Sediment carbon fate in phreatic karst (Part 2): Numerical model development and application


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Abstract

The authors develop a numerical model to elucidate time-distributed processes controlling sediment carbon fate in phreatic karst. Sediment carbon processes simulated in the new numerical model include conduit erosion and deposition, sediment carbon transport, surficial fine grained laminae evolution, carbon pool mixing, microbial oxidation, and the understudied process of sediment carbon exchange during equilibrium transport. The authors perform a model evaluation procedure that includes generalized likelihood uncertainty estimation to quantify uncertainty of the model results. Modeling results suggest that phreatic karst conduits sustain sediment transport activity long after surface storm events cease. The sustained sediment transport has the potential to shift the baseflow sediment yield of the phreatic karst to be on par with stormflow sediment yield. The sustained activity is suggested to promote the exchange of sediment carbon between the water column and subsurface karst deposits during equilibrium sediment transport conditions. In turn, the sediment carbon exchange impacts the mixing of new and old carbon pools and the flux of carbon from phreatic karst. Integrated numerical model results from this study support the concept that phreatic karst act as a biologically active conveyor of sediment carbon that temporarily stores sediment, turns over carbon at higher rates than surface streams, respires carbon dioxide to the water column, and recharges degraded organic carbon back to the fluvial system. The numerical modeling method adopted in this paper shows the efficacy of coupling carbon isotope fingerprinting with water quality modeling to study sediment carbon in phreatic karst.

1. Introduction

The authors’ motivation for Part 2 of these two companion papers was to advance numerical modeling of sediment carbon in phreatic karst. The conceptual model developed in Part 1 was carried forward and further tested with a new numerical simulation. The conceptual model from Part 1 suggests that phreatic karst acts as a biologically active conveyor of sediment carbon that temporarily stores sediment, turns over carbon at higher rates than surface streams, respires carbon dioxide to the water column, and recharges degraded organic carbon back to the fluvial system. Karst morphologic and hydrologic features for which the conceptual model, and hence the numerical model herein, are deemed applicable includes active sediment carbon delivery from surface streams to subsurface karst, the presence of a phreatic system that promotes carbon storage and turnover, and active recharge of sediment back to the fluvial network. The authors’ arguments for research that warrants improving numerical modeling of phreatic karst systems is described in the following paragraphs.

Karst terrain covers 12% of the Earth’s land surface (Ford and Williams, 2007) underscoring the importance of numerical modeling to better elucidate the role of karst systems within fluvial carbon cycling. Nevertheless, we find that few studies have performed numerical modeling of sediment carbon in karst. A number of authors have performed hydrologic and hydraulic modeling of karst aquifers that has led to the development of many methods to estimate spring discharge such as the application of pipe flow models (Thraikill, 1974; Jeannin, 2001), watershed modeling tools (Baffaut and Benson, 2009; Palanisamy and Workman, 2014), and equivalent porous media models (Scanlon et al., 2003; Panagopoulos, 2012; Hartmann et al., 2014). However, the development of numerical models to estimate sediment transport is a relatively uninvestigated area of karst research save for a recent study that used results of a watershed modeling simulation and sediment measurements at a springhead to indirectly estimate...
sediment discharge (Nerantzaki et al., 2015). With respect to carbon, Simon and Benfield (2001) modeled stream metabolism and carbon processing in a karst cave and found that rates of benthic organic carbon turnover are high in caves compared to surface streams. However, no studies, to our knowledge, have focused on modeling sediment carbon fate in karst.

The development of numerical modeling tools for sediment has a number of advantages for karst systems. One advantage is that numerical modeling can help to elucidate coupled physical and biological processes that exhibit interdependence and non-linearity and cannot be studied with data alone. The surficial fine grained laminae is a feature of phreatic karst that exhibits such complexity for which numerical modeling is deemed useful. The physically-active surficial fine grained laminae is partially controlled by the sediment transport carrying capacity of the fluid to transport sediment carbon in phreatic karst. Within a numerical model, the transport capacity can be calibrated using sediment measurements (Guo and Jin, 1999; Russo and Fox, 2012). Further, the biologically-active surficial fine grained laminae is partially controlled by the inrush of labile carbon and microbial oxidation. Within a numerical model, carbon source quality that is input to the system can be simulated with carbon fingerprinting while carbon measurements can be used to constrain oxidation (Ford and Fox, 2014; Fox and Ford, 2016). Thereafter, continuous simulation of the processes can be integrated to understand their net influence on phreatic karst.

A second advantage of numerical modeling of sediment carbon in phreatic karst is that processes that cannot feasibly be measured in a phreatic setting can be simulated to appreciate their role, or lack thereof, to carbon fate. Sediment exchange between suspended sediments and bed deposits has long been known to occur in fluvial systems during equilibrium sediment transport (i.e., net-zero erosion/deposition, Chang, 1988), yet rarely has been included in sediment transport modeling because emphasis was on prediction of bed morphology or sediment transport rates. In the case of sediment carbon, sediment exchange from turbulent mixing of bed and suspended sediment has the potential to change the overall carbon makeup of each pool even during equilibrium transport conditions. Numerical modeling of phreatic karst allows explicit consideration of sediment carbon exchange between the water and surficial fine grained laminae during transport.

A third advantage of numerical modeling in karst systems is that model calibration and model-integrated results can provide additional lines of evidence to support the conceptual models that underlie our comprehension of karst systems. While the progress of karst research calls for the use of advanced instrumentation and measurements (White, 2002), emphasis on numerical modeling provides a cost-effective alternative to high resolution data collection. Numerical modeling allows the researcher to fill in gaps in data streams when instruments malfunction or are under routine maintenance. These continuous estimates of processes are then integrated to provide sediment carbon budgets. Thereafter, numerical modeling results can provide an additional line of evidence to reinforce, or refute, postulations made during conceptual model development. In this context, it will be shown that the numerical model applied in this study gives further evidence to support the concept that karst pathways act as biological conveyors that temporarily trap and release surface-derived sediment (see Paper 1: Conceptual Model).

