{18} O of river flow during recession was strongly correlated with river flow (Figure 4), so C_0 during the model run was estimated as a linear function of flow measured at each time-step. This approach assumes that evaporative effects on river δ^{18} O during recession were the same during storm events, which is consistent with the observations of δ^{18} O in the Econlockhatchee River during both storm and recession conditions (Gremillion and Wanielista, 2000).

The assumption of variable C_0 affected estimates of new-water contribution for stations HR (Figure 5) and the subcatchment defined by the reach between HR and FR (Figure 7). The linear regression models for C_0 , solved separately for HR and FR (Figure 4), indicated that old water became depleted during the storm hydrograph in response to higher flow. At peak flow C_0 was 0.73% more depleted than baseflow C_0 at HR and 1.0% more depleted at FR. The use of a linear function for C_0 , rather than a constant baseflow value, reduced the signal strength of the separation ($C_N - C_0$ was a smaller absolute value), and increased the estimate of old water contribution, as the signal-strength term ($C_N - C_0$) appeared in the denominator of the hydrograph separation equation (Equation (3) or (11)).

Steady-state model

Equations (11) and (12) were solved for each sampling observation after the start of the storm event on 29 May 1993. Time-step duration varied depending on sampling times, but was approximately 12 h during the storm event and 24 h otherwise. Figure 5 presents the SS modelling results for stations HR and FR, respectively. Oxygen isotope data indicated that end members were significantly different throughout the storm event at HR and FR. The value of C_0 averaged -0.27% at station HR and -0.51% at station FR, and C_N averaged -4.46%. The 2σ analytical precision for δ^{18} O was approximately 0.2‰, so a significant isotopic signal was evident between the end members. Old water contribution during the storm event was estimated to be 76 and 77\% of total flow at HR and FR, respectively.

Non-steady-state model

The SS model was essentially a linear interpolation between two δ^{18} O end-members. When the model is derived for non-steady state conditions (Equations (8) and (9)), temporal changes in the quantity and δ^{18} O of channel storage must be estimated and the model becomes more sensitized to measurement errors. To solve the NSS model, channel volumes at the beginning and end of each time-step were required. Channel geometry was known from previous hydrological surveys of the river (Gremillion and Wanielista, 2000). Field measurements of river elevation were combined with channel geometry data to arrive at estimates of



Figure 4. Regression of river δ^{18} O from stations HR (a) and FR (b) versus elevation for three sampling periods. Early spring 1993 immediately preceded the storm event analysed in this study. Late spring 1993 was the period during the storm hydrograph, and autumn 1992 sampling occurred in November and December 1992 during a period of extended recession. Regression equations were based on autumn 1992 and early spring 1993 data. Circles represent new water, plus signs represent old water and squares represent measured river water

channel volume for each time-step. The sensitivity of the model to the estimates of channel volume was assessed by varying the initial estimates of channel volume by factors 0.9, 1.0, 1.1 and 1.2 in separate model runs (Figure 6).

To compare the results of the SS and NSS models, the old water fraction, or ratio of old water to total volume, was computed for each time-step. In the SS model, the fraction of old water was computed as the quantity of old water divided by river discharge from the control section

$$f_{\rm O(SS)} = \frac{V_{\rm O}}{V_{\rm R}} \tag{14}$$

For the NSS model the fraction of old water at a given time-step was the volume of old water divided by the net flow out of the control section, which consisted of channel discharge out of the control section (V_R) plus the net change in channel storage

$$f_{\rm O(NSS)} = \frac{V_{\rm O}}{V_2 + V_{\rm R} - V_1}$$
(15)

Figure 6a plots the old water fraction for the SS and the NSS models at station HR. Figure 6b plots channel discharge (V_R) , old water estimates assuming steady state (V_{SS}) and non-steady state (V_{NSS})



Figure 5. Hydrograph separations using the steady-state model for stations HR (a and c) and FR (b and d). The δ^{18} O of new water was computed using Equation (13) and the δ^{18} O of old water was computed from regression equations in Figure 4

conditions, change in channel storage (dV) and absolute storage (V). All quantities except absolute channel storage were expressed as flows (V/dt) because sampling intervals were not uniform. The NSS model predicted the same average fraction of old water for the storm event, although several point values for f varied dramatically from the steady-state estimates (e.g. 4, 6 and 7 June). In spite of rapidly increasing storage volume on the ascending limb of the hydrograph and decreasing storage volume on the descending limb (dV, Figure 7b), the SS and NSS models predicted roughly the same fraction of old water in the river (V_R).

