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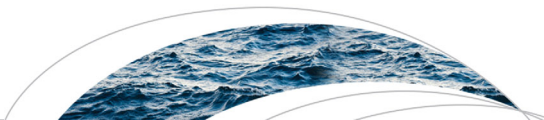
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RESEARCH ARTICLE

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Isotope-based Fluvial Organic Carbon (ISOFLOC) Model: Model formulation, sensitivity, and evaluation

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Key Points:

- A new isotope-based fluvial organic carbon budget model is formulated
- Sensitivity analysis suggests high uncertainty reduction of the carbon budget
- The isotope subroutine parameterizes the critical shear stress of algae

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Abstract Watershed-scale carbon budgets remain poorly understood, in part due to inadequate simulation tools to assess in-stream carbon fate and transport. A new numerical model termed *ISOTOPE*-based *FLU*-vial Organic Carbon (*ISOFLOC*) is formulated to simulate the fluvial organic carbon budget in watersheds where hydrologic, sediment transport, and biogeochemical processes are coupled to control benthic and transported carbon composition and flux. One *ISOFLOC* innovation is the formulation of new stable carbon isotope model subroutines that include isotope fractionation processes in order to estimate carbon isotope source, fate, and transport. A second innovation is the coupling of transfers between carbon pools, including algal particulate organic carbon, fine particulate and dissolved organic carbon, and particulate and dissolved inorganic carbon, to simulate the carbon cycle in a comprehensive manner beyond that of existing watershed water quality models. *ISOFLOC* was tested and verified in a low-gradient, agriculturally impacted stream. Results of a global sensitivity analysis suggested the isotope response variable had unique sensitivity to the coupled interaction between fluvial shear resistance of algal biomass and the concentration of dissolved inorganic carbon. Model calibration and validation suggested good agreement at event, seasonal, and annual timescales. Multiobjective uncertainty analysis suggested inclusion of the carbon stable isotope routine reduced uncertainty by 80% for algal particulate organic carbon flux estimates.

1. Introduction

Quantifying fluvial carbon budgets at the watershed-scale remains difficult due to a lack of mechanistic understanding of how physical and biogeochemical processes alter the composition of carbon species during transit from source to sink [Cole *et al.*, 2007; Battin *et al.*, 2009; Regnier *et al.*, 2013]. One area of particular interest is streams where high nutrient loads such as from agriculture and urban land uses and low canopy cover promote autochthonous benthic carbon production and turnover. Recent findings suggest that autochthonous carbon production and turnover can be on the same order of magnitude or greater than allochthonous carbon inputs in some agriculture and urban streams [e.g., Tank *et al.*, 2010]. The significance of understanding autotrophic carbon dynamics has been recently highlighted through a contemporary macro scale study that estimates stream and river derived autochthonous carbon fluxes from land to ocean equal 0.3 PgC y^{-1} , yet the spatial distribution and fate of autochthonous carbon via burial, turnover, or transport remains an open question [Regnier *et al.*, 2013]. The traditional assumption that stream generated carbon is turned over and can be neglected in energy utilization studies has been refuted recently by studies that highlight burial and long-term storage as a prominent fate mechanism of autochthonous carbon [Ford and Fox, 2014; Hotchkiss and Hall, 2015]. The critical role that autochthonous carbon plays in fluvial carbon budgets as well as fueling ecosystem function suggests these under-represented systems need further study. Numerical modeling of the fluvial carbon budget that includes spatially explicit accounting for autochthonous processes serves as a practical method to address autochthonous carbon questions. Numerical modeling can be combined with recently developed data-driven methods such as stable isotope measurements of carbon pools. The motivation of the present study is to improve watershed-scale water quality modeling technology for estimating fluvial organic carbon budgets for systems where autochthonous benthic carbon processes play a substantial role in the fluvial carbon cycle.

Carbon cycling in streams that include autochthonous production and turnover is governed by a complex mixture of physical and biogeochemical processes that promote exchange between carbon pools and phases (Figure 1). Autotrophic algal biomass assimilates DIC and temporarily fixes it as algal POC, herein

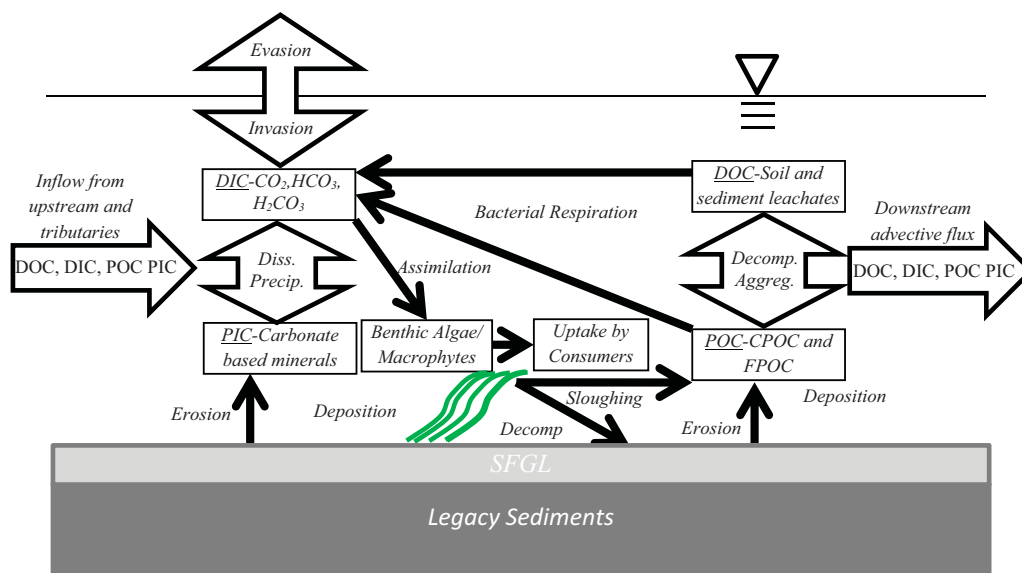


Figure 1. Reach-scale conceptual model of the fluvial carbon cycle in low-order streams including carbon pools and the physical, chemical, and biological processes impacting their composition.

referred to as APOC. APOC can be decomposed to fine POC (FPOC) or DOC, respired to DIC through autotrophic and heterotrophic respiration, transfer to consumers through feeding, or advect downstream via sloughing (i.e., physical detachment). FPOC is an amalgamation of carbon contained in silt and clay sized particles eroded from upland soils, streambanks, and generated within the stream channel either from breakdown of coarse POC or aggregation of DOC. FPOC is subjected to similar physical and biogeochemical processes as APOC, including further decomposition, respiration, and downstream transport. DOC is predominantly composed of soil leachates from the upland subsurface seepage but can also contain leachates from APOC and FPOC. Inorganic carbon composition directly impacts newly generated organic matter and can reflect levels of respiration and dissolution from the streambed. PIC can be dissolved to DIC or precipitated depending on pH conditions, and DIC composition is dependent upon in-stream organic carbon respiration, dissolution of PIC, and gaseous exchange with the atmosphere.

Currently available watershed-scale water quality models have attempted to estimate some fluxes and transformations of the organic carbon budget depicted in Figure 1; however a model that is formulated to consider organic carbon detachment and advection as well as growth and turnover processes characteristic of streams with high autotrophic cycling has not been developed previously. Watershed-scale water quality models applicable to water, sediment, carbon, and nutrient loadings to streams such as SWAT, AnnAGNPS, and SPARROW, tend to be focused on upland production and routing using 1-D hydrologic and sediment transport subroutines. SWAT and AnnAGNPS neglect in-stream contributions; suggesting carbon composition is a function of upland soil carbon and erosion dynamics only [Bingner et al., 2011; Neitsch et al., 2011; Oeurng et al., 2011]. SPARROW utilizes a heavily empirical regression model coupled with semitheoretical growth and first-order decay reactions for organic carbon to simulate total organic carbon composition at watershed outlets; however SPARROW does not adequately account for temperature dependent decomposition processes or exchange processes between carbon pools [White et al., 1991; Shih et al., 2010; Ford and Fox, 2014].

A second class of water quality models including AQUATOX, QUAL2K, and WASP are more heavily focused on in-stream water quality and have been applied to low order streams at the watershed-scale, although perhaps often erroneously given that these C and nutrient model formulations are based on theory derived from benthic layers in large, slow moving water bodies. AQUATOX, QUAL2K, and WASP conceptualize the benthos as a two layer, 1 mm aerobic and 10 cm anaerobic, well-mixed system that receives inputs from detrital carbon of varying quality, i.e., labile algal detritus, refractory detritus, and nonreactive detritus [DiToro, 2001; Wool et al., 2006; Chapra et al., 2008; Park and Clough, 2012]. An underlying assumption of these models is that POC is contained solely in the anaerobic layer under steady state, thus the models

ignore the impact of fluvial erosion on benthic carbon composition. Further, the active aerobic layer is typically an order of magnitude larger in low-gradient streams with loosely compacted surface fine-grained laminae, SFGL [Droppo and Stone, 1994; Droppo et al., 2001; Walling et al., 2006; Russo and Fox, 2012; Ford and Fox, 2014].

A lack of watershed-scale water quality models applicable to streams with pronounced autochthonous production suggests new model formulations are needed that account for upland carbon loading, simulate inter-pool transfer, continuously simulate the carbon composition of the benthos, account for algal growth and turnover, and simulate the impacts of advection. Therefore, the present work aims to enhance the water quality modeling technology for fluvial organic carbon budgets through incorporation of the model feedbacks shown in Figure 1. Specifically, we account for and couple the aforementioned physical and biogeochemical processes.