The authors had the objective to develop and apply a sediment carbon numerical simulation model to phreatic karst. The main contributions of this paper are: (1) advancement of sediment carbon modeling for karst by coupling physical processes, biological processes, and carbon isotope fingerprinting; (2) the use of the numerical model to simulate sediment transport and sediment carbon exchange processes that have not been investigated previously for karst systems; and (3) integrated results of the numerical simulation that provide additional lines of evidence towards a conceptual model of sediment carbon within karst pathways.

2. Methods

2.1. Model formulation

The authors formulate the numerical model by considering the existence of karst morphologic and hydrologic features, including active sediment carbon delivery from the surface to subsurface karst, the presence of a phreatic system that promotes carbon storage and turnover, and active recharge of sediment back to the fluvial network (Atkinson, 1977; Drysdale et al., 2001; Massei et al., 2002; White, 2002; Fleury et al., 2007, 2013; Bakalowicz et al., 2008; Herman et al., 2008). The authors assume sediment carbon originating from urban/suburban and agricultural landscapes and streams is transported within the fluvial load (<53 μm in diameter) to a phreatic karst conduit. Quick flow from surface streams to a phreatic conduit (i.e., tertiary porosity pathways) are formulated to dominate sediment carbon inputs based on the data results in the companion Paper 1 as well as by the results of others (Ryan and Meiman, 1996; Katz et al., 1998; Mahler and Lynch, 1999; Pronk et al., 2006; Simon et al., 2007). Based on the potential for a mixture of land uses and stream conditions, the authors consider that sediment carbon can be from a mixture of carbon pools with varying levels of quality (e.g., litter-derived, soil carbon, algae). The authors formulate the model considering that boundary condition measurements of sediment carbon inflowing to a phreatic karst system (i.e., at swallets or sinking streams) and carbon recharged from the phreatic karst (i.e., at springheads) provide information for model inputs and model evaluation, respectively.

The authors formulate the continuity equation to simulate sediment organic carbon (SOC) fate within a phreatic conduit as

\[
\frac{d(SSOC)}{dt} = Q_{SOCin} - Q_{SOCout} + Q_{SOCitr} + \sum_{i=1}^{n_i} E_{SOCi} - D_{SOC} + X_S - X_{SS}
\]

and

\[
\frac{d(SOC)}{dt} = -\sum_{i=1}^{n_i} E_{SOCi} + D_{SOC} - X_S + X_{SS} - DEC_{SOC}.
\]

where each term has dimensions of mass per time (kg s\(^{-1}\)). Eqs. (1) and (2) represent sediment carbon fate within suspended sediment (SS) and storage (S), respectively, within a phreatic conduit. In Eq. (1), suspended sediment carbon may transport into \(Q_{SOCin}\) and out of \(Q_{SOCout}\) a section of a phreatic conduit or may arrive within the conduit from swallets that pirate sediment carbon from surface streams \(Q_{SOCitr}\). Sediment carbon can move between suspended sediment and storage with the surficial fine grained laminae by physical mechanisms, including erosion from surface storage and deep storage \(E_{SOC}\), where \(n_i\) vertical depths of sediment are stored), deposition to the stored sediment carbon \(D_{SOC}\), and the exchange (X) during equilibrium sediment transport. During storage within the surficial fine grained laminae, sediment carbon can undergo microbial oxidation \(DEC_{SOC}\), and carbon fingerprinting can be used to discretize incoming labile and recalcitrant pools that can be tracked within a phreatic conduit and simulated using pool-specific oxidation rates.

The authors formulate erosion within a phreatic conduit based on the physical limitations of shear, transport, and supply as

\[
E_{SOC} = S_{SOC}S^{-1}\min[a(\tau_a - \tau_c)^{\beta}B(T_cT_e - SSR^{-1}S_t^{-1})],
\]

where \(S_{SOC}S^{-1}\) is the density of carbon within the stored sediment (gC g\text{sed}^{-1}) since the erosion and deposition mechanics are based
on both the inorganic and organic portions of the fluvial load, \( \tau_o \) is the fluid shear stress at the bed of the phreatic conduit (Pa), \( \tau_c \) is the critical shear stress of sediment (Pa), \( a \) and \( b \) are empirical coefficients, \( L \) is the bed length (m), \( W \) is the bed width (m), \( T_c \) is the transport carrying capacity (kg \( m^{-1} s^{-1} \)), and \( t \) is the time step (s). The fluid shear stress for conduit flow can be estimated by the Darcy-Weisbach formula as

\[
\tau_o = \frac{f \rho V^2}{8},
\]

where, \( f \) is the Darcy friction factor (unitless), \( \rho \) is the density of water (kg \( m^{-3} \)), and \( V \) is the velocity of fluid in the conduit (m \( s^{-1} \)). The erosion rate in Eq. (3) also relies on the excess transport capacity expressed as the difference between the sediment transport carrying capacity of the flow (\( T_c \)) and the suspended sediment load per time. \( T_c \) (kg \( m^{-1} s^{-1} \)) can be expressed (Julien and Simons, 1985; Hessel and Jetten, 2007) as

\[
T_c = C_T \frac{1}{T_o},
\]

where \( C_T \) (m \( 1/2 s^2 kg^{-1/2} \)) is an empirical coefficient typically calibrated with suspended sediment measurements. The available storage of sediment (kg) within the phreatic conduit is the final erosion rate-limiting process as the surficial fine grained laminae source can be exhausted as a result of erosion.

