Abstract

Here, we present the implementation of the freshwater carbon (C) cycle in the Dynamic In-stream Chemistry module (CARBON-DISC), which is part of the Integrated Model to Assess the Global Environment-Dynamic Global Nutrient Model (IMAGE-DGNM). A coupled hydrology-biogeochemistry approach with 0.5 by 0.5-degree resolution accounts for the spatial and temporal variability in dynamic conditions in the aquatic continuum using independent global databases. This process-based model resolves the concentrations, transformations and transfer fluxes of dissolved inorganic carbon (DIC), dissolved organic carbon (DOC) and terrestrial and autochthonous particulate organic carbon (POC) from headwaters to river mouth with a time step of 1 month for the period 1950-2000.

This is a major step forward in basin scale modelling of the C processing in freshwater systems, since simulated results can be validated at every location and point in time, and the model can be applied for retrodiction and to analyse future scenarios. Validation of the model with long-term measurement data shows a fair agreement, considering that this is a global model. To analyse the performance of the full production-respiration DISC module, two other schemes are presented, including an abiotic system excluding any in-stream processing of DOC and allochthonous production, and an extended abiotic system including heterotrophic respiration, but excluding production. Furthermore, a sensitivity analysis shows that many parameters, such as temperature, solar radiation, organic sediment mineralization rate and C inputs, including particulate organic carbon from terrestrial vegetation and dissolved inorganic carbon from groundwater, strongly affect atmosphere-freshwater exchange of CO₂.
1. Introduction

Only recently, (Cole et al., 2007) identified rivers as significant components of the global carbon (C) cycle and recognized that river systems function as globally important sources of CO2. Since then, multiple studies have confirmed the significance of freshwater systems in global carbon cycling, but there is substantial uncertainty on the magnitude of fluxes and the human perturbation (Cole et al., 2007; Battin et al., 2009; Tranvik et al., 2009; Bastviken et al., 2011; Raymond et al., 2013; Regnier et al., 2013; Borges et al., 2015; Holgerson and Raymond, 2016; Sawakuchi et al., 2017).

Carbon in freshwater originates from terrestrial (allochthonous) sources and from aquatic within system (autochthonous) production (Prairie and Cole, 2009). Allochthonous C is delivered to surface water as dissolved or particulate organic C (plant litter, leached material) or dissolved inorganic C (carbonates produced during weathering or soil respiration) (Cole et al., 2007). After delivery to streams, rivers, lakes or reservoirs, organic C is metabolized to inorganic carbon, buried in sediment or laterally transported towards oceans. The inorganic carbon delivered or generated within the system is transported downstream or emitted to the atmosphere as CO2 since aquatic systems are predominantly supersaturated in CO2 relative to the atmosphere (Kempe, 1984; Frankignoulle et al., 1998; Duarte and Prairie, 2005).

Many studies have been published on local C processing in headwaters, rivers, lakes, reservoirs and floodplains (Tranvik et al., 2009; Crawford et al., 2013, 2016; Wallin et al., 2013; Hotchkiss et al., 2015; Wollheim et al., 2015; Holgerson and Raymond, 2016). These local assessments have identified the key governing processes and their sensitivity to perturbations. Global assessments of riverine carbon cycling, and in particular CO2 partial pressure and global CO2 effluxes have been very important to quantify the role of rivers in the global C cycle. However, these budgeting approaches fail to describe the rapid changes in the global C-cycle (Ciais et al., 2013) and are not appropriate for retrodictions (predictions of the past) or making informed projections. Many existing river biogeochemistry models lack spatio-temporal input and hydrological constraints.

Moreover the models usually lump the various compartment of the aquatic continuum and regress modelled and observed C export at the scale of whole river basins (Beusen et al., 2005; Mayorga et al., 2010; Kroeze et al., 2012) After upscaling, such approaches yield a first order quantification of C fluxes to the coastal ocean. However, they contribute little to advance our understanding of the C cycle in river basins. To describe the interactions between land-use changes, interventions in the hydrology (dam construction, reservoirs, water extraction), and wastewater discharge, and their consequences for riverine C cycling, we need a model that spatio-temporally resolves the biogeochemical processes coupled to hydrology.