It is well recognized that simulation of DOC, POC, and APOC fate and transport at the watershed-scale requires a numerical modeling environment that is highly parameterized. In an effort to assist with model parameterization of physical and biogeochemical rates, we introduce the use of stable carbon isotopes within our watershed-scale water quality modeling. $\delta^{13}\text{C}$ is the isotopic signature of a carbon pool and reflects the ratio of ^{13}C to ^{12}C atoms in a given sample as

$$\delta^{13}\text{C}_{\text{Sample}} = \left(\frac{(^{13}\text{C}/^{12}\text{C})_{\text{Sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}}} - 1 \right) \times 1000, \quad (1)$$

where δ is the standard isotope notation, and VPDB is the reference standard Vienna Pee Dee Belemnite. Measuring and modeling of $\delta^{13}\text{C}$ of carbon pools provides an extra set of source and transformation equations to water quality studies and thus carbon stable isotopes have been extensively applied in recent years, primarily within data-driven approaches. $\delta^{13}\text{C}$ measurements of FPOC have been used to apportion sources of carbon in aquatic systems ranging from small streams to coastal waterbodies [Fox and Papanicolaou, 2007; Fox, 2009; Kendall et al., 2010; Schindler Wildhaber et al., 2012; Sarma et al., 2012]. Source apportionment studies have placed heavy emphasis on the ability of $\delta^{13}\text{C}$ to differentiate soil organic carbon (SOC) sources derived from C3 and C4 plants due to their significantly different $\delta^{13}\text{C}$ signatures of -24 to -29‰ and -10 to -14‰ , respectively [Smith and Epstein, 1971; Onstad et al., 2000; Palmer et al., 2001; Fox and Papanicolaou, 2007; Fox, 2009; Jacinthe et al., 2009; Brunet et al., 2011].

While the aforementioned studies highlight the strength of using $\delta^{13}\text{C}_{\text{FPOC}}$ as an environmental tracer, McGuire and McDonnell [2008] point out that few studies have incorporated stable isotopes into catchment scale models. The few studies that have implemented stable isotope technology in water quality modeling have focused on either nutrients [e.g., Fox et al., 2010] or short time scales [e.g., Tobias and Bohlke, 2011]. Synthesizing recent insights suggests $\delta^{13}\text{C}_{\text{FPOC}}$ can help constrain the fluvial organic carbon budget since $\delta^{13}\text{C}_{\text{FPOC}}$ is effective at tracing C sources, and is sensitive to isotope fractionation processes. With regard to source tracing, $\delta^{13}\text{C}$ values of autochthonous and allochthonous sources have been shown to be statistically differentiable with $\delta^{13}\text{C}$ ranges of -28 to -42‰ and -10 to -29‰ , respectively [Onstad et al., 2000; Palmer et al., 2001; Dalzell et al. 2007; Sakamaki and Richardson, 2011; Schindler Wildhaber et al., 2012]. With regard to in-stream transformations, large isotope fractionations of the DIC pool during assimilation (0 – 20‰), and low isotope fractionation during decomposition of organic carbon (0 – 2‰) suggest $\delta^{13}\text{C}_{\text{FPOC}}$ can help constrain parameters associated with APOC assimilation [Jacinthe et al., 2009; Dubois et al., 2010].

Our goal is to advance watershed-scale, water quality modeling for estimating the fluvial organic carbon budget within streams with benthic autochthonous carbon by introducing the ISOTOPE-based FLuvial Organic Carbon, or ISOFLOC, model. ISOFLOC couples existing one-dimensional hydraulics and sediment transport, benthic algae, and FPOC mass-balance models to new DIC and $\delta^{13}\text{C}$ mass-balance submodels that include isotope fractionation processes. Model evaluation techniques including sensitivity analysis, model calibration and validation, and uncertainty analysis are presented for evaluating ISOFLOC applications. Thereafter, an ISOFLOC case study is applied in a low-gradient, agriculturally impacted watershed with prominent autochthonous cycling. An 8 year data set of carbon content (C_{FPOC}) and the stable carbon isotopic composition ($\delta^{13}\text{C}_{\text{FPOC}}$) of fine transported sediments are utilized to assist with evaluating the modeling framework.

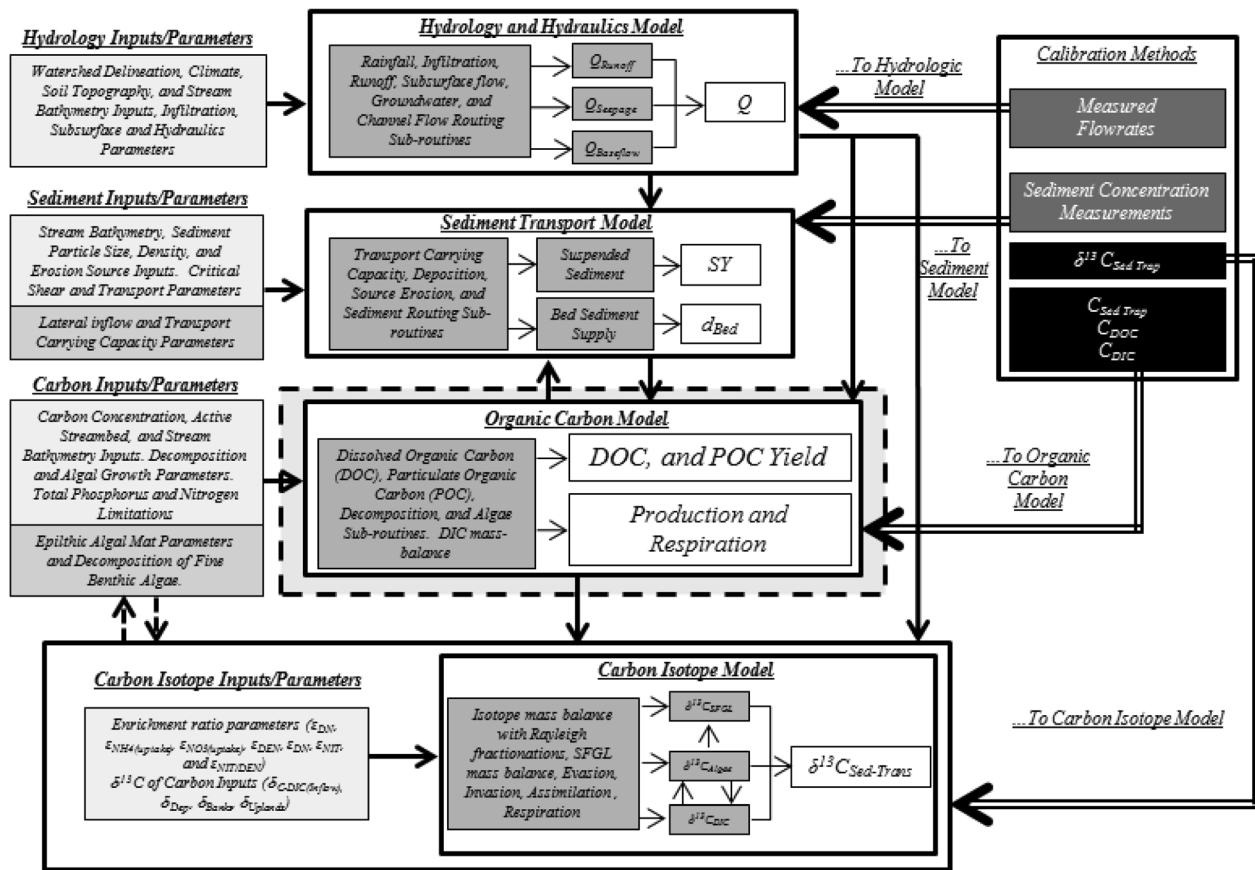


Figure 2. Model flowchart for ISOFLOC which details inputs, outputs, and calibration procedures. The flowchart provides the framework for coupling hydrologic, hydraulic, sediment transport, organic carbon, and carbon isotope subroutines.

2. ISOFLOC Model

2.1. Model Formulation

Figure 2 provides a flowchart summarizing connectivity of the submodels in ISOFLOC. Water and sediment transport subroutines provide the basis for advective transport of dissolved and particulate carbon phases. ISOFLOC simulates reaction equations for APOC, FPOC, and DIC simultaneously to estimate coupled feedbacks between the different pools. Organic carbon pools simulated in ISOFLOC include DIC, DOC, APOC, and FPOC. In the following, we describe the formulation for the total elemental inorganic and organic phases, and then we describe the new isotope mass balance formulations.

The ISOFLOC model incorporates a mass balance equation for DIC and flux equations for DIC and DOC. ISOFLOC models advection of DIC and DOC using model input of volumetric water flowrate, Q_j^i , for a given spatial reach, j , and time step, i , and Q_j^i can be modeled using data-driven, conceptual, or process-based hydrologic models calibrated for a watershed. ISOFLOC models DIC fate in a given reach to account for reactions with the streambed and assimilation and respiration impart changes to the DIC composition through a mass balance for DIC (kgC) as

$$DIC_i^j = DIC_{in_i}^j - DIC_{out_i}^j + (Dis_i^j + El_i^j + Re_i^j - Fix_i^j - Pr_i^j) SA_{Bed} \Delta t, \quad (2)$$

where in represents the advective upstream influx of DIC, out represents the advective downstream outflux of DIC, El ($\text{kgC m}^{-2} \text{d}^{-1}$) is the rate of CO_2 evasion from the stream channel or invasion from the atmosphere, Dis ($\text{kgC m}^{-2} \text{d}^{-1}$) is the rate of particulate carbonate dissolution in the stream bed, Res ($\text{kgC m}^{-2} \text{d}^{-1}$) is the respiration rate of the algal mat, Fix ($\text{kgC m}^{-2} \text{d}^{-1}$) is the carbon fixation rate, Pre ($\text{kgC m}^{-2} \text{d}^{-1}$) is the precipitation rate of new particulate carbonate material, and SA (m^2) is the surface area of the erosion source. ISOFLOC includes parameters surrounding benthic algae dynamics (i.e., Fix and Res) utilizing the

equations presented in *Rutherford et al.* [2000]; these equations are widely used to simulate algal biomass dynamics [*Flynn et al.*, 2013]. Specifically, ISOFLOC models *Fix* as a function of light, temperature and density of biomass and *Res* as a function of density of biomass and temperature. When the stream is under-saturated in CO_2 , *EI* is positive and the model assumes CO_2 diffusion from the atmosphere to the stream until P_{CO_2} is equal to that of the atmosphere (e.g., until it reaches saturation conditions). Conversely, when the stream is super-saturated in CO_2 , *EI* is negative due to evasion. ISOFLOC models evasion from the stream channel based on the flux equation which is widely used in stream evasion studies [e.g., *Wallin et al.*, 2013, and references within] as

$$E_i^j = - \frac{\left((P_{CO_2-Water} - P_{CO_2-Atm}) \times k_{H_i}^j \times .012 \right) \times w_{CO_2} \times V_{Water_i}^j}{H_i SA_{Bed}} \quad (3)$$

where k_H (mol CO_2/L atm) is the Henry's law coefficient and varies as a function of temperature [*Masters and Ela*, 2008], P_{CO_2} (atm) is the partial pressure of CO_2 , w_{CO_2} ($m\ s^{-1}$) is the gas transfer velocity, and Δt is the model time step. The coefficient, 0.012 (kgC/mol CO_2), accounts for the atomic mass of carbon present in aqueous CO_2 . ISOFLOC models partial pressure of CO_2 in the water utilizing carbonate equilibrium kinetics [*Masters and Ela*, 2008; *Doctor et al.*, 2008]. While beyond the scope of this study, data sets that are sensitive to evasion should test the efficacy of the model presented herein against more sophisticated evasion models that can provide site-specific parameterization [e.g., *Raymond et al.*, 2012]. ISOFLOC assumes that if CO_2 is not super saturated, assimilation is the sole removal process of DIC since an influx of atmospheric CO_2 will make the water acidic, favoring algal production over calcium precipitation. For the invasion rate, the model assumes CO_2 diffuses from the atmosphere to the stream until P_{CO_2} is equal to that of the atmosphere (e.g., until it reaches saturation conditions). ISOFLOC neglects the DOC reactions with the streambed since autochthonous carbon from algal exudates are turned over quickly and make up a small portion of transported DOC [*Cole et al.*, 1982; *Lyon and Ziegler*, 2009; *Hotchkiss and Hall*, 2015]. ISOFLOC estimates DOC flux by multiplying DOC concentrations ($kg\ C\ m^{-3}$) by streamwater Q at the watershed outlet at each time step.

