

Solute dynamics during bank storage flows and implications for chemical base flow separation

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[1] Chemical base flow separation is a widely applied technique in which contributions of groundwater and surface runoff to streamflow are estimated based on the chemical composition of stream water and the two end-members. This method relies on the assumption that the groundwater end-member can be accurately defined and remains constant. We simulate solute transport within the aquifer during and after single and multiple river flow events, to show that (1) water adjacent to the river will have a concentration intermediate between that of the river and that of regional groundwater and (2) the concentration of groundwater discharge will approach that of regional groundwater after a flow event but may take many months or years before it reaches it. In applying chemical base flow separation, if the concentration in the river prior to a flow event is used to represent the pre-event or groundwater end-member, then the groundwater contribution to streamflow will be overestimated. Alternatively, if the concentration of regional groundwater a sufficient distance from the river is used, then the pre-event contribution to streamflow will be underestimated. Changes in concentration of groundwater discharge following changes in river stage predicted by a simple model of stream-aquifer flows show remarkable similarity to changes in river chemistry measured over a 9 month period in the Cockburn River, southeast Australia. If the regional groundwater value was used as the groundwater end-member, chemical base flow separation techniques would attribute 8% of streamflow to groundwater, as opposed to 25% if the maximum stream flow value was used.

1. Introduction

[2] Over the past 30 years or more, solute mass balance methods have been widely used for quantifying the rate of groundwater discharge to rivers. If concentrations of the solute in surface water and groundwater end-members are known, then measured concentrations in the stream can be used to determine the fraction of each end-member in streamflow using a solute mass balance approach. Where end-member concentrations are constant and stream concentrations are measured over time, then changes in the proportion of the end-members over time can also be determined. Most usually, changes in proportions of surface runoff and groundwater discharge are determined during and immediately following rainfall events. A range of different solutes have been used, but silica, chloride, and stable isotopes of water ²H and ¹⁸O are most common [e.g., Turner

et al., 1987; Jordan, 1994]. Because the method partitions discharge into that derived from the rainfall event (“event water,” often equated with surface runoff) and that attributable to water that resided in the catchment prior to the rainfall event (“pre-event water,” often ascribed to groundwater), the method has become known as base flow separation. We here refer to it as chemical base flow separation, to distinguish it from base flow separation methods based only on flow hydrographs.

[3] Results of previous chemical base flow separation studies have been recently reviewed by *Genereux and Hooper* [1998] and *Jones et al.* [2006]. Most studies have concluded that more than 30% of river discharge during flow events is due to pre-event water. However, as pointed out by *Kirchner* [2003] and *Jones et al.* [2006], this finding appears to be inconsistent with groundwater hydraulic calculations, which suggest that groundwater does not respond rapidly to rainfall events, and so there should not be a significant increase in groundwater discharge to streams on the time scale for surface runoff. A number of papers have attempted to explain this apparent paradox, and the reader is referred to reviews by *Genereux and Hooper* [1998] and *Jones et al.* [2006] for detailed discussion of these. Most recently, *Chanat and Hornberger* [2003] and *Jones et al.* [2006] have proposed mechanisms involving mixing between end-members before they discharge to the stream,

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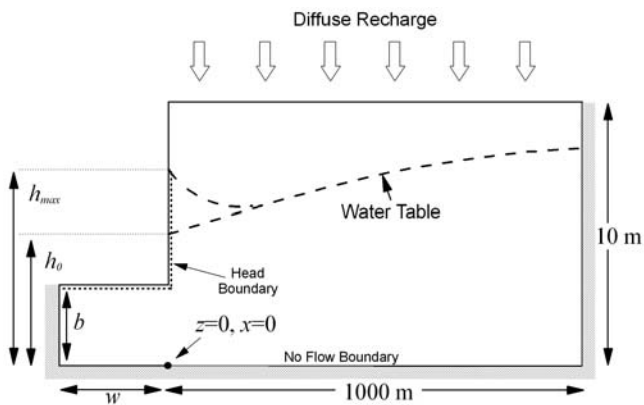


Figure 1. Model setup. (For fully penetrating rivers, $b = w = 0$.)

to explain the discrepancy. *Chanat and Hornberger* [2003] proposed a reservoir mixing model, whereby a near-stream zone mixes surface runoff and groundwater discharge before they enter the stream, although the physical processes causing this mixing are not clearly described. *Jones et al.* [2006] invoke mixing between surface runoff and groundwater by diffusion and dispersion, in areas where the water table is at or near the land surface. In this paper we discuss a mixing mechanism related to bank storage processes to explain the discrepancy.

[4] One of the implicit assumptions with the chemical base flow separation technique is that the groundwater and surface water end-members are constant in time. However, the method is applied during streamflow recession, when this assumption is least likely to hold. During high river stage, river water will enter the aquifer, where it may mix with regional groundwater. When the river stage falls, groundwater flows into the river. These bank storage processes have been studied for more than 50 years, and the hydraulics are reasonably well understood [*Cooper and Rorabaugh*, 1963; *Hall and Moench*, 1972; *Moench and Barlow*, 2000]. Only a very small number of papers, however, have specifically examined solute transport during this exchange process. *Squillace et al.* [1993] determined that return flow of bank storage contributed a significant amount of atrazine and deethylatrazine to the Cedar River, IA, under base flow conditions. The concentrations from bank storage were distinguishable from groundwater recharge due to higher concentrations. The authors did not consider the implications of differing concentrations of discharge water for chemical base flow separation. *Chen and Chen* [2003] used particle tracking to delineate the region of aquifer where groundwater is replaced by stream water during high river stages and analyzed how this region varied with stream and aquifer properties. However, they did not simulate solute transport or the mixing processes between the stream water and the regional groundwater. *Desilets et al.* [2008] investigated the interaction of a river and a stream under varying levels of stream-aquifer connection and how the composition of near stream water was impacted by this. They did not however investigate the implications of this for groundwater discharge concentrations. *Lin and Medina* [2003] simulated the transport of a pulse of contaminant released during a river flood event, as a means of illustrating the capabilities of a coupled surface water-groundwater

model. Their results showed that the contaminant, which entered the aquifer during the high river stage, would continue to discharge from the aquifer back into the river for an extended period of time. However, the paper did not provide an analysis of how the concentration of groundwater discharge was affected by stream and aquifer parameters nor did it consider the implications for chemical base flow separation methods.