In this paper we present the implementation of freshwater C cycling in the Dynamic In-stream Chemistry module (CARBON-DISC), which is part of the Integrated Model to Assess the Global Environment (IMAGE (Stehfest et al., 2014)) Dynamic Global Nutrient Model (IMAGE-DGNM (Vilmin et al., 2019)). This new model is specifically designed for global applications.
and describes the spatial and temporal variability of carbon concentration and fluxes based on the river basin hydrology from headwaters to mouth and carbon cycling processes. Here, we present the main features of the CARBON-DISC module, we apply the module in the stream network of the Rhine basin and evaluate its characteristics with a sensitivity analysis.

2. Model and data used

2.1 General aspects

The IMAGE-DGNM model framework integrates the PCR-GLOBWB dynamic global hydrology model (Sutanudjaja et al., 2018) with the IMAGE model (Stehfest et al., 2014) that provides C, nitrogen (N) and phosphorus (P) delivery to inland waters (streams, rivers, lakes, reservoirs, floodplains) for the period 1900-2000. The biogeochemistry within the streams, rivers, lakes, reservoirs and floodplains is modelled using the DISC module, which is part of the IMAGE-DGNM framework (Vilmin et al., 2019). The IMAGE-DGNM has a global coverage with a 0.5 degree spatial resolution and includes spatially resolved biogeochemical input data ((Beusen et al., 2015); (Vilmin et al., 2019)). IMAGE-DGNM uses ancillary information of air temperature from a CRU dataset (Mitchell and Jones, 2005) as a 1:1 proxy for the water temperature. Although the temporal scale of the model framework is adjustable, here we focus on monthly-scale processes.

IMAGE provides land cover data to PCR-GLOBWB and wastewater, suspended particulate matter (SPM) and allochthonous organic carbon loads to CARBON-DISC; PCR-GLOBWB provides water flows, depth and volume of water bodies for streams of Strahler order > 5. The hydrology for smaller streams and rivers is parameterized in IMAGE-DGNM using the approach proposed by (Wollheim et al., 2008), as described in Beusen et al., 2015 (Fig. 1). DGNM explicitly accounts for spatio-temporal distribution of sources for the different forms of C. These include wastewater, erosion, weathering, vegetation in riparian areas and floodplains (details are provided in Table 1). After delivery of C in the form of particulate organic carbon (POC), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC, the sum of CO₂, HCO₃⁻ and CO₃²⁻) and alkalinity (ALK) to streams and rivers (see Table 1), the DISC model calculates in-stream biogeochemistry and transport from Strahler order 1 to the mainstream for each grid cell, and from upstream cells to the coastal ocean.
Figure 1: Scheme of the IMAGE-DGNM framework including CARBON-DISC for the in-stream biogeochemical carbon processes

IMAGE-DGNM explicitly resolves the mass and fluxes of suspended particulate matter (SPM) and sedimented particles. The pool of sedimented particles represents the mass of particles that have settled that can be resuspended as a result of exposure of the sediment surface to flowing waters. SPM is an important factor for light attenuation in the water column. (Kirk, 2011). SPM is delivered from land to surface waters through soil erosion and from litterfall by terrestrial vegetation and during transport, it is produced within the water column through primary production. SPM consists of non-reactive, particulate inorganic matter (PIM) and reactive particles, particulate organic matter (POM). All suspended particulate species also exist in the sediment form. Calcium carbonate particles are not identified as a distinct unit.