Discrete reach model

The twin peaks of the storm hydrograph at station FR, superimposed over the single-peak hydrograph of station HR (Figure 3b) indicate that either a component of rapid runoff entered the river between HR and FR or that rainfall was locally heavy in the HR–FR subcatchment. Precipitation gauges placed at widely spaced locations in the Econlockhatchee river (Gremillion, 1994) recorded approximately the same amount of rainfall on 30 May, 1993 (3.77, 3.80 and 2.59 cm), indicating low spatial variability in that precipitation event and high translation of rainfall to runoff in the subcatchment between stations HR and FR.

The isotopic response at FR (Figure 3c) concurrent with the second peak suggests that this quickly translated component was isotopically depleted relative to river water at station HR. To estimate the δ^{18} O



Figure 6. Analysis of non-steady-state model. The steady-state (SS) and non-steady-state (NSS) solutions are plotted in (a) as fraction of old water, f (Equations (14) and (15)). Channel volume (V) was varied from 90% to 120% to assess sensitivity to channel storage. River flow and estimates of old water using SS and NSS models (b) are overlaid with instantaneous change in storage, dV, and channel storage volume. Volumes are expressed as a flow (Q/dV) because sampling intervals varied during the study period.

of water entering the river between stations HR and FR, mass-balance models were derived for a discrete river reach

$$\frac{\mathrm{d}V}{\mathrm{d}t} = Q_{\mathrm{HR}} + Q_{\mathrm{G}} - Q_{\mathrm{FR}} \tag{16}$$

$$\frac{\mathrm{d}CV}{\mathrm{d}t} = C_{\mathrm{HR}}Q_{\mathrm{HR}} + C_{\mathrm{G}}Q_{\mathrm{G}} - C_{\mathrm{FR}}Q_{\mathrm{FR}} \tag{17}$$

which reduces algebraically to

$$C_{\rm G} = \frac{C_2 V_2 + C_{\rm FR} V_{\rm FR} - C_1 V_1 - C_{\rm HR} V_{\rm HR}}{V_2 + V_{\rm FR} - V_1 - V_{\rm HR}}$$
(18)

where inflow and outflow subscripts reflect station names: HR for channel inflow and FR for channel outflow. Equation (18) reduces to the steady-state form

$$C_{\rm G} = \frac{C_{\rm FR} V_{\rm FR} - C_{\rm HR} V_{\rm HR}}{V_{\rm FR} - V_{\rm HR}}$$
(19)

Equation (19) estimates the concentration of the *gaining* tracer, which describes water entering the reach by means other than channel inflow. McKenna *et al.* (1992) examined the release of bank storage in the Truckee River, Nevada using a form of Equation (19) to separate bank storage (old water) and snowmelt (new

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Figure 7. Solution of the discrete reach model to estimate the δ^{18} O of water entering the reach between stations HR and FR (a) and the hydrograph separation using the SS two-component model (b)

water) sources. Because Equation (19) is an end-member mixing model, like to two-component models discussed previously, the difference between $C_{\rm FR}$ and $C_{\rm HR}$ must be significant to produce an accurate estimate of $C_{\rm G}$. For modelling purposes, it was assumed that a minimum signal strength of $\delta^{18}O_{\rm FR} - \delta^{18}O_{\rm HR} > 0.5\%$ was necessary. This value was selected arbitrarily as five times the analytical precision of the $\delta^{18}O$ analysis (Gremillion and Wanielista, 2000). McDonnell *et al.* (1991) defined minimum signal strength as two times the standard deviation of five sample replicates. Using this definition, the minimum signal strength would be 0.2‰; thus the 0.5‰ criterion is somewhat more conservative. Only four observations during the spring 1993 storm event met this criterion (Figure 7), and all of these occurred during the gaining portion of the hydrograph ($Q_{\rm FR} - Q_{\rm HR}$). River δ^{18} O at stations FR and HR prior to and following this episode were not significantly different at any given sampling time, which is consistent with observations of spatial homogeneity in the river during autumn 1992 monitoring (Gremillion and Wanielista, 2000).