The authors simulate sediment carbon deposition within the phreatic conduit for hydraulic conditions when excess transport capacity is not met. Deposition of sediment carbon can be expressed using a sediment deposition function (Russo and Fox, 2012) as

\[
D = SS_{SOC} SS^{-1} \times \max \left[ \frac{W_r}{k_p H} (SS_{r1} - T_c t), 0 \right],
\]

where \( SS_{SOC} SS^{-1} \) is the density of carbon in the suspended sediment (gC g Sed^{-1}), \( W_r \) is the settling velocity of sediment (m \( s^{-1} \)), \( k_p \) is the deposition coefficient based on the Rouse concentration profile (unitless), and \( H \) is the height of the phreatic conduit (m).

The authors formulate Eqs. (1) and (2) by accounting for the exchange (X) of sediment carbon during equilibrium sediment transport. It is recognized that during equilibrium sediment transport there is a net-zero effect on the mass of suspended sediment or mass of stored sediment within the conduit bed, however, instantaneous turbulence allows for near-continuous exchange of sediment from the water column to the bed and vice versa (e.g., Chang, 1988). The equilibrium exchange is included to potentially change the overall makeup of carbon quality in the suspended and stored carbon pools as

\[
X_{SS} = (e_s SS) \times (SS_{SOC} SS^{-1}) \ \ t^{-1},
\]

and

\[
X_S = (e_s SS) \times (SS_{SOC} SS^{-1}) \ \ t^{-1},
\]

where, \( e_s \) is the exchange rate (unitless) between suspended and stored surficial fine grained laminae sediment carbon. The physical mass of sediment mixed (\( e_s SS \)) is equal (i.e., equilibrium mixing) in Eqs. (7) and (8), but the quantity of sediment carbon within the water column or bed (i.e., \( SS_{SOC} SS^{-1} \) and \( SS_{SOC} SS^{-2} \), respectively) can vary.

The authors formulate sediment carbon fate by considering that temporarily stored carbon within the surficial fine grained laminae of the phreatic conduit undergoes oxidation by heterotrophic bacteria. The authors formulate a first-order decomposition function for each carbon pool

\[
DEC_{SOC} = \sum_{j=1}^{n_p} k_j SS_{SOC}.
\]

where \( j \) is an index for carbon pool (i.e., litter, soil, algae), \( n_p \) is the total number of carbon pools, \( k \) is the soil decomposition rate (d^{-1}) of each pool, and \( SS_{SOC} \) is the supply of organic carbon associated with each pool in the surficial fine grained laminae (kg).

### 2.2. Model setup and discretization

The authors test the sediment carbon numerical formulation in Eqs. (1) through (9) within the coupled Cane Run Creek Watershed and Royal Spring Groundwater Basin located in the Bluegrass Region of central Kentucky, United States. The reasons for choosing the fluviokarst system and the physiogeographic features of the system are described in Fig. 3 and the methods section of our companion Paper 1. In brief, a landscape with urban/suburban and agricultural land uses drains to the Cane Run Creek and its tributaries. The phreatic subsurface conduit is approximately 16 km in length, generally aligned with the main stem of the surface channel of Cane Run, and pirates nearly all surface flow during low to moderate hydrologic conditions. The phreatic conduit is approximately 20 m below the ground surface, is hydraulically controlled by a subsurface dam, and recharges at the Royal Spring springhead, which has the highest average discharge of any perennially spring in the highly karstic region of central Kentucky, USA (Currens et al., 2015).

The authors applied the numerical model for sediment carbon to the primary phreatic conduit, and discretized the model formulation as follows. The authors specified three sediment carbon pools, including fine-sized litter, recalcitrant soil carbon, and stabilized algae, that can be transported to the phreatic conduit and vary in recalcitrance and microbial oxidation rates (Thorpe and Delong, 2002; Marin-Spiotta et al., 2014). The authors specified two vertical depths of sediment carbon in the phreatic conduit including the highly active surficial fine grained laminae and a deeper more consolidated storage with higher critical shear stress (Ford and Fox, 2014). The authors discretized the transport carrying capacity using the residual \( T_c \) concept (Chang, 1988) such that the surficial fine grained laminae would be eroded first followed by the deeper, more consolidated stored bed carbon. The authors discretized the transport calibration coefficient to differentiate between baseflow and stormflow transport in the phreatic conduit (Russo and Fox, 2012), which reflects three orders of magnitude difference in fluid energy. The authors discretized the phreatic conduit into sixteen, 1 km in length, spatial cells and simulated the model at a one hour time step. The temporal discretization reflected the authors’ confidence in the time series data. The spatial scale was selected in order to satisfy the Courant-Friedrichs-Lewy condition such that the average velocity of suspended sediment carbon within the model is on the same order of magnitude as the downstream transmission of information (Islam and Chaudhry, 1997).

The authors used data, including water, sediment, sediment carbon measurements and carbon fingerprinting results, from surface streams as upstream inputs to the model (see Fig. 1). The authors solved the numerical model for sediment carbon flux and sediment carbon storage for each spatial cell and time step by estimating erosion and deposition as a function of hydraulic variables and sediment concentration and by performing the calculation steps outlined in Russo and Fox (2012) and Husic (2015). The authors used data, including sediment and sediment carbon measurements, within the conduit at the Groundwater Station (see Paper 1, Fig. 3) and at the springhead (Royal Spring) as downstream boundary conditions and for model evaluation.