The CARBON-DISC module describes the biogeochemical transformations of DOC and POC to DIC. These instream processes depend on hydrology, temperature and solar irradiance (Fig. 1). POC comprises hundreds of different compounds varying from easily decomposable to recalcitrant (Middelburg, 1989; Bianchi, 2011). To account for the diversity in POC reactivity, we distinguish among allochthonous, terrestrial POC (POC_terr and SEDOC_terr) and aquatic, autochthonous POC (POC_auto and SEDOC_auto), because the mineralization of terrestrial organic matter with structural carbohydrates and lignins is slower than that of aquatic organic matter, rich in N and P (Middelburg, 2019). Physical dynamics of POC are governed by simplified deposition and resuspension equations.
Alkalinity (ALK) is generated by weathering of soils and rocks and delivered to streams. Although ALK is the sum of excess bases in solution in natural environments carbonate alkalinity ($\text{HCO}_3^- + 2 \text{CO}_3^{2-}$) tends to make up most of the total alkalinity. In our model ALK is delivered to surface water and combined with model generated DIC to calculate $\text{pCO}_2$ and pH, but it is not modified by chemical reactions within the river. Consequently, CARBON-DISC ignores ALK production and consumption by primary production, respiration, nitrification and calcium carbonate precipitation and dissolution within the stream network (Soetaert et al., 2007), since we assume that large scale alkalinity concentrations are governed by weathering of soils and rocks.

The performance of the model is validated by comparing simulation results of DIC, ALK, $\text{pCO}_2$, pH, DOC and TOC with literature data along the main stream (Fig. 2). Literature data were acquired from the GLORICH database (Hartmann et al., 2014) (https://www.geo.uni-hamburg.de/en/geologie/forschung/geochemie/glorich.html). We compare monthly simulations and two weekly measurements of DIC, alkalinity, $\text{pCO}_2$, pH, DOC and TOC for the station in Lobith, located on the German-Dutch border. The model can simulate at any temporal resolution, but here we discuss the monthly aggregated results.

Figure 2: Map of Rhine basin with available in-stream carbon measurement locations for GLORICH (Hartmann et al., 2014)
2.2 Model description

CARBON-DISC provides the concentration of any C species $i$ [Mmol/km$^3$] in each waterbody (i.e. a stream, lake, reservoir or floodplain) in each grid cell and for each time step (here 1 month) by calculating the total (tot) change in Mmol per time step of all C species $i$ in each waterbody (i.e. a stream, lake, reservoir or floodplain) in each grid cell, as an effect of biogeochemical (bgc) interactions between C species and as a result of hydrological (hyd) transport from waterbody to waterbody, within a grid cell as well as from grid cell to grid cell, as follows:

$$\frac{dC_i}{dt_{tot}} = \begin{cases} \frac{dC_i}{dt_{bgc}} + \frac{dC_i}{dt_{hyd}} & \text{if species is dissolved or suspended in water column} \\ \frac{dC_i}{dt_{bgc}} & \text{if species is attached or sedimented onto bed surface} \end{cases} \quad (1)$$

Hydrological advection of any dissolved or particulate C species $i$ in the water column, being DIC, DOC, POC and ALG, is calculated as follows:

$$\frac{dC_i}{dt_{hyd}} = L_i - Q * [C_i] \quad (2)$$

with $L_i$ representing the upstream load [Mmol/yr] of species C $i$. $Q$ represents the water discharge [km$^3$/yr] and $[C_i]$ represents the concentration of carbon species $i$ [Mmol/km$^3$], which we obtain from dividing the total amount of species $i$ [Mmol] in the water body by the volume [km$^3$] of that water body (acquired from hydrological model data). From 1$^{st}$ to 5$^{th}$ Strahler orders, discharge and water volumes are calculated through the approach proposed by (Wollheim et al., 2008), as described in Vilmot et al. (submitted). For 6$^{th}$ Strahler order and higher, discharge and water body dimensions as well as floodplain area and depth data are provided by PCR-GLOBWB (Sutanudjaja et al., 2018) at a 0.5° spatial resolution. Floodplains are only exchanging water with the 6$^{th}$ Strahler order and higher in the same grid cell, and we assume their flow velocity is 10% of the main stream velocity. Hydrological transport from low to higher Strahler orders, and from one grid cell to the next grid cell, is calculated as long as these species are in the surface water column. POC, when sedimented as SEDOC (see below in Eq. (18)) remains where it is settled until it is resuspended. ALG$\_benth$ is not being transported downstream, as it is considered attached to the stream bed.