The δ^{18} O of water entering the reach between stations HR and FR was estimated to range from -2.5%in the ascending limb of the gaining hydrograph to -3.0% at the end of the recession of the gaining hydrograph (Figure 7a). Variable $C_{\rm G}$ represents the combined effects of new water, old water and evaporative influences. These effects may be separated by applying a two-component model, such as Equation (11). Variable $C_{\rm N}$ was computed using Equation (13) and is plotted in Figure 7a. For the SS and NSS modelling runs described previously, $C_{\rm O}$ was estimated separately for stations HR and FR. For this application, $C_{\rm O}$ was estimated as the average of the two values produced by the regression equations in Figure 4 for each observation. Applying Equations (11) and (12) to the gaining hydrograph, old water fractions were estimated to range from 38 to 53%, with an average value of 47% (Figure 7a). This is substantially lower than the basin-wide estimate of 76% determined for station HR.

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DISCUSSION

This study applies the widely used two-component hydrograph separation model to assess changing flow paths in a watershed undergoing urbanization. Two areas of focus in this study are examining the validity of the steady-state assumption of the model and interpreting the modelling results within the context of watershed management.

Model performance

The assumption that a SS model adequately represents watershed conditions is supported by the modelling results. However, conceptually the NSS model (Equations (8) and (15)) may provide very different results than the SS model (Equations (11) and (14)). The sensitivity of these equations to their variables can be examined by setting up spreadsheet solutions using simulated data. Table II shows one such solution for a model run of 12 days, with fixed channel volume (V), river flow (V_{R}) and isotopic concentrations of old and new water. River water δ^{18} O changed by 1 per mille during the run, indicating a shift from old water to new water. The equations show that if inflow and storage volumes are fixed, but the isotopic values change over time, then the steady-state and non-steady-state solutions may differ, depending on the residence time of water in the river. Figure 8 shows the solution of the model in Table II for different values of river flow. As residence time decreases, the difference between the steady and non-steady state solutions diminishes. In general, the NSS state model is highly sensitive to temporal changes in any isotopic value, but only sensitive to changing flows if they result in changing residence time. If isotopic values do not change over time, both models will produce identical fractions of old water regardless of changes in flow or residence time. For the storm event monitored in this study, both models produced similar results and the steady-state assumption was reasonable. In summary, the SS model may produce different results than the NSS model, but only under conditions of rapidly changing isotopic concentrations or long channel residence times. Other errors associated with time-scale, measurement, or governing assumptions are likely to be of comparable or greater magnitude.

Watershed management

The hydrograph-separation models derived for this study provided estimates of old water contribution for two subcatchments in the same watershed for the same storm event. This data resolution allows some inferences to be made about runoff mechanisms with the watershed. For the subcatchment upstream from station HR (215 km²), approximately 76% of river flow during the event was composed of pre-event water.



Figure 8. Solution of the steady (SS) and non-steady (NSS) state models for varying river flow (V_r) . Parameters other than river flow are summarized in Table II

Time (days)	V (m ³)	V_{R} (m ³)	C _N (‰)	С _о (‰)	С _в (‰)	f SS	fNSS
1	100	10	-6.0	-3.0	_ 3.9	0.70	
2	100	10	-6.0	-3.0	-4.0	0.67	0.33
3	100	10	-6.0	-3.0	-4.1	0.63	0.30
4	100	10	-6.0	-3.0	-4.2	0.60	0.27
5	100	10	-6.0	-3.0	-4.3	0.57	0.23
6	100	10	-6.0	-3.0	-4.4	0.53	0.20
7	100	10	-6.0	-3.0	-4.5	0.50	0.17
8	100	10	-6.0	-3.0	-4.6	0.47	0.13
9	100	10	-6.0	-3.0	-4.7	0.43	0.10
10	100	10	-6.0	-3.0	-4.8	0.40	0.07
11	100	10	-6.0	-3.0	-4.9	0.37	0.03
12	100	10	-6.0	-3.0	-5.0	0.33	0.00