### 2.3. Model inputs and parameterization

The friction factor was estimated by solving for the conservation of energy from within the conduit to the springhead (see...
model inputs in Table 1). The maximum supply of the surficial fine grained laminae was estimated by assuming that the neutrally buoyant mixture reaches a maximum depth of 5 mm (Droppo and Stone, 1994; Stone and Droppo, 1994; Droppo and Amos, 2001). The bulk density of the deeper bed sediment is estimated as $1.5 \times 10^3$ kg m$^{-3}$ (Russo and Fox, 2012). The exponent in the erosion calculation (Eq. (3)), $b$, is assumed to be 1 for all fluvial erosion sources, which agrees with the concept of erosion being a shear driven process (Hanson and Simon, 2001; Sanford and Maa, 2001; Wynn et al., 2008; Simon et al., 2009). Erodibility and critical shear stress for these equations, $a$ and $\tau_c$, are parameterized uniquely for each erosion source based on literature reported values and equations (Droppo and Amos, 2001; Hanson and Simon, 2001; Sanford and Maa, 2001; Simon and Thomas, 2002; Russo and Fox, 2012). Sediment settling velocity was modeled using Stoke’s Law and the settling depth coefficient was estimated based on a uniform concentration profile (Russo and Fox, 2012). The boundary flow rate reflects changes in sediment transport behavior.

Fig. 1. Fluviokarst sediment and carbon transport modeling framework. STAGE 1: model preparation. Sediment pirated from tributaries ($Q_{SS}$), conduit flow rate ($Q_i$), and hydraulic and hydrologic input were calculated for use in model. STAGE 2: Sediment Transport Model (STM). Transport coefficients ($C_{tc}$) were calibrated to match STM results with TSS data. STAGE 3: Carbon Model (CM). The generalized likelihood uncertainty estimation (GLUE) method was performed to estimate the distribution of results, model domain, and optimal model run for the CM.
between baseflow and storm flow and is dependent on hydraulic watershed characteristics (Russo and Fox, 2012).

Sediment carbon quality varies within the watershed due to land use. Fingerprinting results (see Table 3, companion Paper 1) were used to unmix soil, algal, and litter carbon contributions to urban and agricultural tributaries. The proportion of urban ($P_{urban}$) and agricultural ($P_{ag}$) land use in each model cell is shown in Table 2. The flux of sediment by surface tributaries into the main Cane Run creek was modeled using Einstein’s Approach (Chang, 1988) which integrates the vertical velocity and sediment concentration profiles over the flow depth. Sediment and flow pirating from the surface channel into the subsurface conduit was estimated as a function of swallet density ($P_{swallet}$), surface sediment concentration, and conduit flow rate and satisfied the conservation of mass within each model cell (Husic, 2015). Conduit bathymetry at the Groundwater Station (cell 10) was estimated from the results of multiple quantitative dye, Doppler sonar, and video experiments. The geometry at other cells (see Table 2) was estimated by optimizing net dynamic equilibrium of sediment over the simulation period.

Model parameterization ranges that were carried forward to the model evaluation relied on measurements within the study region or ranges reported in the literature for similar systems. The percent algae ($P_{algae}$) in surface-derived sediment was modeled using a distribution from a nearby agriculturally dominated watershed (Ford et al., 2014, also see Paper 1). Decomposition rates for soil, litter, and algal carbon were parameterized based on results from literature (Webster et al., 1999; Six and Jastrow, 2002; Ford and Fox, 2014). Liu et al. (2010) investigated sediment exchange ratio ($e_x$) variation using grain-size distributions within an estuary dominated by clayey silt and estimated that the exchange ratio is <0.10 for unidirectional flows. While the exchange rate is likely to vary with turbulence intensity, mean bursting and sweeping behavior was approximated by a single rate within the model.

2.4. Model evaluation

Model evaluation was facilitated using measured datasets detailed in our companion Paper 1. In brief, flow, sediment, and sediment organic carbon data were collected over a two year period to calibrate and validate model results. Flow and turbidity data were sampled at 15 and 10 min intervals, respectively, and sediment organic carbon samples were collected approximately every fortnight. Surface streams were continuously monitored using staff gages while a Marsh McBirney® 201-D magnetic water flow-meter was deployed in the subsurface conduit to collect continuous velocity data. Depth integrated sediment samples were collected and analyzed for total suspended solids (TSS). Turbidity and TSS were correlated to provide a continuous record of sediment transport. Sediment organic carbon values of the tributaries and outlets were measured using in situ trap samplers (Phillips et al., 2000).

Calibration parameters for the sediment model included the transport capacity coefficients for low and high flows. Regarding
Fig. 3. (a) Sediment model results at the Groundwater Station, and (b) longitudinal surface fine grained laminae (SFGL) depth changes in conduit.