The formulation for benthic algae (APOC) growth and fate accounts for algal DIC fixation during growth, C lost from the algal pool during respiration and decomposition, and algal transport from the benthic region due to sloughing. This subroutine of the formulation stems from the *Ford and Fox* [2014] model which was a modification of the original *Rutherford et al.* [2000] framework. APOC (kgC) is simulated as

$$APOC_i^j = APOC_{i-1}^j + (Fix_i^j + APOC_{Col}^j - Re\ s_i^j - DEC_{APOC_i}^j) SA_{Bed} \Delta t - Slough_i^j, \quad (4)$$

where $APOC_{Col}$ ($kg\ C\ m^{-2}\ d^{-1}$) is the algal colonization rate and DEC_{APOC} ($kg\ C\ m^{-2}\ d^{-1}$) is the breakdown rate of coarse algae to fine sediment algae and is assumed to vary proportionally with heterotrophic bacterial growth [e.g., *White et al.*, 1991], and *Slough* (kgC) is the carbon eroded from the algal mat. ISOFLOC models algal sloughing using shear and supply limited conditions as

$$Slough_i^j = \min \left[k \left(\tau_f^j - \tau_{cr}^{APOC} \right) \rho_s^{APOC} SA_{Bed} \Delta t, APOC_i^j \right]. \quad (5)$$

where k (m^{-1}) is the erodibility coefficient, τ_f (Pa) is the shear stress of the fluid at the centroid of the erosion source, τ_{cr} (Pa) is the critical shear stress of the erosion source, and ρ_s ($kg\ m^{-3}$) is the bulk density of the source. The model assumes sloughed algae is exported from the watershed, since algal material is relatively neutrally buoyant and is not expected to settle out of suspension during flow conditions that induce sloughing.

ISOFLOC simulates sediment transport mechanics as the basis for POC transport and temporary storage. Specifically, the model simulates fine sediment transport for streams with SFGL following the formulation by *Russo and Fox* [2012] and utilized by *Ford and Fox* [2014] as

$$SS_i^j = SS_{i-1}^j + E_{Bank}^j + E_{Bed}^j - D_i^j + Q_{SSin}^j \Delta t - Q_{SSout}^j \Delta t, \quad (6)$$

where SS (kg) is the suspended sediment in the water column, E (kg) is the erosion from streambank and streambed sources, D (kg) is deposition to the bed, Q_{SS} ($kg\ s^{-1}$) is suspended sediment transported into

and out of the modeled reach, and Δt (s) is the time step. ISOFLOC considers shear resistance, the transport carrying capacity of the fluid, and supply of the erosion source as potential limiting factors for sediment entrainment for both the streambed and the streambanks as

$$E_i^j = \min \left[k \left(\tau_{if}^j - \tau_{cr}^j \right) \rho_s S A_l \Delta t, T_{iC}^j - S S_{i-1}^j, S_{i-1}^j \right], \quad (7)$$

where (l) represents the sediment source, T_c (kg) is the transport carrying capacity, and S (kg) is the sediment supply. Parameterization of the erodibility coefficient (k) and fluid shear stress (τ_{if}^j) follow the method of *Hanson and Simon* [2001]. The model estimates T_c using a Bagnold like expression [*Chien and Wan*, 1999] as

$$T_{iC}^j = c_{TC}^j \frac{\left(\tau_{if}^j \right)^2}{w_s} L^j \Delta t, \quad (8)$$

where c_{TC} (s^{-1}) is the transport capacity coefficient, w_s ($m s^{-1}$) is the particle settling velocity, and L (m) is the length of the reach. The model estimates deposition of sediment to the streambed as

$$D_i^j = \frac{w_s \Delta t}{k_p H_i^j} \left[S S_{i-1}^j - T_{iC}^j \right], \quad (9)$$

where k_p is the concentration profile coefficient, and H (m) is the water column height. ISOFLOC assumes bank supply is infinite, but budgets streambed sediment as

$$S_{iBed}^j = S_{i-1Bed}^j - E_{iBed}^j + D_i^j + Gen_i^j. \quad (10)$$

where Gen (kg) is the cumulative mass of inorganic and organic fine sediment generated from APOC (APOC in the SFGL divided by its C content).

ISOFLOC continuously simulates FPOC concentration in the streambed ($C_{FPOC-Bed}$) based on the formulation of *Ford and Fox* [2014] as

$$C_{iFPOC-Bed}^j = \left(\frac{C_{i-1FPOC-Bed}^j * S_{i-1Bed}^j}{100} + (DEC_{APOC_i}^j - DEC_{iFPOC-Algae}^j - DEC_{iFPOC-upland}^j) S A_{Bed} \Delta t + \frac{D_i^j C_{Upland}^j - E_{iBed}^j C_{i-1FPOC-Bed}^j}{100} \right) * 100 / S_{iBed}^j, \quad (11)$$

where $DEC_{FPOC-Algae}$ ($kgC m^{-2} d^{-1}$) is the decomposition rate of algal FPOC, $DEC_{FPOC-Upland}$ ($kgC m^{-2} d^{-1}$) is the decomposition rate of upland soil derived FPOC, and C (%) is the percentage carbon of a given sediment carbon source. The model estimates transported FPOC concentration (C_{FPOC-T}) by multiplying carbon weighted fractions for the total suspended carbon load, derived from the sediment transport model, by C of each source.

ISOFLOC simulates stable carbon isotope mass balances with Rayleigh fractionations [*Sharp*, 2007] for APOC, DIC, and FPOC pools as

$$\delta^{13}C_i^j = \delta^{13}C_{i-1}^j X^C_{i-1} + \sum \delta^{13}C_{inputs_i^j} X^C_{inputs_i^j} - \sum \delta^{13}C_{outputs_i^j} X^C_{outputs_i^j} - \sum \epsilon_{frac_i^j} \ln(f_{frac_i^j}), \quad (12)$$

where X^C represents the fraction of carbon in a given pool and is estimated using outputs from the aforementioned sediment and mass-balance C models, ϵ is the enrichment factor during an isotopic fractionation process. In Rayleigh fractionation, ϵ_{A-B} is defined as

$$\epsilon_{A-B} = \left[\frac{\left(\frac{^{13}C}{^{12}C} \right)_A}{\left(\frac{^{13}C}{^{12}C} \right)_B} - 1 \right] \times 1000 \quad (13)$$

where A is the product and B is the reactant in equation (12). f is the fraction of a substrate remaining after the isotope fractionation process occurs and is derived from the appropriate C mass-balance. Implementing known inputs, outputs, and fractionation processes for APOC, DIC, and FPOC into equations (12)(13), the

isotopic submodel simulates $\delta^{13}C_{APOC}$ as

$$\delta^{13}C_{APOC_i^j} = \delta^{13}C_{APOC_{i-1}^j} X_{APOC}^C i - 1^j - \delta^{13}C_{Slough_i^j} X_{Slough}^C + \delta^{13}C_{Fix_i^j} X_{Fix}^C j - \epsilon_{Res} \ln(f_{Res_i^j}) - \epsilon_{DEC(APOC)} \ln(f_{DEC(APOC_i^j)}), \quad (14)$$

where $\delta^{13}C_{Fix}$ is a function of $\delta^{13}C_{DIC}$ and the fractionation imparted by algal assimilation. $\delta^{13}C_{DIC}$ is estimated as

$$\delta^{13}C_{DIC_i^j} = \delta^{13}C_{DIC_{i-1}^j} X_{DIC}^C i - 1^j + \delta^{13}C_{DIC-in_i^j} X_{DIC-in}^C j - \delta^{13}C_{DIC-out_i^j} X_{DIC-out}^C j + \delta^{13}C_{Res_i^j} X_{Res}^C j + \delta^{13}C_{Dis_i^j} X_{Dis}^C j + \delta^{13}C_{Inv_i^j} X_{Inv}^C j - \epsilon_{Eva} \ln(f_{Eva_i^j}) - \epsilon_{Fix} \ln(f_{Fix_i^j}) - \epsilon_{Pre} \ln(f_{Pre_i^j}), \quad (15)$$

where ϵ_{Fix} varies temporally and spatially since previous studies have shown that enrichment factors at low concentrations of aqueous CO_2 are significantly lower than at high aqueous CO_2 concentrations [e.g., Riebesell et al., 2000]. While the relationship between partial pressure of CO_2 and ϵ_{Fix} is still not clearly defined [Bade et al., 2006], ISOFLOC assumes an exponential decay for ϵ_{Fix} as a function of the inverse of C_{DIC} since findings of Riebesell et al. [2000] suggest low sensitivity of ϵ_{Fix} at moderate-high C_{DIC} and a steep decline for decreasing DIC at low C_{DIC} , reminiscent of an exponential decay relationship. ISOFLOC simulates $\delta^{13}C_{FPOC-Bed}$ as

$$\delta^{13}C_{FPOC-Bed_i^j} = \delta^{13}C_{FPOC-Bed_{i-1}^j} X_{FPOC-Bed}^C i - 1^j - \delta^{13}C_{E_i^j} X_{E_i}^C j + \delta^{13}C_{DEC(APOC)_i^j} X_{DEC(APOC)_i}^C j + \delta^{13}C_{D_i^j} X_{D_i}^C j - \epsilon_{DEC(FPOC-Algae)} \ln(f_{DEC(FPOC-Algae)_i^j}) - \epsilon_{DEC(FPOC-Upland)} \ln(f_{DEC(FPOC-Upland)_i^j}). \quad (16)$$

ISOFLOC estimates the isotopic signature of fine transported sediment ($\delta^{13}C_{FPOC-T}$) using a simple mass balance that calculates the carbon weighted average of source contributions and their associated isotopic signatures (i.e., $\delta^{13}C_{FPOC-Bed}$, $\delta^{13}C_{Upland}$, and $\delta^{13}C_{Bank}$).