[5] There are a number of papers that have modeled solute transport in groundwater in the vicinity of large river systems and that have simulated impacts of rising and falling river and groundwater levels on solute concentrations [e.g., *Jolly et al.*, 1998]. However, the complexity of natural systems sometimes does not allow the role of individual processes to be identified, and so it can be difficult to draw general conclusions from these studies. The object of this study is to investigate how water movement between a river and aquifer due solely to changes in river stage impact on near-stream chemistry and the implications of this for chemical base flow separation. The analysis is done using numerical simulation of an aquifer slice perpendicular to a stream. In the generic simulations, river water that enters the aquifer during high river stages and regional groundwater are assumed to have constant but distinct concentrations. The concentration within the aquifer and the concentration of aquifer discharge are examined following the passage of a single river flood wave (rise and fall of river stage) and following numerous flood waves spaced at regular intervals. The changing concentration of groundwater discharge during these flood waves has significant implications for chemical base flow separation methods. In a field example, concentrations observed within a river over a 9 month period are compared with outputs from this simple model.

2. Modeling

2.1. Conceptualization and Model Setup

[6] To examine changes in groundwater chemistry associated with bank storage processes, we have simulated a slice of aquifer perpendicular to a river. The numerical model HydroGeoSphere (HGS) has been used for flow and transport simulations, as it is capable of simulating saturated and unsaturated flow as well as solute transport [*Therrien et al.*, 2006]. Although this package is also able to simulate river flow, for the perpendicular slice model, we have simulated the river using a specified head boundary. The model domain was 10 m in height and 1 m in width (Figure 1). For simulation of partially penetrating streams ($b > 0$), the model length was $1000\text{ m} + w$, where $2w$ is the river width (i.e., the aquifer beneath the stream was simulated between the middle of the stream and the edge, and the aquifer was simulated for a distance of 1000 m from the edge of the stream). No flow boundaries were used along the base of the model, for the right hand boundary, and for the left hand boundary of the aquifer beneath the stream. The top of the model had a constant flux applied for the duration of each simulation to generate diffuse recharge (R) to the water table. The river stage was simulated using a time varying head (TVH) boundary, which was applied to all model cells at $x = 0$ m and between b and h_{max} in the z direction and also between $-w$ and 0 in the x direction and between b and $(b - 0.1\text{ m})$ in the z direction. For simulation of fully penetrating streams ($b = 0$), the domain length was 1000 m, and the TVH

boundary was applied between 0 and 0.1 m in the x direction and 0 and h_{\max} in the z direction.

[7] The head boundary was varied according to

$$h(0, t) = \begin{cases} h_0, & t = 0 \\ h_0 + \frac{(h_{\max} - h_0)}{2} \left(1 - \cos\left\{2\pi\frac{t}{t'}\right\}\right), & 0 > t \leq t' \\ h_0, & t' > t \leq t_{\max} \end{cases} \quad (1)$$

where h is the hydraulic head (L), t is time (T), t' is the duration of the stage oscillation, h_0 is the head at $t = 0$, and h_{\max} is the maximum head (at $t = t'/2$). This generates a cosine-shaped wave between $t = 0$ and $t = t'$, with amplitude $(h_{\max} - h_0)'$. Two sets of simulations were conducted. For single wave simulations, the initial head (h_0) was set to 5 m, the duration of the stage oscillation (t') was 5 days, and the total length of the simulation (t_{\max}) was 200 days. For multiple wave simulations, the duration of the stage oscillation was $t' = 5$ days, and the oscillation was repeated after time t_{\max} and at regular intervals thereafter, with t_{\max} varying between 10 and 100 days. In these cases, h_0 was set such that the average head of the oscillation and intervening period was equal to 5 m. Except for a small number of simulations that examined sensitivity to wave height, h_{\max} was always set as $h_0 + 1$ m. For multiple wave simulations, the total length of the simulation was 200 days, or 15 oscillations, whichever was the greater. In all simulations, the initial aquifer heads were determined from a steady state simulation with constant recharge R and constant river head $h_0 = 5$ m. In this paper fluxes from the river into the aquifer are considered to be negative, and fluxes from the aquifer into the river are positive.

[8] For solute transport, the whole model domain was assigned an initial concentration of 1 kg/m^3 , and all recharge was added at a concentration of 1 kg/m^3 . All concentrations in groundwater are reported relative to this input concentration and hence are dimensionless. There are two types of concentration boundaries that could be used for the river: a constant concentration boundary or a Cauchy (or third-type) boundary. The constant concentration boundary allows mass to enter the model both by advection and dispersion. Numerous studies have shown that dispersivity increases with scale [Silliman and Simpson, 1987; Gelhar et al., 1992]. The dispersivity at the boundary should therefore be very small. However, because a constant value of dispersivity is used throughout the model, the constant concentration boundary condition probably overestimates the dispersive flux in the initial stages of river inflow (when the concentration gradient across the boundary is high). The Cauchy boundary calculates fluxes and applies mass by advection only. This is unrealistic because diffusion and possibly dispersion will occur across the interface. Furthermore, because dispersion occurs as soon as mass enters the model domain, the Cauchy boundary causes a discontinuity in the concentration between the boundary and the adjacent node. Thus, both types of boundary have problems, and these are exacerbated in our case because we are considering processes near to the interface. We have chosen to use a constant concentration boundary because it avoids the flux (and concentration) discontinuity. A constant concentration of 0 kg/m^3 was applied at the same boundary as the

TVH boundary at times when the water flux was toward the aquifer to simulate the chemical signature of river water. In the base simulation, the dispersive flux across the boundary accounted for 21% of the river water signature added to the model. At times when the flux was from the aquifer to the river, this concentration boundary was removed. This resulted in solutes being removed advectively (at a rate of qC , where q is the rate at which water is removed by the TVH boundary, and C is the concentration of the water removed). We have not used a constant concentration boundary when removing water because the river concentration at this time will be dependent on the discharging groundwater concentrations and so is not known a priori.

[9] The model was discretized based on requirements of the simulation. In the x direction, the model was discretized from 0.01 m in close proximity to the TVH boundary to 200 m away from this boundary. In the z direction, the grid was discretized in three increments: 0.4 m from 0 to 4 m, 0.1 m from 4 to 6.5 m, and 0.7 m from 6.5 to 10 m. Finer discretization was used between 4 and 6.5 m due to the rising and falling water table over fairly short time frames close to the TVH. The grid contained a single 1 m cell in the y direction. (In this paper, fluxes are expressed in units of L^2/T , i.e., volume per time per width of aquifer.)