Table 1
Model inputs, initial conditions, potential calibration parameters in sediment transport model, and calibration parameters in the carbon model.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔL</td>
<td>Spatial step</td>
<td>1 x 10^3</td>
<td>m</td>
</tr>
<tr>
<td>Δt</td>
<td>Temporal step</td>
<td>3600</td>
<td>s</td>
</tr>
<tr>
<td>f</td>
<td>Darcy friction factor</td>
<td>0.3</td>
<td>Unitless</td>
</tr>
<tr>
<td>ρ</td>
<td>Density of water</td>
<td>1 x 10^3 kg m^-3</td>
<td></td>
</tr>
<tr>
<td>ρ_{SFGL}</td>
<td>Bulk density of SFGL sediment</td>
<td>1 x 10^3 kg m^-3</td>
<td></td>
</tr>
<tr>
<td>ρ_{BED}</td>
<td>Bulk density of deep bed sediment</td>
<td>1.5 x 10^3 kg m^-3</td>
<td></td>
</tr>
<tr>
<td>d_{max}</td>
<td>Maximum depth of SFGL sediment</td>
<td>5.0 x 10^-3 m</td>
<td></td>
</tr>
<tr>
<td>c_{SFGL}</td>
<td>Critical shear of the SFGL source</td>
<td>0.05 Pa</td>
<td></td>
</tr>
<tr>
<td>c_{BED}</td>
<td>Critical shear of the bed source</td>
<td>1 Pa</td>
<td></td>
</tr>
<tr>
<td>w_s</td>
<td>Mean settling velocity of suspended material</td>
<td>9.2 x 10^-4 m s^-1</td>
<td></td>
</tr>
<tr>
<td>k_p</td>
<td>Settling depth coefficient</td>
<td>0.5 unitless</td>
<td></td>
</tr>
<tr>
<td>Q_{boundary}</td>
<td>Boundary between low and high flows</td>
<td>1.4 m^3 s^-1</td>
<td></td>
</tr>
<tr>
<td>SOC_{urban}</td>
<td>Carbon content of urban sediment</td>
<td>5.70 gC 100gSed^-1</td>
<td></td>
</tr>
<tr>
<td>SOC_{ag}</td>
<td>Carbon content of agricultural sediment</td>
<td>3.83 gC 100gSed^-1</td>
<td></td>
</tr>
<tr>
<td>d(SFGL,0)</td>
<td>Initial depth of SFGL sediment in the conduit</td>
<td>2.5 x 10^-3 m</td>
<td></td>
</tr>
<tr>
<td>S_{SOC}(0)</td>
<td>Initial organic carbon content of SFGL</td>
<td>2.68 gC 100gSed^-1</td>
<td></td>
</tr>
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</table>

Sediment calibration parameters

<table>
<thead>
<tr>
<th>C_{low}</th>
<th>Transport capacity coefficient for low flows</th>
<th>Min</th>
<th>Optimal</th>
<th>Max</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 x 10^-6</td>
<td>1.2 x 10^-5</td>
<td>4.0 x 10^-5</td>
<td>m^1/2 s^-1 kg^-1/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_{high}</td>
<td>Transport capacity coefficient for high flows</td>
<td>3.0 x 10^-7</td>
<td>3.1 x 10^-6</td>
<td>6.0 x 10^-6</td>
<td>m^1/2 s^-1 kg^-1/2</td>
</tr>
</tbody>
</table>

Carbon calibration parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Min</th>
<th>Median</th>
<th>Max</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_{algal}</td>
<td>Percent of algal carbon</td>
<td>0</td>
<td>0.21</td>
<td>0.4</td>
<td>Unitless</td>
</tr>
<tr>
<td>k_s</td>
<td>Soil carbon decomposition rate</td>
<td>2.6 x 10^-6</td>
<td>1.1 x 10^-4</td>
<td>2.3 x 10^-4</td>
<td>d^-1</td>
</tr>
<tr>
<td>k_l</td>
<td>Litter carbon decomposition rate</td>
<td>2.3 x 10^-4</td>
<td>4.5 x 10^-3</td>
<td>8.0 x 10^-3</td>
<td>d^-1</td>
</tr>
<tr>
<td>k_a</td>
<td>Algae carbon decomposition rate</td>
<td>2.3 x 10^-4</td>
<td>4.0 x 10^-3</td>
<td>8.0 x 10^-3</td>
<td>d^-1</td>
</tr>
<tr>
<td>e_x</td>
<td>Sediment mixing exchange rate</td>
<td>0</td>
<td>0.043</td>
<td>0.10</td>
<td>Unitless</td>
</tr>
</tbody>
</table>
calibration, it is well recognized that sediment transport model yields are highly sensitive to the transport capacity terms with negligible sensitivity to other parameters (Ahmadi et al., 2006; Hessel and Jetten, 2007; Yan et al., 2008; Russo and Fox, 2012). Further, note that the two controlling transport capacity coefficients are independent and do not interact since they are used for mutually exclusive hydrologic conditions (i.e., baseflow vs storm flow). Therefore, sediment transport model results were calibrated with the transport capacity coefficients using the collected data at the Groundwater Station (see “Stage 2” Fig. 1). The Generalized Reduced Gradient method (GRG nonlinear algorithm) was used to optimize sediment transport modeling results (Lasdon et al., 1974). Initial conditions to the algorithm were selected based on manual calibration and visual assessment of the model and data sediment discharge graphs. Sediment transport model results were evaluated using the Nash-Sutcliffe efficiency (Nash and Sutcliffe, 1970) following the guidelines of Moriasi et al. (2007). Nevertheless, the fact that the data range is on the same order of magnitude smaller than that of the algal (k\textsubscript{a} = 4.0 \times 10^{-3} d^{-1}) and litter (k\textsubscript{l} = 4.5 \times 10^{-3} d^{-1}) carbon pools, but near the maximum end of soil decomposition rates published in other studies (Alvarez and Guerrero, 2000; Ford and Fox, 2014). Model results also showed the exchange rate to be 4.3% and the percent of algae in the carbon load to be 21%. The distribution of model results and data results is approximately normal and the minimum, median, and maximum model outputs are shown in Fig. 2b. The sediment carbon model under predicts the range of variability exhibited by the sediment carbon data results reflecting the mean representation of erosion and decomposition in the model (e.g., constant rates over grid cells that are approximately one kilometer in length). For example, it is realized that fluvial sediment carbon data can be highly variable (Ford et al., 2014) reflecting episodic transport of eroded sediment (Fox and Papanicolaou, 2008) and the spatial variability of decomposition hot spots in fluvial systems (Battin et al., 2003). Nevertheless, the fact that the data range is on the same order as the model results and is included within the model domain (Fig. 2c) adds confidence to the results and highlights that the model is able to reflect the mixing of new sediment carbon transported to the subsurface and resuspended sediment carbon that was temporarily stored in the bed.