2.2.1. DIC dynamics

External input of DIC in the DISC module is from weathering (Table 1) and there is in-stream production of DIC through mineralization of organic carbon forms and respiring living biomass. DIC is consumed through primary production. Finally, DIC is added to or removed from the water body in the form of CO$_2$ as a result of atmospheric exchange:
\[
dDIC/dt = WEA_{DIC} + DOC_{MINERALIZATION} + POC_{terre_{MINERALIZATION}} + POC_{auto_{MINERALIZATION}} + SEDOC_{terre_{MINERALIZATION}} + SEDOC_{auto_{MINERALIZATION}} + ALG_{RESPIRATION} + ALG_{benth_{RESPIRATION}} - ALG_{PRIMARY_PRODUCTION} - ALG_{benth_{PRIMARY_PRODUCTION}} - DIC_{ATMOSPHERIC_EXCHANGE} (3)
\]

Atmospheric exchange is calculated from the difference in CO\(_2\) concentrations between the surface water and the atmosphere:

\[
DIC_{ATMOSPHERIC_EXCHANGE} = k_{air} \times (CO_{2water} - CO_{2atmosphere}) \tag{4}
\]

Where \(CO_{2atmosphere}\) is the atmospheric concentration, fixed at 0.0136 mmol L\(^{-1}\) (equivalent of 400 ppmv). \(CO_{2water}\) is the dissolved CO\(_2\) concentration that is calculated (together with pH) from [DIC] [mmol L\(^{-1}\)], [ALK] [meq L\(^{-1}\)] and temperature with the MOCSY2.0 scheme from (Orr and Epitalon, 2015). Here, alkalinity delivery to surface waters is the same as DIC delivery, from WEA\(_{DIC}\). Alkalinity is transported downstream without biogeochemical modifications. \(k_{air}\) is the atmospheric exchange coefficient [h\(^{-1}\)] calculated as follows:

\[
k_{air} = k_{600} / (600/Sc_T)^{0.5} \tag{5a}
\]

where \(k_{600}\) is the normalized \(k_{air}\) at 20°C and \(Sc_T\) is the Schmidt number at temperature \(T\) [C°] (Wanninkhof, 2014), calculated from:

\[
Sc_T = 1911.1 - 118.11T + 3.4527T^2 - 0.04132T^3 \tag{6}
\]

where \(T\) is represented by air temperature (Mitchell and Jones, 2005). The atmospheric exchange coefficient \(k_{600}\) can be estimated from flow velocity (\(v\) [cm s\(^{-1}\)]) for small rivers or from windspeed (\(\bar{u}_{10}\) [m s\(^{-1}\)]) for large rivers (Alin et al., 2011):

\[
k_{600} = \begin{cases} a_1 + b_1 \bar{u}_{10} & \text{if stream width} > 100 \text{ meters} \\ a_2 + b_2 \times v & \text{if stream width} < 100 \text{ meters} \end{cases} \tag{7}
\]

Values for \(a_1, b_1, a_2\) and \(b_2\) are by default set to respectively 4.46, 7.11, 13.82 and 0.35 (Alin et al., 2011).

\(k_{air}\) above floodplains is strongly reduced with factor \(F_{u10_{veg}}\) (0.001) when (a fraction of) high vegetation (\(F_{high_{veg}}\)) covers the floodplain. Vegetation type data from IMAGE (Stehfest et al., 2014) was classified as either high or low vegetation. A spatial fraction of high vegetation (\(F_{high_{veg}}\)) per 30 minutes gridcell was obtained from 5-minutes resolution IMAGE output. Equation (5a) is modified for floodplains as follows:

\[
k_{air_{floodplains}} = (k_{600} / (600/Sc_T)^{0.5}) \times F_{high_{veg}} \times F_{u10_{veg}} + (k_{600} / (600/Sc_T)^{0.5}) \times (1 - F_{high_{veg}}) \tag{5b}
\]

\[7\]
2.2.2. **Organic carbon dynamics**

Surface runoff and waste water deliver DOC (Table 1), which is mineralized during its transport downstream. In-stream DOC production occurs through excretion by pelagic and benthic algae. DOC is consumed by mineralization.