[10] The effect of stream and aquifer parameters on transport processes was determined by systematically varying parameters from a common base case simulation. This base case simulation is for a fully penetrating stream ($w = b = 0$) and uses an aquifer hydraulic conductivity of $K = 5 \text{ m/d}$, porosity of $\theta = 0.4$, recharge rate of $R = 0.08 \text{ m/yr}$, longitudinal dispersivity of $\alpha_L = 0.5 \text{ m}$, and transverse dispersivity of $\alpha_T = 0.05 \text{ m}$. These parameters are considered to be typical of alluvial aquifers composed of coarse sands and gravels. The dispersivity was chosen as representative of a travel distance of 2 m [Gelhar et al., 1992]. Where variations to these parameters are made, this is described in the text. For some of the simulations, a 0.5 m thick zone of low hydraulic conductivity was included immediately adjacent to the river (model cells between 0 and 0.1 m in the x direction). Unsaturated zone parameters were assumed to follow the relationship described by van Genuchten [1980], with $\alpha = 15 \text{ m}^{-1}$, $\beta = 3$, and a residual saturation of 0.04, values that are representative of a sand [Carsel and Parrish, 1988].

[11] The accuracy of the numerical model was tested by comparing simulated flow rates with those derived from the analytical solution of Cooper and Rorabaugh [1963] for a semi-infinite confined aquifer (Figure 2). (Analytical solutions are not available for unconfined aquifers.) A 100 m thick aquifer was simulated to ensure that the rise in head was much less than the thickness of the aquifer. Both fully saturated and unconfined aquifers were simulated in HGS. For these simulations, the aquifer recharge rate was set to zero. The confined simulation and the analytical solution show excellent agreement and are almost indistinguishable. The unconfined model is significantly different. Peak discharge to the aquifer is similar; however, it is delayed when compared to the analytical and confined models. Also, peak return flows are much lower in the unconfined case. The differences are likely due to processes within the unsaturated zone that are not accurately simulated using a constant value of specific yield. In particular, movement into and out of the

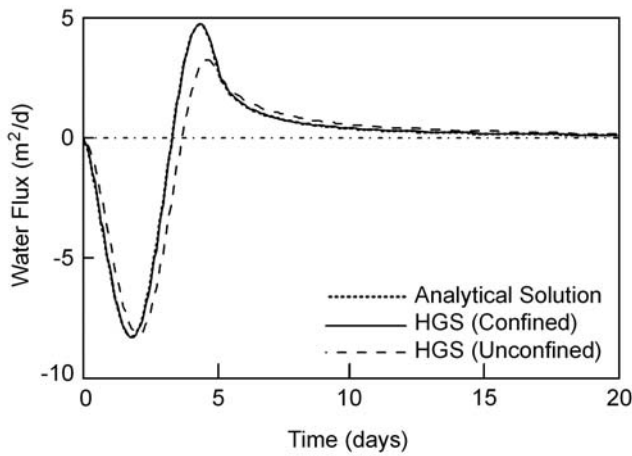


Figure 2. Water fluxes into and out of an aquifer due to river stage variation in a fully penetrating river. Comparison between numerical simulation for a confined aquifer and an unconfined aquifer, and analytical solution for a confined aquifer with a hydraulic conductivity of $K = 5$ m/d [Cooper and Rorabaugh, 1963]. In the confined aquifer solution, an aquifer thickness of 100 m and storativity of 0.24 (equal to the specific yield of the unconfined aquifer) is used. Note that the analytical solution and the confined numerical solution are almost indistinguishable.

unsaturated zone causes the pressure head to propagate much more rapidly in the deep part of aquifer than at the water table resulting in vertical head gradients. This indicates the need to explicitly model the unsaturated zone in the near stream environment to accurately simulate the bank storage process.

2.2. Single Wave Event

[12] The calculated water exchange flux between the river and the groundwater during and following the variation in river stage, as well as the concentration of groundwater immediately adjacent to the river at times of groundwater discharge for the base case are shown in Figure 3. For this particular simulation, flow from the river to the aquifer commences after 0.3 days and continues until 3.3 days. The total flux of river water into the aquifer over this time is 3.91 m^2 . The cumulative return flux is equal to this value after 9.2 days (5.9 days after return flow commenced). Immediately after the flow reverses and groundwater begins to discharge back into the river, the concentration of groundwater discharge would be expected to be close to zero (the river concentration) because groundwater discharge would largely comprise river water that had only recently entered the aquifer. We might also expect that the concentration would remain close to this value until 9.2 days, at which time it should return to the value of regional groundwater. Needless to say, we would expect some transition between these two concentrations. However, Figure 3d shows that the concentration of groundwater discharge is significantly greater than zero almost immediately after the flux direction changes and does not reach a value of 0.9 until 33 days (almost 30 days after the flow direction reverses). Although the dispersivity used in the simulations is not particularly large, very high dispersion is caused by the high ground-

water velocities that occur close to the stream bank. The maximum flow rate between the stream and aquifer occurs at 1.9 days, when groundwater velocities are in excess of 1 m/d. Corresponding dispersion coefficients are thus more than $0.5 \text{ m}^2/\text{d}$. The distribution of concentration within the aquifer at the time of flow reversal is shown in Figure 4a. Although the average distance of penetration of river water into the aquifer is only about 2 m, the effect of dispersion is very noticeable.