3. Results and discussion

3.1. Model evaluation

Sediment transport model results from the phreatic conduit agreed well with sediment data observations during calibration and validation periods (Fig. 2a). Baseflow conditions were reflected well in the model suggesting that the low flow transport capacity coefficient represented the sediment transport dynamics in the conduit adequately. Model results typically underestimated peak sediment discharge: low estimates of peak sediment discharge could arise from heterogeneity of sediment inputs (e.g., swallet geometry, spatial variability, and clogging). The E\textsubscript{N} and R\textsuperscript{2} statistics for calibration and validation perform satisfactorily when compared to sediment modeling results reported in the literature (Moriasi et al., 2007), especially considering that the model was simulated at an hourly time step while most literature values are daily or monthly. Yuan et al., (2001) showed that statistical evaluation values worsen as time steps are shortened.

Sediment carbon model results from Royal Spring were evaluated using the GLUE methodology by which values for the five carbon model calibration parameters were estimated. Of the 20,000 model simulations, approximately half of the parameter sets were found to meet the specified statistical criteria (t-test, \(\alpha = 0.05\)). The parameter median values of the acceptable model results showed that the decomposition rate of soil (k\textsubscript{s} = 1.1 \times 10^{-4} d^{-1}) was one order of magnitude smaller than that of the algal (k\textsubscript{a} = 4.0 \times 10^{-3} d^{-1}) and litter (k\textsubscript{l} = 4.5 \times 10^{-3} d^{-1}) carbon pools, but near the maximum end of soil decomposition rates published in other studies (Alvarez and Guerrero, 2000; Ford and Fox, 2014). Model results also showed the exchange rate to be 4.3% and the percent of algae in the carbon load to be 21%. The distribution of model results and data results is approximately normal and the minimum, median, and maximum model outputs are shown in Fig. 2b. The sediment carbon model under predicts the range of variability exhibited by the sediment carbon data results reflecting the mean representation of erosion and decomposition in the model (e.g., constant rates over grid cells that are approximately one kilometer in length). For example, it is realized that fluvial sediment carbon data can be highly variable (Ford et al., 2014) reflecting episodic transport of eroded sediment (Fox and Papanicolaou, 2008) and the spatial variability of decomposition hot spots in fluvial systems (Battin et al., 2003). Nevertheless, the fact that the data range is on the same order as the model results and is included within the model domain (Fig. 2c) adds confidence to the results and highlights that the model is able to reflect the mixing of new sediment carbon transported to the subsurface and resuspended sediment carbon that was temporarily stored in the bed.

### Table 2

Conduit bathymetry, swallet density, and land use information for model cells. \(P_{\text{swallet}}\) represents the proportion of swallets in the watershed located within a particular model cell. \(P_{\text{urban}}\) and \(P_{\text{ag}}\) represent the percentage of land used for agricultural and urban purposes, respectively, contributing to a given model cell.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Height (m)</th>
<th>Width (m)</th>
<th>(P_{\text{swallet}})</th>
<th>(P_{\text{urban}})</th>
<th>(P_{\text{ag}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.45</td>
<td>3.11</td>
<td>9</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>3.42</td>
<td>6</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>0.59</td>
<td>4.04</td>
<td>11</td>
<td>63</td>
<td>37</td>
</tr>
<tr>
<td>4</td>
<td>0.65</td>
<td>4.51</td>
<td>10</td>
<td>58</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>0.69</td>
<td>4.79</td>
<td>7</td>
<td>52</td>
<td>48</td>
</tr>
<tr>
<td>6</td>
<td>0.73</td>
<td>5.04</td>
<td>6</td>
<td>48</td>
<td>52</td>
</tr>
<tr>
<td>7</td>
<td>0.77</td>
<td>5.35</td>
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<td>54</td>
</tr>
<tr>
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<td>5.72</td>
<td>14</td>
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<td>57</td>
</tr>
<tr>
<td>9</td>
<td>0.86</td>
<td>5.97</td>
<td>12</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>10*</td>
<td>0.90</td>
<td>6.22</td>
<td>15</td>
<td>38</td>
<td>62</td>
</tr>
<tr>
<td>11</td>
<td>0.90</td>
<td>6.22</td>
<td>No surface sediment diverted to the conduit in Cells 11–16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.90</td>
<td>6.22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>0.90</td>
<td>6.22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0.90</td>
<td>6.22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.90</td>
<td>6.22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16*</td>
<td>0.90</td>
<td>6.22</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Cell 10 represents the Groundwater Station (GS) site.

* Cell 16 represents the Royal Spring (RS) site.
carbon in the phreatic conduit. The fate of pirated sediment provides a depiction of sustained fluid energy’s impact on sediment carbon. Sediment is pirated from the surface streams to the phreatic conduit during storm events from September 2011 to April 2012 and from December 2012 to August 2013 while April 2012 to December 2013 is a period of prolonged drought with little to no stormflow (Fig. 3a, $Q_{ss}$). Storage in the surficial fine grained laminae (SFGL in Fig. 3a) increases during the largest storm events because sediment is deposited as the transport carrying capacity of the fluid decreases in the phreatic conduit relative to the surface streams. However, sustained fluid energy exists in the phreatic conduit long after stormflow has ceased in the surface streams. The sustained transport capacity continues to erode the sediment from the surficial fine grained laminae such that sediment transport rates are non-zero for much of the time during September 2011 to April 2012 and December 2012 to August 2013. The sustained sediment transport results in high yields of sediment during baseflow conditions in the surface streams. For example, integrated model results showed that 46% of the total sediment exported from the phreatic conduit to the springhead occurs during periods of no surface stream activity. The sediment carbon eroded from the surficial fine grained laminae and transported during these baseflow periods is lower than newly pirated sediment carbon (i.e., OC in Fig. 4a) and highlights the recharge of degraded sediment carbon back to the surface streams.