\[
dDOC/dt = SRO_{DOC} + WAS_{DOC} + ALG_{EXCRETION} + ALG_{benth.EXCRETION} - DOC_{MINERALIZATION}
\]  

\(^{(8)}\)

\(P_{OC_{terre}}\) has a terrestrial origin and originates from litterfall and soil erosion (Table 1). There is resuspension through in-stream erosion and sedimentation. Finally, \(P_{OC_{terre}}\) can be consumed by mineralization:

\[
dP_{OC_{terre}}/dt = LIT_{POC} + SOL_{POC} + SEDOC_{terre\_INSTREAM\_EROSION} - P_{OC_{terre\_SEDIMENTATION}} - P_{OC_{terre\_MINERALIZATION}}
\]  

\(^{(9)}\)

\(P_{OC_{auto}}\) is the autochthonous particulate organic carbon produced in-stream, via the death of primary producers. Similar to \(P_{OC_{terre}}\), within river produced POC can be resuspended (erosion), deposited, or mineralized.

\[
dP_{OC_{auto}}/dt = ALG_{C\_MORTALITY} + ALG_{C\_benth\_MORTALITY} + SEDOC_{auto\_INSTREAM\_EROSION} - P_{OC_{auto\_SEDIMENTATION}} - P_{OC_{auto\_MINERALIZATION}}
\]  

\(^{(10)}\)

Particulate organic matter that has settled from the water column (\(SEDOC_{terre}\) and \(SEDOC_{auto}\)) can either be resuspended to the water column, transformed into DIC via mineralization or become buried.

The relevant equations are:

\[
dSEDOC_{terre}/dt = P_{OC_{terre\_SEDIMENTATION}} - SEDOC_{terre\_INSTREAM\_EROSION} - SEDOC_{terre\_MINERALIZATION} - SEDOC_{terre\_BURIAL}
\]  

\(^{(11)}\)

\[
dSEDOC_{auto}/dt = P_{OC_{auto\_SEDIMENTATION}} - SEDOC_{auto\_INSTREAM\_EROSION} - SEDOC_{auto\_MINERALIZATION} - SEDOC_{auto\_BURIAL}
\]  

\(^{(12)}\)

The erosion of the individual sedimented C species is a fraction of the total erosion \(\Phi_{ero\_tot}\) [ton/yr]. \(\Phi_{ero\_tot}\) is calculated from the total mass of sediment in the water body (\(SED_{tot}\) [ton]), bed area (\(A\) [km²]), flow velocity (\(v\) [km/yr]), slope (\(S\) [km*km⁻¹]), a fixed erosion coefficient \(k_{ero}\) [ton/km²] of 2*10⁴ and a half-saturation constant \(k_{sed}\) [km] of 1*10⁻⁶:

\[
\Phi_{ero\_tot} = k_{ero} \times (SED_{tot}/A) / (k_{sed} + SED_{tot}/A) \times S \times v \times A
\]  

\(^{(13)}\)
with:

\[
S_{E D_{t o t}} = S_{E D I M} + S_{E D O M_{t e r r e}} + S_{E D O M_{a u t o}}
\]  

(14)

\(S_{E D I M}\) represents the mass [ton] of sedimented inorganic matter and \(S_{E D O M_{t e r r e}}\) and \(S_{E D O M_{a u t o}}\) represent the masses [ton] of organic matter in the sediment of terrestrial and in-stream origin, respectively. Their masses are calculated from \(S_{E D O C_{t e r r e}}\) and \(S_{E D O C_{a u t o}}\) as:

\[
S_{E D O M_{t e r r e}} = \frac{S_{E D O C_{t e r r e}}}{f_{c_{S E D O C_{t e r r e}}} \times M M_C}
\]  