2.2. Model Evaluation

Figure 3 provides a flowchart of methods for evaluation of ISOFLOC. Evaluation of ISOFLOC consists of (1) an exploratory, global sensitivity analysis that utilizes nominal ranges established for site specific conditions, (2) calibration and validation of the model under uncertainty for response variables using well-accepted statistical metrics, (3) estimation of the fluvial organic carbon budget utilizing uncertainty bounds, (4) comparison of the results against literature published values, and (5) rerunning the calibration using additional response variables to reduce uncertainty. In the following subsections, we provide the general procedure for performing sensitivity, calibration, and uncertainty evaluations of ISOFLOC.

2.2.1. Sensitivity Analysis

We recommend global sensitivity of ISOFLOC due to the numerous model parameter interactions that can impact model response variables. Two primary ISOFLOC response variables are $C_{FPOC-T(av)}$ and $\delta^{13}C_{FPOC-T(av)}$ because: (i) it is important to understand how the new isotope submodels add additional information to the carbon mass-balance model; (ii) $C_{FPOC-T(av)}$ and $\delta^{13}C_{FPOC-T(av)}$ have been previously shown to have seasonal and annual oscillations at the watershed scale indicative of source variability and in-stream processes [Ford and Fox, 2014; Ford et al., 2015]; and (iii) the impact of highly nonlinear feedbacks between physical and biological processes, and subsequently parameters, on $C_{FPOC-T(av)}$ and $\delta^{13}C_{FPOC-T(av)}$ are not intuitive and the sensitivity analysis helps to better understand these linkages. ISOFLOC sensitivity analysis uses quantitative apportionment based on a variance-based sensitivity analysis. Variance based methods are widely used in hydrologic and water quality modeling studies [Wang et al., 2006; Nossent et al., 2011; Herman et al., 2013]. ISOFLOC sensitivity uses low discrepancy, quasi-random Sobol sequences to generate a sample and resample ($N \times d$) matrix (A and B respectively) with N rows of sequences, and d columns of sensitive parameters following from the methods of Sobol' [2001] and Saltelli et al. [2010]. The method performs resampling for each potentially sensitive parameter (A_i^j for $i=1, 2, 3, \dots, d$) whereby column i from matrix A is replaced with column i from matrix B to generate A_i^j , with all other columns in A_i^j coming from A (e.g., matrix A without the i^{th} column). The sensitivity method calculates first and total order sensitivity indices since they provide primary effects of a variable and the cumulative effects of a parameter and its covariance with other parameters in a model respectively. Our ISOFLOC evaluation uses both Saltelli and Jansen estimators. The Saltelli et al. [2010] estimator estimates first-order effects, while the Jansen estimator estimates total

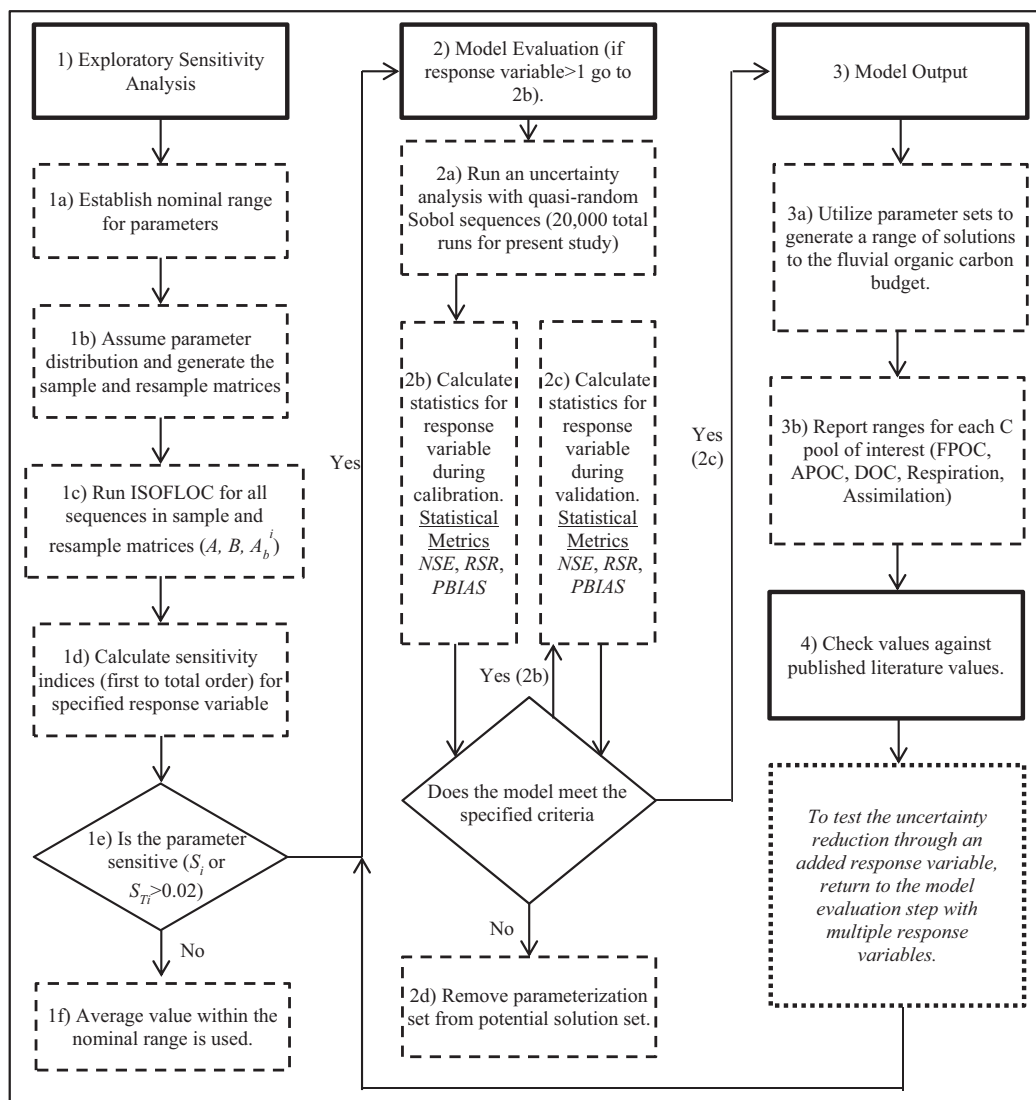


Figure 3. Model evaluation procedure in ISOFLOC for (1) exploratory sensitivity analysis, (2) model calibration/validation, (3) uncertainty analysis, and (4) validation of output through comparisons with similar watershed systems.

order effects as these have been highlighted as best practice for variance-based sensitivity analysis [Jansen, 1999; Salteli et al., 2010].

2.2.2. Model Calibration, Validation, and Uncertainty Analysis

ISOFLOC performs model calibration, validation and uncertainty analysis to generate a model uncertainty range (Figure 3). ISOFLOC utilizes a user defined number of Sobol sequences (set to 20,000 currently), reads in each parameter set, runs ISOFLOC, and outputs model results. A submodel in ISOFLOC compares model and measurement results against statistical metrics for response variables and the parameter set is either accepted as a potential solution or rejected and excluded from uncertainty bounds. ISOFLOC accounts for uncertainty reduction using single-objective, C_{FPOC-T} , and multiobjective approaches, both C_{FPOC-T} and $\delta^{13}C_{FPOC-T}$ [van Griensven and Bauwens, 2003; Rode et al., 2007], by calculating the percent reduction in the range of transported organic carbon pools.

With regard to statistical metrics, statistical metrics to evaluate model performance have typically been developed for loadings, and current guidelines may not be applicable to concentrations or stable isotope signatures [Moriasi et al., 2007]. ISOFLOC uses slight modifications to existing published metrics to be

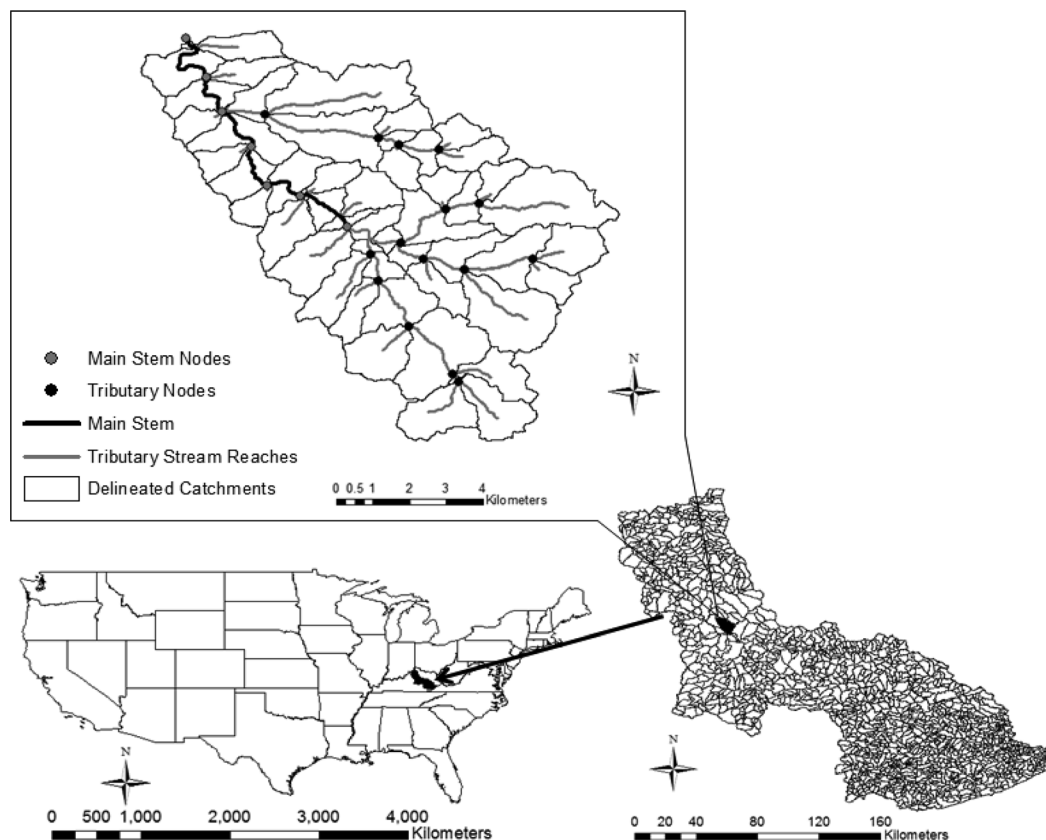


Figure 4. Modeling domain for the main stem of the South Elkhorn watershed (box) and its associated location within the HUC 6 Kentucky River Basin (bottom right). The polygons within the Kentucky River Basin represent HUC 12 watersheds.