The longitudinal variability of sediment storage and sediment carbon transport in the conduit highlights the role of equilibrium sediment exchange in phreatic karst. The surficial fine grained laminae’s evolution shows the highest variability in the first 10 km of the phreatic conduit (i.e., cells 5 and 10 in Fig. 3b). The phreatic conduit in this section is near swallets that deliver sediment. The sediment deposits to the surficial fine grained laminae and later erodes as mentioned above. Moving downstream in the conduit from kilometers 11 to 16, much lower variability of the surficial fine grained laminae’s depth is shown in time (i.e., cells 13 and 16 in Fig. 3b). The phreatic conduit does not gain or lose water or sediment through this section and the cross sectional area is fairly uniform. The fluid energy is relatively constant and the mass rate of suspended sediment stays relatively constant spatially through this section.

While fluid and sediment is conveyed at constant rates in the lower reach of the phreatic conduit, sediment carbon transport varies due to equilibrium sediment exchange. Sediment carbon becomes more and more degraded when moving downstream in the conduit (i.e., $Q_{OC}$ decreases from GW to RS in Fig. 4a). Suspended sediment instantaneously exchanges more labile suspended sediment carbon with more recalcitrant bed sediment carbon. The organic carbon content of suspended sediment is considerably higher than that of the surficial fine grained laminae (i.e., OC in Fig. 4a) due to the fact that heterotrophic bacteria oxidize organic carbon while it is temporarily stored. The sediment exchange during equilibrium sediment transport therefore causes the entrainment of older, more highly decomposed bed sediment and deposition of more labile, newly delivered sediment carbon. The exchange process also impacts the distribution of transported carbon across carbon pools (Fig. 4b). The proportion of soil carbon increases in the surficial fine grained laminae relative to the suspended sediment and remaining algae and litter carbon decrease due to their order of magnitude higher rates of decomposition. Equilibrium sediment exchange increases the proportion of the degraded soil carbon to the sediment carbon load during conveyance through the phreatic conduit, again highlighting a more degraded sediment carbon that is recharged to surface streams.

The mentioned hydrologic processes, including the sustained fluid energy to transport degraded sediment carbon during low flow and the impact of equilibrium sediment exchange upon transporting degraded carbon, are worthy of discussion. Both processes have the potential to help deliver degraded carbon from phreatic karst to surface streams, and neither process has been mentioned previously in the literature, to the authors’ knowledge.

One net effect of sustained fluid energy in phreatic karst is that storm flow deposition coupled together with low to moderate flow erosion results in a near long term equilibrium of the surficial fine grained laminae (Fig. 3a). The surficial fine grained laminae can therefore continuously harbor and oxidize sediment carbon. Another impact is that the phreatic karst often acts as a constant conveyer of sediment carbon through the system regardless of surface stream conditions (i.e., as mentioned, nearly half of sediment is transported during surface baseflow). The sediment transport activity of the phreatic karst highlights the disconnect between surface and subsurface streams in karst terrain. This is particularly interesting because conventional wisdom, or at least the first rule of thumb, is that fluvial systems transport 90% of their sediment load during 5% of the year (Walling and Webb, 1982; Hossain and Eyre, 2002). The phreatic karst obviously does not conform to this conventional wisdom and in turn continually recharges degraded sediment carbon to surface streams.

The equilibrium sediment exchange extends our knowledge of phreatic karst but also highlights the potential importance of a less studied sediment transport physical process. Sediment transport scientists have long understood that suspended sediments in turbulent flow can actively exchange with stored bed sediments although during equilibrium transport it is recognized that the net exchange is zero (e.g., Chang, 1988). The physics of the sediment exchange process has been more recently justified using advanced visualization techniques and it has been found that sediment erosion and deposition is coupled to flow coherency (Cellino and Lemmin, 2004). Cellino and Lemmin (2004) showed that low momentum zones of coherent fluid that transports settling sediment episodically deposits sediment to the bed while fluid ejections associated with the shedding phenomena at the bed episodically re-suspends bed sediment into the water column. However, sediment exchange processes between the water column and bed during equilibrium transport have been rarely included in sediment transport models. One reason for omitting the equilibrium exchange process from models is a lack of need for such detailed information given that the net results sought after for sediment transport models have been the downstream transport rates distributed over time and the net change in the streambed elevation; estimates of sediment equilibrium exchange does not help this goal. A second reason for omitting the exchange process from sediment transport models has likely been a lack of methods to help parameterize the exchange rate, as studies such as those by Cellino and Lemmin (2004) were experimental in nature and limited to the laboratory scale.

The equilibrium exchange of sediment is potentially of high interest in the recent class of scientific studies that emphasize elucidating the role of carbon processes in the inland freshwater carbon budget (Battin et al., 2008; Regnier et al., 2013). In the case of sediment carbon fate and transport in the phreatic karst studied here, the exchange rate appears important given the potential to exchange labile carbon with recalcitrant carbon. It is likely that the net importance of the equilibrium exchange process upon sediment carbon fate varies in other fluvial systems. For example, storm-activated surface stream equilibrium transport can be of a short duration since bed sediments are eroded to the water column during the rising limb of the hydrograph while sediments originating from upstream are deposited to the bed during the falling limb of the hydrograph. For such occurrences, the exchange during equilibrium may be marginalized in importance relative to non-equilibrium exchanges. However, highly regulated rivers such as systems with controlled dam release will have fairly constant...
sediment transport carrying capacity and for such systems the sediment carbon balance might be impacted by equilibrium exchange. With this in mind, it is possible that the phreatic karst conduits represents a class of fluvial systems in which equilibrium exchange is significant due to the fairly limited range of the sediment transport carrying capacity of the flow dictated by an upstream or downstream hydraulic control.