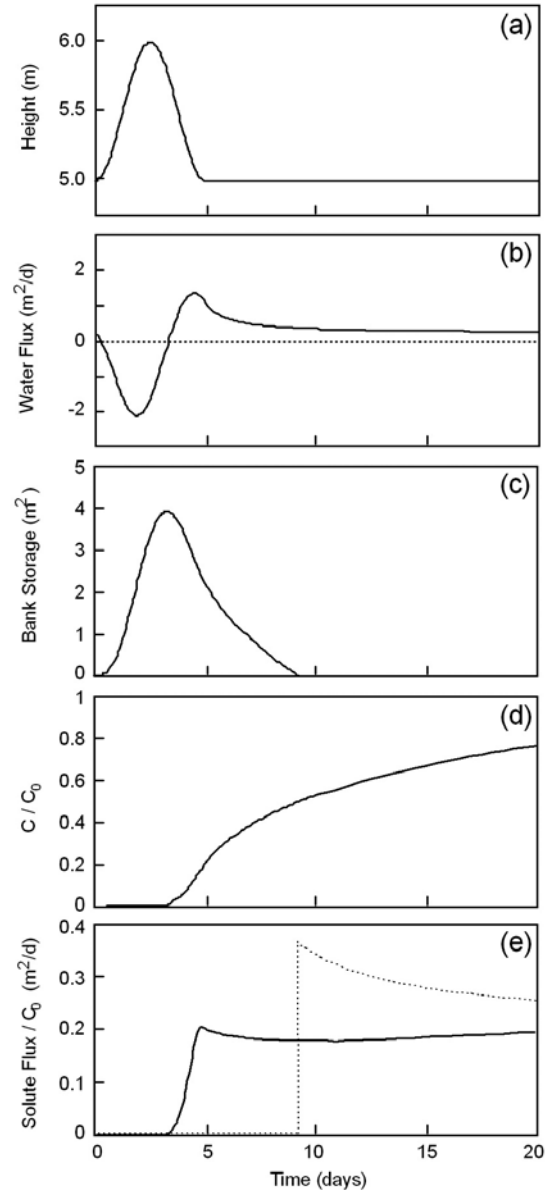


Figure 3. Water and solute fluxes associated with a rise in river stage for a fully penetrating stream. (a) Cosine wave head boundary in the stream used to drive surface water-groundwater exchanges; (b) water flux between the river and aquifer (negative fluxes denote flows from the river to the groundwater.); (c) volume of water in bank storage (d) mean concentration of water exchange; and (e) solute flux. The broken line in Figure 3d indicates the solute flux in the absence of dispersive mixing. The simulation is for $K = 5$ m/d, $\theta = 0.4$, $R = 0.08$ m/yr, $\alpha_L = 1$ m, and $\alpha_T = 0.1$.

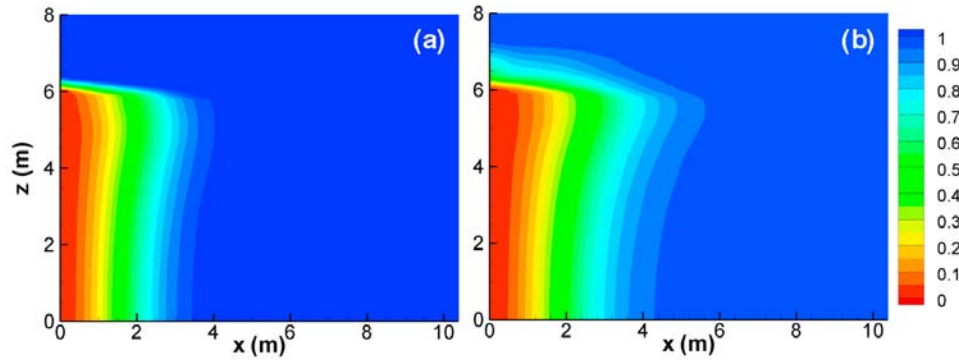


Figure 4. (a) Concentrations within the aquifer after 3.3 days, immediately prior to flow reversal, for the simulation depicted in Figure 3. (b) Concentration in the aquifer immediately prior to flow reversal after 10 flow events (simulation depicted in Figure 6). These plots show the maximum penetration of river water into the aquifer in cases of single and multiple waves, respectively.

[13] Because the groundwater discharge rate is falling as the concentration of groundwater discharge is increasing (compare Figures 3b and 3d), the solute flux to the river can display a more complex pattern. In the case shown here, the normalized solute flux peaks within 1-2 days of flow reversal, before initially declining but then increasing to eventually approach a value of $0.22 \text{ m}^2/\text{d}$ (the steady state groundwater flux) (Figure 3e). The normalized solute flux is equal to the water flux that would be estimated from a base flow separation, if correct values for groundwater and surface water end-members were used. It should be noted, however, that since the base flow separation equations do not include dispersive terms, they will be incorrect if the dispersive flux is significant. The broken line in Figure 3e

shows the solute flux to the river that would be expected in the absence of dispersion, with river water (concentration of zero) discharging from the aquifer until 9.2 days, after which the solute flux would equal the water flux (concentration of one).

2.3. Single Wave Sensitivity Analyses

[14] The concentration of groundwater discharge at any particular time will be a function of aquifer parameters that control solute transport. Effects of variations in dispersivity, hydraulic conductivity, aquifer recharge rate, porosity, river penetration, and clogging layer hydraulic conductivity are shown in Figure 5. Increases in dispersivity result in increased concentration of groundwater discharge in early time periods

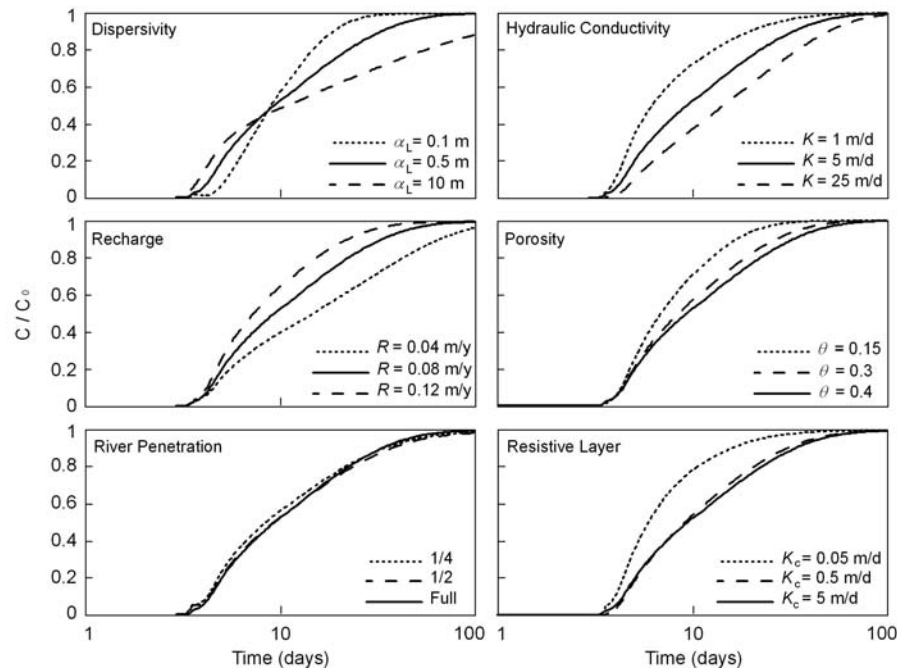


Figure 5. Effect of variation in dispersivity, hydraulic conductivity, recharge rate, porosity, river penetration, and resistive layer hydraulic conductivity on the concentration of groundwater discharge during bank storage return flow. (Transverse dispersivity was maintained at 10% of longitudinal dispersivity, and partially penetrating rivers are 10 m in width.) Model parameters are otherwise the same as in Figure 3.