applicable to the stable isotope and concentration variables including root mean square error of the standard deviation of measured data (RSR), Nash-Sutcliffe efficiency (NSE), and percent bias (PBIAS) [Moriasi *et al.*, 2007]. Inclusion of a parameter set in the uncertainty analysis requires a $RSR < 0.8$ and $NSE > 0.4$ for both calibration (2/3 of the data) and validation (1/3 of the data) of the sediment carbon content signatures and $RSR < 1$ and $NSE > 0$ for calibration and validation of the sediment carbon isotopic signatures. Further, a PBIAS threshold of $\pm 20\%$ ensures model simulations do not consistently over or underestimate measured data. The specified statistics ensure that the model outputs always provide statistically stronger goodness-of-fit to a mean trend suggesting that each of the acceptable model simulations reflect underlying processes.

3. ISOFLOC Case Study

ISOFLOC was applied for an 8 year simulation period in the South Elkhorn watershed (Figure 4) in order to provide a case study of the model formulation, results and evaluation. The South Elkhorn is a low gradient, agricultural and urban impacted, temperate system (62 km²) located in the Bluegrass Region of central Kentucky. In general, sediment erosion rates in the uplands are low in the agriculturally dominated watershed because the region has strict conservation measures in place on the pristine horse farms to support the equine industry. However, the watershed experienced disturbances in 2006–2007 associated with urbanization and construction, as well as storm events and high sediment transport throughout 2006. For ISOFLOC testing, modeling of the benthos focused on the main-stem due to the high residence times and favorable conditions for autochthonous production and decomposition (e.g., shallow water depths, low velocities, and open canopy). We accounted for inflow of water, sediment, and carbon constituents to the modeled stream from the tributaries upstream of the main stem and laterally along the main stem using empirical and physically based relationships published in previous studies in the watershed [Fox *et al.*, 2010; Russo, 2010; Ford, 2011; Russo and Fox, 2012]. The ISOFLOC application simulated a 30 min time step in six

Table 1. Inputs and Parameterization for the South Elkhorn Application of ISOFLOC

Parameter ID	Parameter Description	Range Simulated in Model	Source for Selected Range	Units
<i>Carbon Mass Balance Model</i>				
pH	Streamwater pH	7–8.5	Measured at study site	
C_{DIC-IN}	Concentration of dissolved inorganic carbon in tributaries	10–60	Measured at study site	mgC L ⁻¹
K_1	Speciation constant for carbonate equilibrium kinetics	4.47×10^{-7}	Masters and Ela [2008]	
K_2	Speciation constant for carbonate equilibrium kinetics	4.68×10^{-11}	Masters and Ela [2008]	
$P_{CO_2-Atmosphere}$	Partial pressure of CO ₂ in the atmosphere	380	Wallin et al. [2013]	ppm
w_{CO_2}	Gas transfer velocity of CO ₂	$3.47-6.94 \times 10^{-5}$	Butman and Raymond [2011]	m s ⁻¹
Pre	Precipitation of particulate inorganic carbon	$0-6.67 \times 10^{-8}$	Tobias and Bohlke [2011]	kgC m ⁻² s ⁻¹
Dis	Dissolution of particulate inorganic carbon	$0-1.67 \times 10^{-8}$	Tobias and Bohlke [2011]	kgC m ⁻² s ⁻¹
C_{DOC}	Concentration of streamwater dissolved organic carbon	1.1–1.7	Measured at study site	mgC L ⁻¹
C_{APOC}	Carbon content of newly generated algal biomass	0.41	Gosselain et al. [2000]	gC gSed ⁻¹
ρ_{algae}	Density of algae	1100	Droppo and Stone [1994]	kg m ⁻³
τ_{CF}	Critical shear stress of algae	0.2–2	Droppo and Stone [1994]	Pa
P_{col}	Colonization rate of algal biomass	$1 \times 10^{-6} - 1 \times 10^{-4}$	Rutherford et al. [2000]	kgC m ⁻² d ⁻¹
P_{Max}	Maximum fixation rate of algal biomass	$0.4-7.7 \times 10^{-3}$	Rutherford et al. [2000]	kgC m ⁻² d ⁻¹
I_K	Light Saturation coefficient	230	Rutherford et al. [2000]	μmol m ⁻² s ⁻¹
T_{min}	Minimum temperature for growth	5	Rutherford et al. [2000]	°C
T_{opt}	Optimum temperature for growth	20	Rutherford et al. [2000]	°C
T_{max}	Maximum Temperature for growth	30	Rutherford et al. [2000]	°C
P_{sat}	Density dependence coefficient	2.5×10^{-3}	Rutherford et al. [2000]	kgC m ⁻² d ⁻¹
P_{resp}	Respiration rate of the algal mat	0.025–0.15	Rutherford et al. [2000]	d ⁻¹
PK_{resp}	Temperature coefficient for algal respiration	1.05	Rutherford et al. [2000]	
T_{ref}	Reference Temperature	20	Same as optimum temperature	°C
DEC_{APOC}	Decomposition of coarse to fine algal carbon	$0.1-1.5 \times 10^{-2}$	Lit meta-analysis (see in text citations)	d ⁻¹
$DEC_{FPOC-Algae}$	Decomposition of fine to dissolved algal carbon	$0.01-1 \times 10^{-2}$	Lit meta-analysis (see in text citations)	d ⁻¹
$DEC_{FPOC-Upland}$	Decomposition of fine soil carbon to dissolved inorganic carbon	$0.1-1 \times 10^{-4}$	Lit meta-analysis (see in text citations)	d ⁻¹
C_{Upland}	Carbon content of hillslope sediments	0.02–0.04	Measured at study site	gC gSed ⁻¹
C_{Bank}	Carbon content of bank sediments	0.0104–0.0205	Measured at study site	gC gSed ⁻¹
<i>Stable Carbon Isotope Mass Balance Model</i>				
$\rho_{DEC-APOC}$	Fractionation associated with decomposing algae	0–2	Jacinte et al. [2009]	‰
$\rho_{Assimilation-Max}$	Maximum fractionation associated with algal carbon fixation	15–25	Tobias and Bohlke [2011]	‰
$\delta^{13}C_{DIC-IN}$	Isotopic signature of inflowing dissolved inorganic carbon	–10 to –15	Measured at study site	‰
$\delta^{13}C_{Dis}$	Isotopic signature of dissolved inorganic carbon from dissolution	5 to –8	Sharp et al. [2007]	‰
$\delta^{13}C_{Inv}$	Isotopic signature of atmospheric CO ₂	–7 to –9	Sharp et al. [2007]	‰
$\rho_{Evasion}$	Fractionation associated with stream channel evasion to the atmosphere	0–4	Doctor et al. [2008]	‰
$\delta^{13}C_{Bank}$	Isotopic Signature of bank sediment carbon	–23.9 to –26.1	Measured at study site	‰
$\delta^{13}C_{Upland}$	Isotopic signature of hillslope sediment carbon	–25.7 to –27.4	Measured at study site	‰
$\rho_{DEC-FPOC}$	Fractionation associated with decomposition of fine sediment carbon	0–2	Jacinte et al. [2009]	‰

equivalently sized reaches over the 8 year period to ensure the simulated transport of sediment and dissolved constituents during the time step was on the same order of magnitude as the ambient travel time in-stream.

3.1. South Elkhorn Parameterization and Evaluation Data

Table 1 shows parametrization of ISOFLOC, including parameter IDs, parameter descriptions, references, units, and nominal ranges, for the South Elkhorn application accomplished through field-based measurements. We collected weekly measurements of pH at two sites along the main stem of the study site and for parameterization in the DIC submodel. We collected tributary DIC concentrations (C_{DIC-in}) monthly for 9 months at two tributaries and two main stem locations via instantaneous grab samples that were filtered using GF-F (0.7 μm) filters. Samples were subsequently analyzed using a UIC Carbon Dioxide Coulometer CM5014. We assumed speciation constants (K_1 and K_2) for chemical equilibrium at 25°C since variability associated with temperature fluctuations is small in freshwater streams [Masters and Ela, 2008]. The average gas transfer velocity (w_{CO_2}) was parameterized using ranges of low-order streams in the Midwestern U.S. [Butman and Raymond, 2011; Raymond et al., 2012]. Partial pressure of CO₂ in the atmosphere (P_{CO_2-Atm}) was assumed spatially homogenous and reflects recent estimates. Precipitation of carbonate minerals (Pre) and dissolution of carbonate minerals (Dis) were parameterized using results of a DIC mass balance model application in a low-order agricultural stream [Tobias and Bohlke, 2011]. We collected dissolved organic carbon (DOC) samples monthly for 9 months at two tributaries and two main stem locations via instantaneous grab samples that were filtered using GF-F (0.7 μm) filters. Samples were subsequently analyzed using a Teledyne

Tekmar Torch TOC analyzer. Results suggest conservative transport of DOC in the stream since measurements in the main stem fell between tributary end-members at both high and low flow conditions. Further, DOC concentrations did not show major temporal trends; hence an average concentration was used to estimate the DOC.