3.3. Phreatic karst actively convey sediment carbon

Hydrologic processes discussed in companion Paper 1 and this paper allow the authors to justify and further update the conceptual model of sediment carbon in phreatic karst. The biologically active phreatic karst conveyor temporarily stores newly delivered sediment carbon within the surficial fine grained laminae because the sediment transport carrying capacity of phreatic karst water is orders of magnitude less than the surface streams. Labile carbon including algae and litter carbon turnover within the surficial fine grained laminae at higher rates than soil carbon, so degraded soil carbon is sequestered while carbon dioxide is respired to the water column. The sustained fluid energy to transport sediment and equilibrium sediment exchange act to transport more and more highly degraded sediment carbon during low flows and longitudinally in the phreatic karst. In turn, degraded organic carbon is almost continuously recharged back to the fluvial system at perennial springheads.

Integration of the numerical modeling results to estimate a sediment carbon budget (Fig. 5) further support the conceptual model as the authors are able to estimate the mentioned processes for the phreatic system studied in this paper. Evidence of the ability of the karst conduit to limit transport capacity was shown by the result that sediment deposition within the conduit was similar to the total amount of sediment pirated from surface pathways. In turn, 84% of the pirated sediment carbon was deposited to the surficial fine grained laminae. The biological activity of the surficial fine grained laminae to oxidize sediment carbon is evidenced by the substantial carbon turned over, which is 46% of the carbon recharged to the surface stream. The similarity of net erosion and deposition in the phreatic conduit highlights the sustained energy of the fluid during low flows. Net deposition of sediment to the surficial fine grained laminae slightly exceeded erosion, which was attributed to the fact that the two years studied contained about 15% more rainfall events than average (e.g., the 2013 hydrologically active summer period was atypical). The potential importance of equilibrium exchange is evidenced by the modeling result that sediment suspended during equilibrium exchange had 29% less carbon than sediment deposited during equilibrium exchange. The recharge of degraded sediment carbon by the phreatic karst to surface streams is highlighted by the modeling results that estimate that recharged sediment carbon is just 57% of pirated sediment carbon.

3.4. Advancement in numerical modeling of karst systems

As one final contribution of this paper, the authors make a note regarding the advancement of water quality modeling that couples
carbon fate in fluviokarst watersheds. The stable carbon isotopic composition of sediment provides an independent method to assess with allocating sources of surface derived sediments to the karst subsurface and justify the consistency of the sediment pool studied in the surface and subsurface environments.

The research method applied here provides another example of a branch of hydrologic modeling that relies on the application of stable carbon isotopes for inputs and verification purposes. The stable carbon isotope composition of sediments has been long used for gaining an understanding of sediment carbon provenance in estuary and marine sciences (e.g., Martinotti et al., 1997). Over the past fifteen years, stable carbon isotopes have been increasingly applied within the sediment fingerprinting methodology in order to understand erosion sources at catchment and watershed scales (Papanicolaou et al., 2003; Bellanger et al., 2004; Fox, 2005, 2009; Fox and Papanicolaou, 2007; Jacinthe et al., 2009; Imberger et al., 2014; Ford et al., 2015).

With the stable carbon isotopes of sediment carbon now as a consistent tool applied within the hydrologic sciences, we expect to see more and more examples of coupling fingerprinting technology, where stable isotopes are used as tracers, with traditional water quality modeling that simulates sediment and sediment carbon continuity. Ford and Fox (2015) showed the use of the ISOFLOC model for such purposes, to simulate algal growth and turnover to sediment carbon; and showed how algal sloughing could be calibrated with stable carbon isotopes in order to help simulate the fluvial organic carbon budget. Fox and Martin (2015) showed how stable isotopes could be used to assist with calibration of model parameters including the sediment delivery ratio and sediment transport capacity with a soil erosion and sediment yield model applicable to watersheds with mixed land uses. Coupling of stable isotopes and water quality modeling is a fairly new class of research, and it is expected that model advancement and lessons learned from the present study as well as the aforementioned studies will assist researchers as they apply the stable isotope tools to assist with reducing numerical model uncertainties.

4. Conclusions

The main conclusions of this paper are as follows:

1. Phreatic karst conduits are suggested to sustain sediment transport activity long after surface storm events cease. The sustained sediment transport has the potential to shift the baseflow sediment yield of the phreatic karst to be on par with stormflow sediment yield. For example, in the present study almost 50% of the sediment conveyed by the phreatic conduit was during time periods when no flow existed in the surface streams of the watershed.

2. Exchange of sediment carbon between the water column and subsurface karst deposits is suggested to occur during equilibrium sediment transport within phreatic karst. In turn, the sediment carbon exchange impacts the mixing of new and old carbon pools and the flux of carbon from phreatic karst. Phreatic karst provides a hydrologic phenomenon where equilibrium sediment transport is likely sustained for rather long periods of time (see point 1 above). The understudied equilibrium exchange of sediment is potentially of high interest for scientific studies that emphasize elucidating the role of carbon processes in the inland freshwater carbon budget.

3. The integrated numerical model results from this study support the conceptual model proposed in Paper 1 of these two companion papers. Phreatic karst are suggested to act as a biologically active conveyor of sediment carbon that temporarily stores sediment, turns over carbon at higher rates than surface streams, respires carbon dioxide to the water column, and recharges relatively depleted organic carbon back to the fluvial system.

4. The method adopted in this paper shows the efficacy of coupling carbon isotope fingerprinting with water quality modeling to study sediment carbon in phreatic karst. It is expected that such methods can be built upon in future research studies.

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References