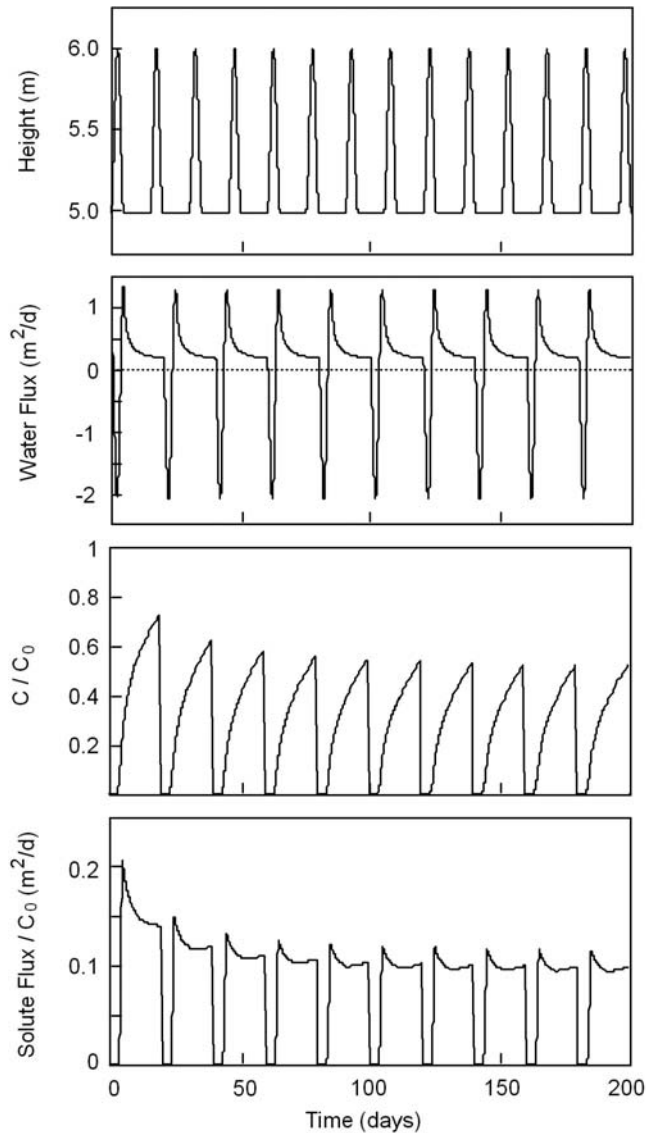


Figure 6. Water and solute fluxes associated with a regular variation in river stage. (a) Head boundary in the stream, (b) water flux between the river and aquifer, (c) mean concentration of water exchange, and (d) solute flux. A recharge rate of $R = 0.04$ m/yr has been used for these simulations. Other parameters are the same as in Figure 3.

but decreased concentration in later times. Decreases in hydraulic conductivity and increases in aquifer recharge rate both result in increases in the concentration of groundwater discharge (the concentration of groundwater discharge returns to the ambient groundwater concentration more rapidly). As the diffuse recharge rate increases, the bank storage penetrates a shorter distance into the aquifer and also returns to the river more quickly (because the ambient groundwater velocity toward the river is higher). Similarly, decreasing the hydraulic conductivity results in decreased penetration of bank storage into the aquifer. Decreases in wave height and aquifer thickness (not shown) have a similar effect to decreases in hydraulic conductivity, with a smaller flux of water into the aquifer, and hence decreased mixing with ambient groundwater. The concentration of groundwater discharge returns to the value of regional groundwater more

rapidly. Decreases in porosity result in the concentration of aquifer discharge returning to the value of regional groundwater more rapidly, and this is due to an increased regional groundwater velocity. (If the groundwater flux is constant, then a decrease in porosity causes an increase in velocity.) Interestingly, while variation in river penetration has a significant influence on the distribution of concentrations within the aquifer, it has only a very small effect on the concentration of groundwater discharge. (River penetration refers to the ratio of the river depth (before the stage oscillation) to the sum of river depth and aquifer thickness below the river. Thus, one-fourth penetration is $(h_0 - b)/h_0 = 0.25$, one-half penetration is $(h_0 - b)/h_0 = 0.5$, and full penetration is $(h_0 - b)/h_0 = 1$.) As expected, the inclusion of a highly resistive “clogging” layer adjacent to the river greatly reduces the magnitude of bank storage exchanges, and hence also, the rate at which the concentration of groundwater discharge returns to the ambient groundwater concentration.

2.4. Multiple Flow Events

[15] Where multiple river flow events occur, the groundwater concentration adjacent to the river may not return to the ambient groundwater concentration between the passage of consecutive waves. In most systems, river flow events will be of variable magnitude and duration, and the water chemistry adjacent to the river will be dynamic, reflecting the variation in this forcing function. For simulation purposes, however, we consider a series of flow events that have a consistent size and concentration and regular frequency. In this case, the concentration within the aquifer will approach a dynamic equilibrium and the concentration of groundwater discharging to the river will increase with time after each flow event, reaching a consistent, maximum value immediately before the passage of the next flow event. The water and solute fluxes and concentration of groundwater discharge as a function of time, for a flow event with a return period of 20 days ($t' = 5$ days, $t_{\max} = 20$ days) are shown in Figure 6. The concentration of groundwater discharge immediately before the passage of the next wave decreases over time but stabilizes after about 10 waves. At this time, the maximum concentration of groundwater discharge is only about 0.4. This maximum concentration will be a function of the model parameters, particularly the wave height, aquifer recharge rate, return

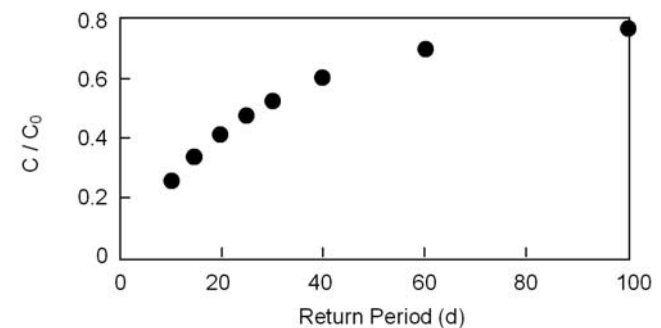


Figure 7. Sensitivity of maximum observed concentration of groundwater discharge to return period, for a regular variation in river stage. A recharge rate of $R = 0.04$ m/yr has been used for these simulations. Other parameters are the same as in Figure 3.

period of the wave, and the dispersivity. Sensitivity of maximum concentration to groundwater parameters is the same as for a single wave (Figure 5). Variations in the maximum concentration as a function of return period are shown in Figure 7. As expected, longer periods of time between consecutive waves result in higher concentrations.