Carbon content of coarse algal biomass (C_{APOC}) was parameterized from elemental signatures of riverine algal biomass [Gosselain *et al.*, 2000]. We parameterized physical parameters of the algal mat, including bulk density and critical shear stress (ρ_{Algae} and τ_{cr}^{algae}), using ranges for laboratory studies of surface fine grained laminae [Droppo and Stone, 1994]. Rates and thresholds for algal production and respiration including colonization rate of algae (P_{Co}), the maximum fixation rate of algal biomass (P_{Max}), light saturation coefficient (I_K), minimum temperature for algal growth (T_{Min}), optimum temperature for algal growth (T_{opt}), maximum temperature for algal growth (T_{max}), the density dependence coefficient governing maximum algal biomass (P_{sat}), autotrophic respiration rate (P_{resp}), temperature coefficient for algal respiration (Pk_{resp}), and reference temperature for algal growth (T_{ref}) were based on a synthesis of measurements from autochthonous dominated stream ecosystems and model parameterization in a similar low-order, agricultural watershed [Rutherford *et al.*, 2000, and references within]. We performed a meta-analysis of field studies reporting decomposition of coarse and fine organic carbon to provide ranges for breakdown rates of different carbon pools including algal carbon (DEC_{APOC}), fine particulate organic carbon associated with a labile pool ($DEC_{FPOC-Algae}$), and fine particulate organic carbon associated with the stable organic pool ($DEC_{FPOC-Upland}$) [Sinsabaugh *et al.*, 1994; Webster *et al.*, 1999; Alvarez and Guerrero, 2000; Jackson and Vallaire, 2007; Yoshimura *et al.*, 2008]. Carbon concentrations of upland hillslope soils and bank sediments (C_{Upland} and C_{Bank}) were measured in the watershed using transported sediment samples collected from upland tributaries during storm flows and grab samples from scouring banks. Samples were analyzed through combustion on an elemental analyzer.

With regard to the stable isotope mass balance model, the enrichment ratio associated with decomposition of algae ($\epsilon_{DEC-APOC}$) and the enrichment ratio associated with decomposition of fine sediment carbon ($\epsilon_{DEC-FPOC}$) were assumed analogous to fractionations associated with terrestrial organic matter decomposition and were parameterized using values observed in soil carbon profiles in a watershed with similar characteristics [Jacinthe *et al.*, 2009]. We parameterized the maximum fractionation associated with fixation of dissolved inorganic carbon ($\epsilon_{Assim-Max}$) using results of a DIC mass balance model application in a similar, low-order agricultural stream [Tobias and Bohlke, 2011]. For DIC, the carbon isotopic signature of tributary DIC ($\delta^{13}C_{DIC-IN}$) was measured using 0.45 μm filtered grab samples that were acid-digested with 5% phosphoric acid, and analyzed on a GC column interfaced with an isotope ratio mass spectrometer (IRMS), similar to the method discussed by Doctor *et al.* [2008]. The carbon isotopic signature of dissolved carbonate minerals ($\delta^{13}C_{Dis}$) and isotopic signature of DIC from invasion from the atmosphere ($\delta^{13}C_{Inv}$) were estimated using well accepted values for carbonate minerals, the dissolution source, and atmospheric CO_2 [Sharp *et al.*, 2007]. We parameterized fractionation associated with evasion of CO_2 to the atmosphere ($\epsilon_{Evasion}$) conservatively using estimates from a headwater stream where evasion is a dominant mechanism in DIC dynamics [Doctor *et al.*, 2008]. Carbon isotopic signatures of upland and bank sediments ($\delta^{13}C_{Upland}$ and $\delta^{13}C_{Bank}$) were measured in the watershed using transported sediment samples collected at high flows and grab samples from scouring banks respectively and were analyzed on an IRMS. To account for surficial erosion during the period of upland disturbance between 2006 and 2008, the $\delta^{13}C_{Upland}$ and C_{Upland} were altered to fit the shift observed in the data. A $\delta^{13}C_{Upland}$ of -24‰ and C_{Upland} of 1.3% were used from 30 May 2006 to 31 December 2007 to generate the best model fit.

We collected 8 years of semiweekly elemental and isotopic signatures of transported FPOC to calibrate and validate the numerical model using temporally and spatially integrated transported sediment samples [Phillips *et al.*, 2000]. A total of 327 samples were collected from 2006 to 2013. In the lab samples were centrifuged, decanted, frozen, freeze dried, wet sieved to isolate the fines fraction, ground, acidified with 6% sulfurous acid, and analyzed on a Costech elemental analyzer interfaced with a GC column and IRMS [Verardo *et al.*, 1990; Rowe *et al.*, 2002]. Samples were removed from the evaluation data set if they were too small to wet sieve or the sediment trap inlet was clogged in the field. In total, 209 samples were available for model evaluation, of which two-thirds were used for model calibration and one-third was used for validation. We randomly selected the subsets of data used for model calibration and validation. For elemental

Table 2. First and Total Order Sensitivity Indices for $C_{FPOC-T(av)}$ and $\delta^{13}C_{FPOC-T(av)}$ for Each of the Sensitive Parameters in the C and ^{13}C Mass Balances^a

Parameter	First-Order Index S_i		Total Order Index S_{Ti}	
	$C_{FPOC-T(av)}$	$\delta^{13}C_{FPOC-T(av)}$ ^b	$C_{FPOC-T(av)}$	$\delta^{13}C_{FPOC-T(av)}$ ^b
C_{DIC-IN}	0.01	0.24	0.02	0.35
τ_{cr}^{algae}	0.08	0.00	0.09	0.28
$\epsilon_{Assimilation-Max}$	0.00	0.10	0.00	0.13
P_{resp}	0.05	0.15	0.06	0.12
P_{Max}	0.16	0.12	0.21	0.09
$DEC_{FPOC-Algae}$	0.37	0.00	0.56	0.09
$\delta^{13}C_{DIC-IN}$	0.00	0.09	0.00	0.08
DEC_{APOC}	0.14	0.10	0.23	0.07
$\epsilon_{i-Assim}$	0.00	0.00	0.00	0.03
pH	0.00	0.00	0.00	0.02
$\epsilon_{DEC-APOC}$	0.00	0.00	0.00	0.01
$\delta^{13}C_{Upland}$	0.00	0.00	0.00	0.01
C_{Upland}	0.01	0.00	0.01	0.00
Total	0.82	0.83	1.18	1.28

^aValues that were less than zero and associated with numerical integration of the Monte-Carlo method in the sensitivity analysis are assumed to have no impact on the model and thus are assumed equal to zero.

^bNote that indices for $\delta^{13}C_{FPOC-T(av)}$ are subject to error from both Monte-Carlo integration and removal of erroneous values (average $\delta^{13}C_{FPOC-T(av)} < -100$) however still provide adequate assessments of sensitive variables despite having slightly higher first as compared to total order indices for specific variable. Additional simulations did not improve first order estimates of $\delta^{13}C_{FPOC-T(av)}$.

by coupled interactions between variability of algal shear stress and DIC concentration (Table 2). When compared to the average isotopic signature of transported sediment carbon, negative relationships were observed for τ_{algae}^{cr} , P_{resp} , DEC_{APOC} , C_{DIC} , $\epsilon_{Assim-max}$, and positive relationships were observed for P_{max} , $\delta^{13}C_{DIC}$, and $DEC_{FPOC-Algae}$ (Figure 5). When compared to the average carbon content of transported sediment carbon, positive relationships were observed for C_{DIC-IN} , τ_{algae}^{cr} , P_{max} , and $DEC_{FPOC-Algae}$ and negative relationships were observed for P_{resp} and DEC_{APOC} . As evidenced in the relationship between average carbon content of transported sediment and the maximum fractionation associated with algal assimilation ($\epsilon_{Assim-max}$), variables that were insensitive displayed noisy relationships with no distinct increasing or decreasing trends.

Results for the average isotopic signature of transported sediment carbon were of particular interest in that coupling DIC and isotope mass-balances promote coupled feedbacks between concentrations of tributary DIC inputs (C_{DIC-IN}) and the critical shear stress of algal biomass (τ_{algae}^{cr}). The critical shear stress of algal biomass showed a shift in the response of the minimum value for $\delta^{13}C_{FPOC-T(av)}$ from -26‰ to -30‰ occurring at 0.7 Pa. The reason that $\delta^{13}C_{FPOC-T(av)}$ output by the model was sensitive to the inherent shear stress of the algae to resist detachment was due to the linkage of biological and physical processes in the benthic algal layer. Holding all other parameters constant, low critical shear stress conditions, e.g., 0.3 Pa, produced relatively high rates of algal sloughing and in turn pronounced algal growth toward equilibrium resulting in net DIC assimilation by algae of 94 tC yr^{-1} and an average $\delta^{13}C_{APOC}$ of -27‰ . High critical shear stress conditions, e.g., 1.3 Pa, produced relatively low algal sloughing rates and less algal growth resulting in net DIC assimilation by algae of 51 tC yr^{-1} and an average $\delta^{13}C_{APOC}$ of -31‰ . As a result when DIC concentrations and critical shear stress of algae were low, an unrealistic scenario was achieved ($\delta^{13}C_{FPOC-T(av)} > -26\text{‰}$). Conversely when DIC concentrations and critical shear stress of algae were high, a more realistic scenario was achieved ($-26\text{‰} < \delta^{13}C_{FPOC-T(av)} < -31\text{‰}$). The coupled, nonlinear, behavior was reflected in Table 2 by higher total order indices for DIC concentration and algal shear resistance (0.35 and 0.28, respectively) relative to first order indices (0.24 and 0.00, respectively).

Visual observation of the model calibration time series of transported sediment carbon suggested good agreement between modeled and measured $\delta^{13}C_{FPOC}$ and C_{FPOC} results on seasonal, annual, and multiannual timescales (Figure 6). Seasonally, the model captured increases in C_{FPOC} and decreases in $\delta^{13}C_{FPOC}$ during summer and fall when accumulation of algal POC in the surface fine-grained laminae was pronounced while decreases in C_{FPOC} and increases in $\delta^{13}C_{FPOC}$ occurred during winter and spring when decomposition

and isotopic signatures, standard deviations of reference materials were 0.82% and 0.04‰, respectively, while standard deviations of unknowns were 0.07 % and 0.04‰, respectively.