Table II. Solution of the SS and NSS models (Equations (14) and (15)) for simulated data

An isotope mass-balance of the river reach between stations HR and FR (135 km²) estimated approximately 47% old water. Antecedent conditions at the onset of the storm may be characterized as exceedingly dry. Whereas the average daily flow at the SH gauging station (Figure 1) from October 1987 to October 1993 was $8.5 \text{ m}^3 \text{ s}^{-1}$ (n = 2181, USGS National Water Information System, http://water.usgs.gov), flow at HR preceding the storm was less than $0.3 \text{ m}^3 \text{ s}^{-1}$. As a result, storage in the surficial aquifer and river channel was extremely low. Thin upland soils, characteristic of scrub pine forests, and high permeability surficial sands combined with low storage may well have led to rapid infiltration. The physical mechanisms involved in runoff generation, then, probably consisted of rapid infiltration of precipitation to the surficial aquifer, followed by increased hydraulic gradient toward the river and increased flow. The estimated 24% of new water reaching the river consisted of a combination of surface runoff and interflow, or water recharging the surficial aquifer near enough to the river to be discharged as surface flow.

The lower percentage of old water entering the reach between stations HR and FR may reflect land use differences between the basins. The headwater catchment upstream of station HR consisted primarily of wetlands, range and sand-pine scrub, with very little urban development. The catchment between stations FR and HR has undergone some urbanization, with almost one-third of the upland area occupied by single-family residences (Table I). Urban development appears to have exerted two effects on the watershed: an increased proportion of surface runoff in the storm hydrograph and a shorter time of concentration.

One clear result of this study was that overland surface runoff did not comprise a significant amount of river flow during the dry-period storm event monitored in May 1993. This observation alone points toward the importance of riparian areas in the hydrology of watersheds undergoing urbanization. Very little of the riparian wetlands in the Big Econlockhatchee system have been disturbed, and wetland regulations are likely to protect much of these areas. The results of this study indicate, however, that these wetlands may be affected by upland development. This study did not specifically address the hydrology of riparian wetlands, so additional research will be necessary to detect changes in the availability and quality of subsurface water following upland development near rivers in highly permeable areas, such as central Florida. Similarly, water quality responses to these practices must be investigated.

CONCLUSIONS

A study was conducted on the Econlockhatchee River in east-central Florida to estimate the contribution of *new* storm-event water relative to total flow during a storm hydrograph. Environmental oxygen-18 was used as a conservative tracer in a series of mass-balance models. Steady-state and non-steady state models

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were derived at the catchment scale and applied at two sites on the Big Econlockhatchee River. Results of steady-state analyses indicated that approximately 76% of the total storm hydrograph was composed of *old*, or pre-storm, water.

Previously studies have widely applied the two-component hydrograph-separation model, although the assumption of steady-state conditions has not been addressed in the literature. Comparison indicates no substantial difference between SS and NSS modelling results under most conditions, including abrupt increases in flow associated with the rising limb of the hydrograph. The SS and NSS models produced similar estimates of old water contribution to the total storm hydrograph, indicating that the assumption of steady-state conditions was reasonable in this study. In general, other sources of error in the two-component model are likely to be equal to or greater than the assumption of steady-state. A separate model was derived to estimate indirectly the δ^{18} O of water entering a discrete river reach (C_G) using a mass-balance on δ^{18} O entering and leaving the reach. The model indicated that slightly less than 50% of the flow entering the river in the reach was new water. This increased amount of new water was attributed to a greater degree of urban development in the subcatchment draining the reach.

Increased proportions of new water with urban development implies a fundamental change in flow paths to the river. Groundwater flow through riparian zones may be altered, which may affect river water quality and change the ecology of riparian ecosystems. Although stormwater management regulations in much of the USA assure that the timing and volume of runoff leaving a parcel of land undergoing development does not change, the importance of preserving pre-development proportions of groundwater and surface water has been overlooked and the long-term impacts of these changes are unclear.

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