3. Implications for Chemical Base Flow Separation

[16] The traditional approach for estimating changes in groundwater discharge to streams during river flow events using chemical base flow separation involves comparison of the measured stream chemistry, with that of rainfall and groundwater sources. If there are only two sources of streamflow, the conservation of mass dictates that the total solute flux in streamflow must equal the sum of the fluxes contributed from the two sources:

$$F_T = F_S + F_G, \quad (2)$$

where F is the solute flux (mass per time), and subscripts S and G refer to the two sources. Most usually, it is assumed that advection dominates the flux, and so both the component flux and the total fluxes can be written as $F = Qc$. Substituting, and invoking conservation of water ($Q_T = Q_S + Q_G$), gives the traditional two-component base flow separation equation:

$$\frac{Q_G}{Q_T} = \frac{(c_T - c_s)}{(c_G - c_s)}, \quad (3)$$

where Q_G is the streamflow attributable to water stored within the catchment prior to the rainfall event (sometimes equated with regional groundwater), Q_T is the total river flow rate, c_T is the tracer concentration in the river, c_s is the surface runoff end-member concentration, and c_G is the pre-event (or groundwater) end-member concentration.

[17] The groundwater concentration is often assumed equal to the river concentration during base flow conditions (e.g., prior to the rainfall event, *Jordan* [1994]). The surface runoff concentration is most usually assumed to be equal to the rainfall concentration, which is determined from rainfall sampling within the catchment [*Joerin et al.*, 2002]. Most frequently the stable isotopes of water (^{18}O and ^2H) have been used as tracers, but chloride, silica, and electrical conductivity have also been used. The assumptions inherent in application of equation 3 are that the tracers are conservative and that the end-members are constant with time and can be accurately defined.

[18] The numerical simulations presented in this paper have shown

[19] 1. that there will usually be a zone of water adjacent to the river, with a concentration intermediate between that of the river and that of the aquifer; and

[20] 2. that the concentration of groundwater discharge will increase with time after a flow event but may take many months or years before it reaches the concentration of regional groundwater.

[21] Our simulations are for a generic tracer, and so the results are applicable to isotopic as well as ionic tracers. The implications for chemical base flow separation are twofold. First, the concentration of groundwater discharging to the

river is likely to be less than the mean pre-event concentration and much less than the regional groundwater concentration unless the aquifer recharge rate is very high and/or an extremely long period of time has elapsed since the last river flow event. Otherwise, the use of the river concentration prior to the flow event for c_G in equation 3 will result in overestimation of the pre-event contribution to streamflow and even greater overestimation of the contribution of regional groundwater. (The pre-event water will include bank storage from previous river flow events, and hence, the pre-event contribution will be higher than the regional groundwater contribution.) In the case of regional groundwater, the magnitude of this overestimation may be an order-of-magnitude or more. Consider, for example, that $c_T = 0.28$, $c_s = 0.25$, $c_G = 1$ but where c_G is incorrectly assigned a value of 0.3, based on the river chemistry prior to the flow event. The proportion of flow due to groundwater is estimated to be 60% but is actually only 4%.

[22] Second, if the regional groundwater concentration is used as c_G , then equation 3 will underestimate the total discharge of groundwater to the river and will also underestimate the pre-event contribution to streamflow. It will, however, correctly estimate the flux of regional groundwater. The total discharge of groundwater will comprise return of bank storage from the current rainfall event, return of bank storage from previous rainfall events, and discharge of regional groundwater. The latter two components can be considered to comprise pre-event water. Use of the regional groundwater concentration for c_G will correctly estimate the discharge of regional groundwater. If dispersion is negligible, the flux obtained from equation 3 must equal the groundwater discharge rate, provided that the end-members have been correctly specified (conservation of mass). When averaged over a long period of time, it will also equal the mean groundwater discharge rate since bank storage flows sum to zero.

4. Field Example

[23] To determine if the results obtained from the modeling are consistent with trends observed in the field, we here compare simulation results with electrical conductivity data for the Cockburn River. The Cockburn River is a semipermanent stream in the Southern Highlands of New South Wales, southeastern Australia, which drains into the Peel River immediately upstream of the town of Tamworth. A gauging station at Mulla Mulla (31.03°S, 151.07°E), in the upper part of the Cockburn River has a catchment area of 907 km², and a mean annual flow of approximately 5.5×10^7 m³. Mean annual rainfall at Tamworth is 670 mm and is reasonably evenly distributed throughout the year, with all months having a mean rainfall of at least 44 mm.

[24] The majority of the Cockburn Catchment is part of the New England Fold Belt and consists of a Cambrian to Silurian ophiolitic sequence, which was uplifted and subjected to mild metamorphism in the Late Carboniferous. Groundwater samples have been collected from eight bores screened within these Carboniferous sediments, most of which are upstream of the gauging station. The electrical conductivity (EC) of these samples ranged between 674 and 1800 $\mu\text{S}/\text{cm}$, with a mean of 1170 $\mu\text{S}/\text{cm}$ [*Cook et al.*, 2006].

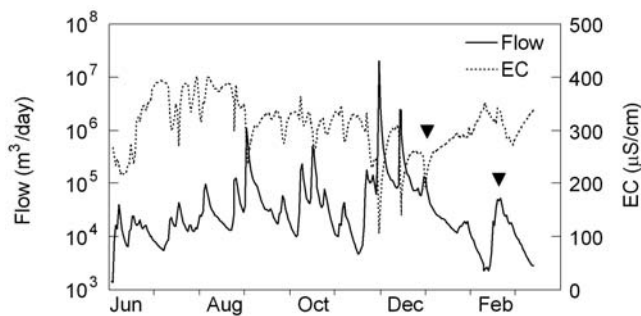


Figure 8. River flow and electrical conductivity measured at Mulla Mulla gauging station between 1 June 2008 and 15 March 2009. Flow events on 1 January and 20 February 2009 are indicated by solid triangles.