3.2. South Elkhorn Application Results

Results of the global, variance-based sensitivity analysis for the average carbon content of transported sediment carbon ($C_{FPOC-T(av)}$) and the average carbon isotopic signature of transported sediment ($\delta^{13}C_{FPOC-T(av)}$) show the nonlinearity of the model as evidenced by the sum of first order indices ($S_i = 0.8$), total order indices ($S_{Ti} = 1.2-1.3$), and the high scatter in the plots (Table 2 and Figure 5). Variance of average carbon content of transported sediment carbon was primarily governed by coupled interactions between the variability in decomposition of organic matter and maximum algal biomass, while variance of $\delta^{13}C_{FPOC-T(av)}$ was primarily governed

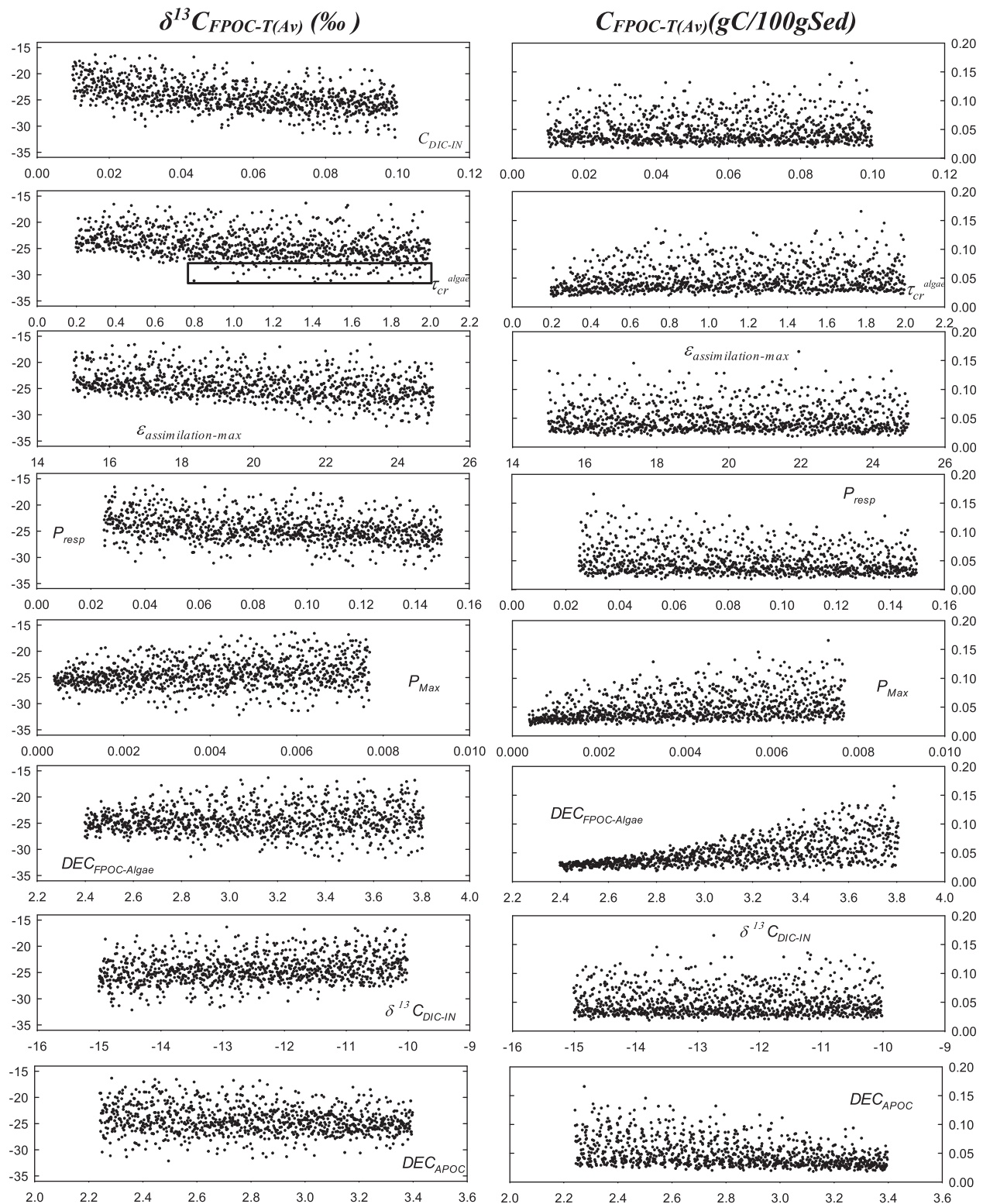


Figure 5. Sensitivity analysis of the ISOFLOC model displays the response of (left) $\delta^{13}C_{FPOC-T(av)}$ and (right) $C_{FPOC-T(av)}$ to the eight most sensitive model parameters. The values plotted the average specified parameter value for that run.

of algal biomass outweighed production and transport of eroded hillslope sediments. Annual variability of peaks in the transported carbon signature corresponded to frequency of storm events during the growing season as can be observed by smaller peaks during the wet summer of 2009 and enhanced peaks during

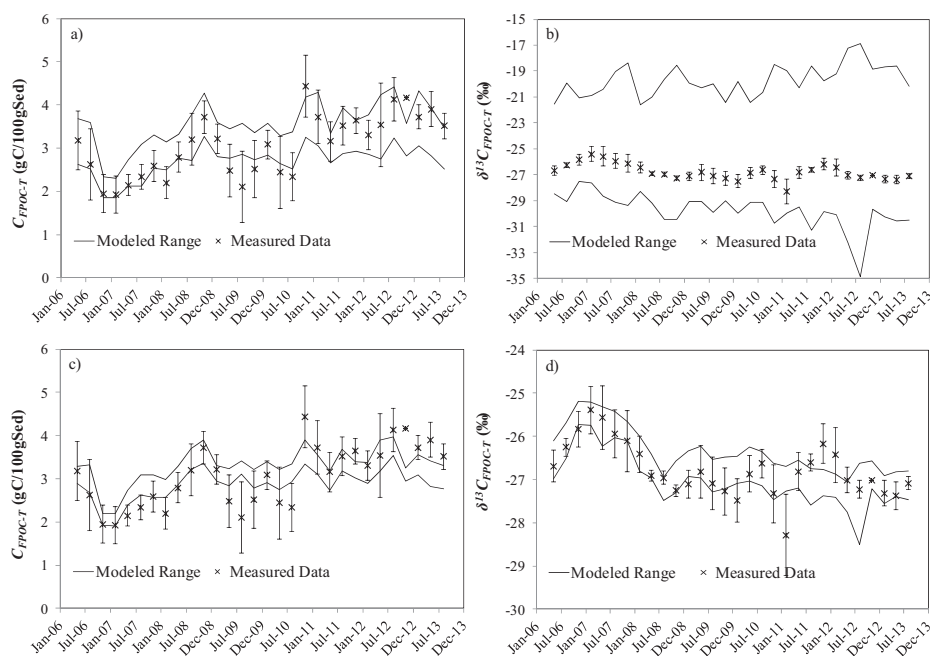


Figure 6. Seasonally averaged uncertainty analysis using the model evaluation framework with (a, b) carbon content of transported fine sediments and (c, d) both carbon content of transported fine sediment and stable carbon isotopic signature of transported fine sediment.

the dry summer of 2008. Lastly, positive increasing trends for C_{FPOC-T} and decreasing trends for $\delta^{13}C_{FPOC-T}$ were consistent for measured data and model simulations throughout the 8 year model evaluation. Thus, the model showed the ability to capture variability of transported organic carbon at numerous temporal scales for the watershed application. Quantitatively, statistical comparison of measured and modeled results (Table 3) showed that two hundred and thirty potential solutions exist for the single-objective application and ten potential solutions exist for the multiobjective application. This result is further reflected in the reduction in range of simulated $\delta^{13}C_{FPOC}$ when utilizing the multiobjective evaluation (Figure 6).

Simulated values were significantly higher than measured values during the growing season of 2007, coinciding with the watershed disturbances. During 2006–2007 there were pronounced upland land-use change disturbances and frequent storms promoting upland erosion. $\delta^{13}C$ of transported sediment were relatively high during the time period ranging from -24 to -26 ‰ and reflecting a deep soil source or bank source ($\delta^{13}C$ ranges from -24 to -25 ‰ for soils at depth and banks). On the contrary, $\delta^{13}C$ was relatively low in 2008–2013 when watershed disturbance was not as pronounced with $\delta^{13}C$ of transported sediment ranging from -26 to -30 ‰ and more reflective of surface soils ($\delta^{13}C \sim -26$ to -27 ‰) and algal biomass ($\delta^{13}C$ ranges from -30 to -40 ‰ for algae). Further, the ability to capture between event variability was tested for the model evaluation period using scatter plots of differences between datapoints (Figure 7). Points that plotted in the I or III quadrant suggest the model adequately captured between event variability whereas points that plotted in the II or IV quadrant suggest low accuracy at capturing between event variability. Model performance from 2006 to 2007 did not estimate between event variability in either data set as well as results from 2008 to 2013, which did capture between event variability very well. Linear regression of the scatter plots showed that for 2008–2013 the coefficient of determination for the elemental and isotopic model results were 0.38 and 0.15 respectively with slopes of 1.0 and 0.6 respectively. Further for 2006–2007 the coefficient of determination for the elemental and isotope signatures were 0.07 and 0.03 respectively with slopes of 0.3 and -0.2 respectively.