[25] Mean daily river flow and electrical conductivity of the Cockburn River between 1 June 2008 and 15 March 2009 is shown in Figure 8. Over this period, mean daily flow rates ranged between 1.4×10^3 and 2.0×10^7 m³/d, and electrical conductivity was between 107 and 403 μ S/cm. As expected, peak river flows are associated with low stream electrical conductivities. It is noteworthy, however, that at all times the electrical conductivity of the river is significantly less than the lowest value measured in any of the groundwater monitoring bores and less than half the mean groundwater value. It is also apparent that the river EC increases only slowly after river flow events, a pattern that is most notable following high flow events on 1 January and 20 February 2009. In fact, the EC of the river was still increasing on 15 March, following the mid-February event. Both of these observations are consistent with the modeling results.

[26] Simulations have been carried out using our simple cross section model in an attempt to reproduce the river electrical conductivity data shown in Figure 8 (although our model only represents the groundwater component of streamflow). For these simulations, the observed river stage is used as the TVH boundary. During major flow events, when flow occurs from the river to the aquifer (a total of 58 days, out of 288), a specified concentration equal to the observed river EC is applied to this boundary. (The maximum river stage often does not coincide with the lowest observed electrical conductivity. This is largely because of time delays associated with flow in the river, which is not considered in our 2-D, slice model. For this reason, we have used the minimum electrical conductivity over the 3-day period centered on the flow event as the concentration of the river for the period when the river is recharging the aquifer rather than the actual concentration measured on that day.) The model uses the same soil parameters as for the generic simulations. Other model parameters are given in Table 1. The simulated concentration of groundwater discharge as a

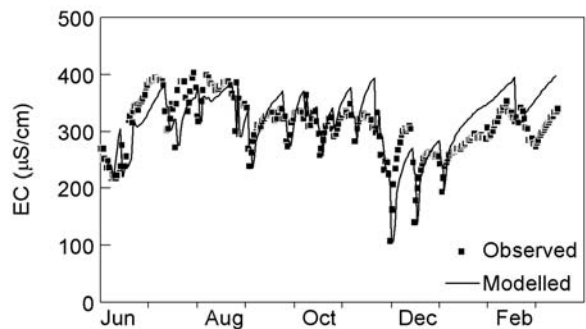


Figure 9. Comparison between observed and simulated values of electrical conductivity of the Cockburn River, between 1 June 2008 and 15 March 2009.

function of time is shown in Figure 9. Considering that the model is for a homogeneous aquifer, only represents 2-D flow and uses a constant concentration for regional groundwater, the fit between the model and the observed data is considered to be very good. In most cases, the observed changes in river concentration are reproduced by the model, although the model does not always accurately predict the rate at which concentration increases following flow events. Different rain events may produce different changes in river level at different points along the river, in part due to differences in the locations of rainfall within the catchment. The electrical conductivity of regional groundwater discharge also shows spatial variability. For these reasons, the electrical conductivity of groundwater discharge will vary along the river, and so the rate of increase in electrical conductivity following a flow event is likely to be different for different events. This variation cannot be captured using a 2-D slice model. Nevertheless, the model explains 60% of the observed variation in the data for the period until 10 January 2009. Although river heads were high during a flow event on 20 February, electrical conductivity did not decrease significantly until 27 February. The higher electrical conductivity values during the higher flows may be due to a number of processes, which are not simulated by our model, and it results in a poorer fit for the February period. It should be noted that almost identical fits could be obtained using different model parameters (using higher values for dispersivity and lower values of porosity, for example). Our purpose is not to uniquely determine aquifer parameters but to show that exchange flows resulting from bank storage processes using reasonable values of parameters can reproduce the main features of the data. On the basis of the results of this modeling, we believe that the process of bank storage offers a plausible explanation to the behavior of stream EC following flow events in Cockburn River.

[27] As discussed above, results of base flow separation are strongly affected by the value used for the groundwater end-member concentration. For the 288 day period shown in Figure 9, the total river flow is 4.43×10^7 m³. The electrical conductivity of the river varied between 107 and 403 μ S/cm (c_T). If we used the maximum observed concentration in the river (403 μ S/cm) for c_G and the minimum observed concentration (107 μ S/cm) for c_S , then equation 3 calculates a total groundwater contribution to streamflow of 1.13×10^7 m³ or 25% of the river flow. However, if instead

Table 1. Parameters Used in Simulation Depicted in Figure 9

Parameter	Description and Units	Value
R	Diffuse recharge rate (m/yr)	0.01
K	Hydraulic conductivity (m/d)	10
ϵ	Porosity (dimensionless)	0.4
α_L	Longitudinal dispersivity (m)	2.5
α_T	Transverse dispersivity (m)	0.25

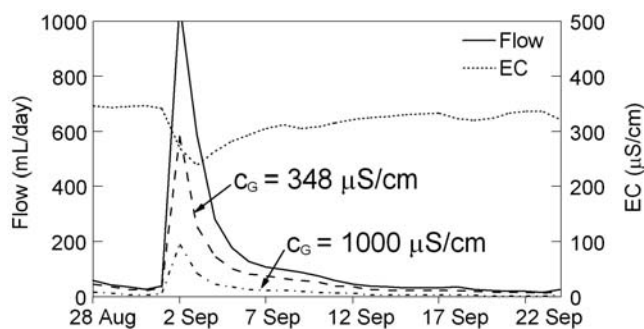


Figure 10. River flow and electrical conductivity of the river during a large flow event in September 2008. Results of base flow separations using groundwater end-members of 403 and 1000 $\mu\text{S}/\text{cm}$ are compared.

we use the mean value measured in regional groundwater ($\sim 1000 \mu\text{S}/\text{cm}$) for c_G , then we get a groundwater contribution to streamflow of $3.74 \times 10^6 \text{ m}^3$ or less than 8% of the river flow.

[28] A chemical base flow separation for a large flow event in early September 2008 is shown in Figure 10. The electrical conductivity of base flow immediately prior to this event was $348 \mu\text{S}/\text{cm}$, and during the event, this dropped to $237 \mu\text{S}/\text{cm}$. A total of $2.35 \times 10^6 \text{ m}^3$ of flow occurred over the 6 day period between 2 and 7 September (inclusive). If a value of $c_G = 348 \mu\text{S}/\text{cm}$ is used in the hydrograph separation, then it is concluded that $1.54 \times 10^6 \text{ m}^3$ (or 65% of the total river flow) can be attributed to groundwater discharge. If instead we use $c_G = 403 \mu\text{S}/\text{cm}$ (the maximum measured value over the period of record), we get $1.25 \times 10^6 \text{ m}^3$ (53%). However, if we use the mean regional groundwater value of $1000 \mu\text{S}/\text{cm}$, then we get $4.15 \times 10^5 \text{ m}^3$ (18%).