4. Discussion

4.1. Model Advancement

Our results suggest that coupling numerical models of sediment carbon mass balance to dissolved inorganic carbon and isotopic mass balances provide model feedbacks that allow for a unique calibration of the

Table 3. Goodness-of-Fit Metrics for the ISOFLOC Case Study With Single-Objective (C_{FPOC}) and Multiobjective (C_{FPOC} and $\delta^{13}C_{FPOC}$) Model Evaluation

Single-Objective	C_{FPOC}	$\delta^{13}C_{FPOC}$
<i>Calibration</i>		
NSE	0.40–0.72	
RSR	0.53–0.78	
PBIAS	–9.9 to 8.3%	
<i>Validation</i>		
NSE	0.40–0.61	
RSR	0.63–0.80	
PBIAS	–10.5 to 7.0%	
Multiobjective	C_{FPOC}	$\delta^{13}C_{FPOC}$
<i>Calibration</i>		
NSE	0.40–0.55	0.17–0.54
RSR	0.67–0.78	0.68–0.91
PBIAS	–6.2 to 4.9%	–1.1 to 1.3%
<i>Validation</i>		
NSE	0.42–0.57	0.00–0.45
RSR	0.65–0.76	0.73–1.00
PBIAS	–7.2 to 4.0%	–0.9 to 1.3%

water quality modeling framework that may not have been realized otherwise. Results of the South Elkhorn sensitivity analysis highlighted that the average isotopic signature of transported sediment carbon ($\delta^{13}C_{FPOC-T(av)}$) was uniquely sensitive to coupled interactions between critical shear stress of algae and DIC concentration (Table 2) which required a shear stress exceeding 0.7 Pa and high dissolved inorganic carbon concentrations to attain an average $\delta^{13}C_{FPOC-T(av)}$ lower than -26‰ (Figure 5). Under-estimating critical shear stresses resulted in overestimation of DIC assimilation by algae, and low DIC concentrations promoted fuller assimilation of the dissolved inorganic carbon pool by algae. As the fraction of the dissolved inorganic pool that assimilated by algal biomass increased, the isotopic signature of the algal biomass moved toward that of dissolved

inorganic carbon ($\delta^{13}C_{DIC} \sim -13.5\text{‰}$) because isotopic fractionation of the lighter ^{12}C became less pronounced. As a result, model goodness of fit for the carbon isotopic signature of transported sediment carbon was poor during simulations in which both critical shear stress of algae and dissolved inorganic carbon concentration were low (<0.8 Pa, and $<0.3\text{kg m}^{-3}$).

In addition, we found that the new isotope submodel reduced uncertainty in fluvial organic carbon budget estimates for the case study presented. Sensitivity analysis results for the South Elkhorn application suggest that the additional isotope submodel only added two additional sensitive parameters that were not sensitive components of the elemental model [Ford and Fox, 2014] while adding three equations. Quantitatively, the ability of the isotope routine to constrain uncertainty in the organic carbon budget was observed for the South Elkhorn case study through reducing the model uncertainty range from two hundred and thirty to ten potential solutions (Figure 6). When using the single objective calibration with only C_{FPOC} , average sloughed algae fluxes had uncertainty bounds of $0.18\text{--}4.15 \text{ tCkm}^{-2}\text{yr}^{-1}$ and FPOC fluxes had uncertainty bounds of $0.28\text{--}0.34 \text{ tCkm}^{-2}\text{yr}^{-1}$. When performing multiobjective calibration with the additional stable isotope routine, uncertainty of FPOC flux was not reduced significantly, however algal biomass sloughing uncertainty range was reduced by 80% to $0.41\text{--}1.16 \text{ tCkm}^{-2}\text{yr}^{-1}$. The result suggests the need for caution when calibrating solutions using solely C_{FPOC} without simultaneously budgeting feedbacks from the carbon source.

4.2. Modeling Needs and Limitations

Despite the major advancements of the model and its ability to capture variability at different time scales, results of the case study suggest some needs for future model improvements. First, the inability of the numerical model to simulate the shift of the isotopic and elemental signatures in October 2006, the subsequent return to predisturbance conditions (Figure 6), and between event variability from 2006 to 2007 (Figure 7) suggest poor performance during nonequilibrium streambed conditions. Nonequilibrium conditions in 2006–2007 stemmed from upland construction in the watershed and a high density of storms throughout 2006. High magnitude flows, coupled with disturbed upland soils promoted deposition to the streambed, burying existing SFGl and APOC [Russo and Fox, 2012]. As evidenced by the shift in the calibration data to more positive $\delta^{13}C$ values, soil carbon eroded from the uplands during this period was predominantly deep terrestrial FPOC. Deep sources of FPOC are less bioavailable than APOC or surface soil FPOC because they contain higher contents of recalcitrant, complex carbon compounds such as lignin and cellulose [Vieira and Mykkestad, 1986; Waite et al., 1995; Lyon and Ziegler, 2009; Lane et al., 2013]. As a result, it is conceivable that microbial pools were subject to nonequilibrium conditions following the deposition events as heterotrophs are sensitive to carbon quality. Further, higher simulated values of C_T relative to measured values during the 2007 growing season suggest that extensive deposition limited accrual of algal biomass for a full growing season, which has been previously

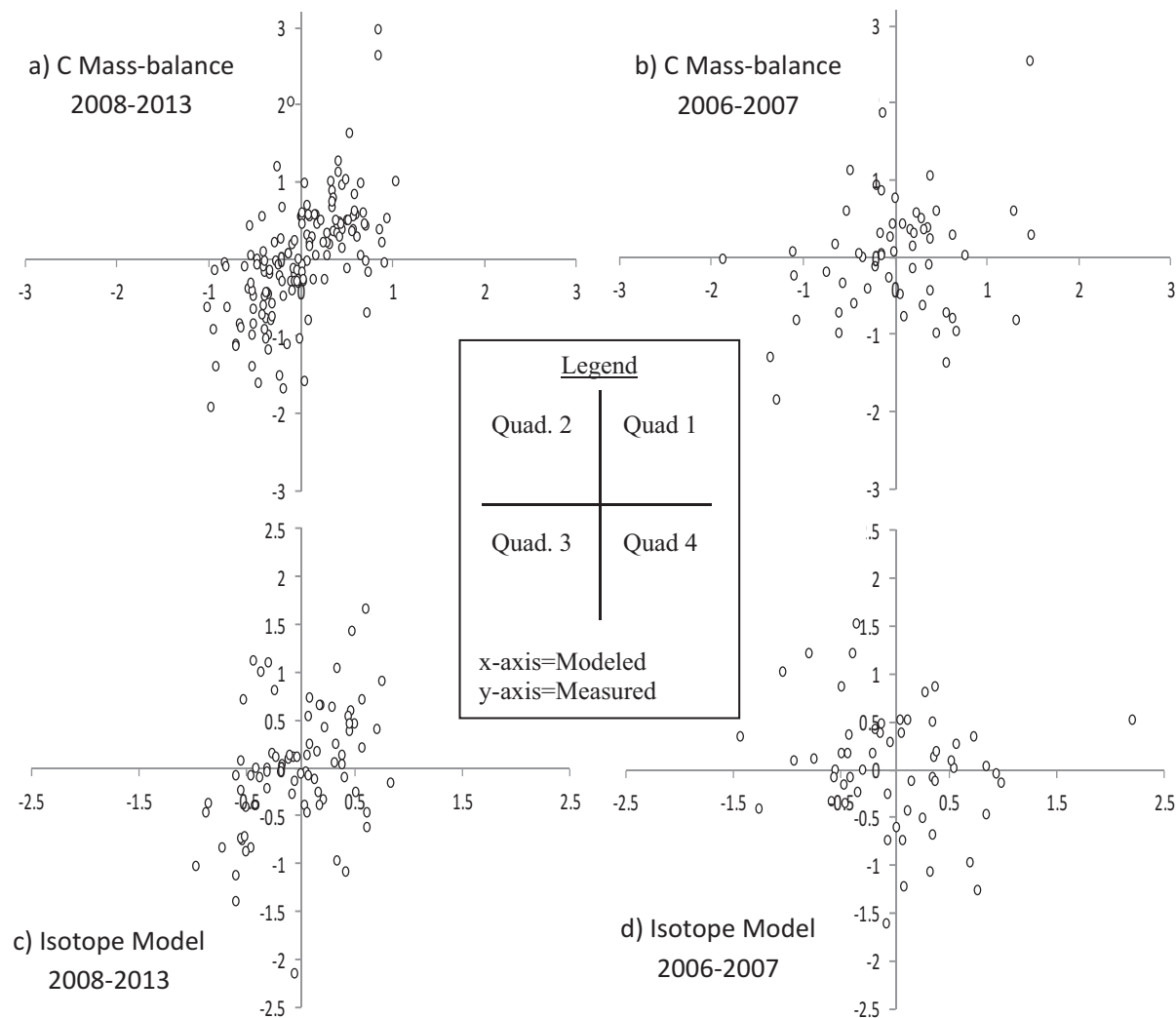


Figure 7. Event variability for the (a, b) elemental and (c, d) isotope models. Plotted values are deviations between calibration points for measured (y axis) versus modeled (x axis). Points that plot in first and third quadrants indicate the model adequately captures between-event variability. Points that plot in the second and fourth quadrants indicate that the model does not capture between event variability.

hypothesized to occur as a result of limited light, oxygen, and nutrient delivery to existing stocks of algal biomass buried under sediment deposits [Peterson, 1996].

In addition to limitations associated with modeling streambed disequilibrium, a limitation is possible regarding the equilibrium conditions of the stable isotope subroutine. Although the stable isotope routine had major advantages associated with its ability to trace sources of carbon, and help develop a unique calibration, the Rayleigh formulations have limitations associated with representing nonequilibrium conditions as highlighted by Maggi and Riley [2010]. Further work is needed to assess potential alternatives to represent dis-equilibrium conditions for watershed-scale models and to gain a more process based understanding of disequilibrium conditions. That said, reliable fractionation data sets to parameterize the transient processes associated with the nonequilibrium type model are not currently available and hence limit the ability for model validation.

5. Conclusion

ISOFLOC and its innovative features, including the stable carbon isotope model subroutines and the coupling of transfers between carbon pools, provide a stream carbon modeling framework that estimates carbon source, fate, and transport results for hydrologists and ecologists. The following conclusions of this study are:

1. Global sensitivity analysis suggest that benthic rates, including algal growth, critical shear stress of algae, and algal decomposition, are the most sensitive parameters impacting the isotope subroutines in ISO-FLOC for the case study presented. Adjusting the benthic rates during calibration and matching observed and model isotopic signatures reduces uncertainty of sloughed algal fluxes in ISOFLOC by 80%.
2. Results of transported elemental and isotopic carbon signatures from ISOFLOC and observed samples show good to very good agreement on event, seasonal, and annual time scales for the case study application. The result suggests that the coupling of DIC and POC phases and the strength of the stable isotope calibration may be useful in future stream applications such as assessing "hot-moments" of nutrient biotransformations, seasonal hypoxia in receiving water bodies, and large-scale annual C budgets.

We qualify the use of ISOFLOC for stream systems where benthic carbon processes including autochthonous production and decomposition are prominent. Although not included in this study, rate limiting nutrient conditions can be easily implemented, and the model parameterization can account for shifts in stream-bed gradients. While the model is designed generally for application in a broad range of systems, the usefulness of ISOFLOC in contrasting systems, e.g., forested systems, other urban and agricultural systems with different transformation rates than those here, needs to be evaluated in order to highlight extent of applicability.

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