5. Discussion

[29] Solute transport processes in aquifer-stream environments are likely to be highly complex. However, our understanding of these complex processes can be improved using simple models that isolate the various processes. In this paper we focus on how bank storage processes may influence the chemistry of groundwater discharge to a stream following flow events. Our results have important implications for assessment of groundwater discharge to streams using chemical base flow separation methods.

[30] End-member analyses of water sources will be correct provided that (1) all the various sources have been identified, (2) concentrations of end-members are constant in time and have been accurately estimated, (3) tracers used are conservative, and (4) dispersion is negligible. Conservation of mass ensures that this is the case. In end-member mixing between surface runoff and groundwater discharge to streams, the problem occurs when the river concentration prior to the rainfall event is used to estimate the groundwater inflow end-member concentration.

[31] Groundwater discharge to the river following passage of a flood wave will comprise (1) return of bank storage that entered the aquifer during the event, (2) return of bank storage from previous flow events, and (3) discharge of regional groundwater. Streamflow comprises these three sources and surface runoff. In reality, the concentrations of

all of these end-members will vary in space and time. However, during flow events, the concentration of river water will be similar to that of surface runoff. Before it mixes with groundwater, the concentration of bank storage will be the same as river water. Thus, if the concentration of surface runoff is much less than that of groundwater, then a two-component end-member mixing analysis can be used to distinguish regional groundwater discharge from the other sources. Furthermore, small variations in concentrations of these source components (surface runoff, river water, and bank storage) will not introduce large errors. (This assumes that although there is variation in concentrations of streamflow between different events, these differences are much less than the differences between streamflow and regional groundwater.) However, the mass balance will be highly sensitive to the estimated concentration of regional groundwater discharge. Often, the concentration in the river immediately prior to the river flow event is used to indicate the groundwater end-member. Our simulations have shown that if this value is used in the hydrograph separation, then the results will greatly overestimate the contribution of regional groundwater. On the other hand, if the concentration of regional groundwater is used as an end-member, then (provided that dispersion is negligible) the contribution of regional groundwater discharge to the river flow will be correctly estimated.

[32] Accurate estimation of the regional groundwater concentration, however, may not be straightforward. Our results suggest that the groundwater concentration is probably best determined by collecting groundwater samples a sufficient distance from the river, so that the influence of river water is unlikely and the samples can be considered to represent regional groundwater. It is difficult to determine what this critical distance will be; it will depend not only on the size of the river and the magnitude of variations in river stage but also on the aquifer hydraulic conductivity and diffuse recharge rate.

[33] In some cases, the base flow separation is used to calculate proportions of event and pre-event water (rather than specifically runoff and groundwater). However, our results suggest that this is unlikely to yield accurate results because pre-event water includes both regional groundwater and bank storage. The concentrations of bank storage and regional groundwater are likely to differ greatly, and the relative proportion of each in pre-event water discharge will change over time. Thus, the concentration of pre-event water discharging to the river will change with time.

[34] The role of dispersion in surface water-groundwater exchange is difficult to assess. River concentrations will change more rapidly than groundwater concentrations. This will lead to sharp concentration gradients across the interface during flow events, which will drive diffusive and dispersive fluxes. However, because dispersivity is scale dependent, the magnitude of these fluxes may be less than simulated using our model. If we had used a Cauchy boundary condition, then the distribution of mass adjacent to the river would have been different. However, since the purpose of this paper is to illustrate a process rather than estimate precise values of dispersivity, this would not have affected our conclusions. Nevertheless, if the dispersive flux across the interface is significant, then it would need to be specifically accounted for in the mass balance equation.

[35] Our study has not addressed spatial variability of concentrations of regional groundwater. In most systems, some spatial variation in regional groundwater concentrations will occur due to other processes (including spatial variations in recharge). This can also lead to temporal changes in the concentration of groundwater discharge, if the areas contributing groundwater discharge to the stream change over time. In some systems, evapotranspiration near the stream may increase the concentration of groundwater discharge [e.g., *Stewart et al.*, 2007], and in some cases, the concentration of groundwater discharge may even be greater than the concentration of regional groundwater. We have not considered this issue, although it is clear that if evapotranspiration of groundwater is a constant fraction of groundwater discharge, then this process could lead to overestimation of the groundwater discharge rate by an amount proportional to the evapotranspiration loss. (If 10% of groundwater discharge is lost to evapotranspiration, then the groundwater discharge rate would be overestimated by $0.1/(1 - 0.1) = 11\%$.) We have also not considered possible variation in rainfall and runoff end-member concentrations, which may be considerable.

[36] There are a number of limitations with our model. We have simulated only a slice of aquifer perpendicular to the river, with a constant rate of diffuse recharge, and with a specified head boundary to represent the river. Our model, therefore, does not include effects of transport within the stream itself, and our simulations only indicate changes in concentration of groundwater discharge and not concentrations in the river. Because we assume a constant rate of diffuse recharge, we have not simulated the increase in height of the water table that would occur due to the same rainfall event that produces the increase in river flow. However, to properly consider this process would require a 3-D model, which would explicitly simulate surface runoff and flow in the river channel. This is beyond the scope of the current paper. Also, we have simulated a rectangular river section and so do not consider overbank flows, and the potential for infiltration of floodwaters to mobilize near-stream groundwaters. These processes can be very important in systems with large floodplains [e.g., *Jolly et al.*, 1998]. Nevertheless, our simple model provides a reasonable fit to the observed electrical conductivity of the Cockburn River over a period of 9 months. The good fit between the observed and modeled data suggests that the exchange flows between the river and groundwater induced by river stage variations offer a plausible explanation for stream water chemistry, at least in this environment.

6. Conclusions

[37] Chemical base flow separation methods rely on accurate quantification of end-member concentrations and assume that these concentrations are constant with time. However, this is unlikely to be the case during and immediately following large river flow events. River water that enters the aquifer during high river stages mixes with regional groundwater, before discharging from the aquifer back to the river after the river stage falls. Where the groundwater has a higher concentration than the river, the concentration of groundwater discharge will increase with time after a flow event but may take many months or years before it reaches the concentration of regional groundwater.

The implications of this for chemical base flow separation are twofold. First, if the concentration in the river prior to a flow event is used to represent the pre-event or groundwater end-member, then the groundwater contribution to streamflow will be overestimated. Second, if the concentration of regional groundwater a sufficient distance from the river is used as the groundwater end-member, then the pre-event contribution to streamflow (regional groundwater discharge plus bank storage from previous events) will be underestimated, but the regional groundwater discharge will be accurately estimated.

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