(15)

\[
S_{E D O M_{a u t o}} = \frac{S_{E D O C_{a u t o}}}{f_{c_{S E D O C_{a u t o}}} \times M M_C}
\]  

(16)

with \(f_{c_{S E D O C_{t e r r e}}}\) and \(f_{c_{S E D O C_{a u t o}}}\) the mass fractions of C in \(S_{E D O M_{t e r r e}}\) and \(S_{E D O M_{a u t o}}\) respectively, assumed to be 0.5. \(M M_C\) is the molar mass of C (12 g/mol).

To calculate erosion of individual particulate species we use:

\[
\Phi_{e r o, P O C_{t e r r e}} = \frac{(S_{E D O C_{t e r r e}} / S_{E D_{t o t}}) \times \Phi_{e r o, t o t}}{D}
\]  

(17a)

\[
\Phi_{e r o, P O C_{a u t o}} = \frac{(S_{E D O C_{a u t o}} / S_{E D_{t o t}}) \times \Phi_{e r o, t o t}}{D}
\]  

(17b)

Sedimentation of POC (terrestrial and autochthonous) is calculated with:

\[
P O C_{t e r r e, S E D I M E N T A T I O N} = \frac{v_{s e d_{P O C_{t e r r e}}}}{D} \times P O C_{t e r r e}
\]  

(18a)

\[
P O C_{a u t o, S E D I M E N T A T I O N} = \frac{v_{s e d_{P O C_{a u t o}}}}{D} \times P O C_{a u t o}
\]  

(18b)

where \(v_{s e d_{P O C}}\) is the sediment deposition velocity which is assumed to be 4.38 [km yr\(^{-1}\)] or 0.5 m h\(^{-1}\) (Vilmin et al., 2019) for both the terrestrial and autochthonous POC. \(D\) is the stream depth [km].

The temperature-dependent mineralization rates for \(D O C\), POC (terrestrial and auto) and SEDOC (terrestrial and auto) are formulated as follows:

\[
D O C_{M I N E R A L I Z A T I O N} = f_{m i n}(T) \times k_{D O C_{m i n}} \times D O C
\]  

(19)

\[
P O C_{t e r r e, M I N E R A L I Z A T I O N} = f_{m i n}(T) \times k_{P O C_{t e r r e, m i n}} \times P O C_{t e r r e}
\]  

(20a)

\[
P O C_{a u t o, M I N E R A L I Z A T I O N} = f_{m i n}(T) \times k_{P O C_{a u t o, m i n}} \times P O C_{a u t o}
\]  

(20b)

\[
S E D O C_{t e r r e, M I N E R A L I Z A T I O N} = f_{m i n}(T) \times k_{S E D O C_{t e r r e, m i n}} \times S E D O C_{t e r r e}
\]  

(21a)

\[
S E D O C_{a u t o, M I N E R A L I Z A T I O N} = f_{m i n}(T) \times k_{S E D O C_{a u t o, m i n}} \times S E D O C_{a u t o}
\]  

(21b)

The temperature dependency is described with a standard Q10 function:
\[ f_{\text{min}} (T) = \exp \left( \frac{T - T_{\text{ref}}}{10} \right) \ln (Q10) \]  

with \( T_{\text{ref}} \) as 15°C Celsius and Q10 set to 2 for all non-living organic species (Soetaert and Herman, 2008).

Burial is calculated with:

\[ SEDOC_{\text{terre}}\text{BURIAL} = k_{\text{burial}} \ast SEDOC_{\text{terre}} \tag{23a} \]
\[ SEDOC_{\text{auto}}\text{BURIAL} = k_{\text{burial}} \ast SEDOC_{\text{auto}} \tag{23b} \]

Burial only occurs when the \( SED_{\text{tot}} \) per bed area is more than 50 kg/m².

### 2.2.3. Primary producers

\( \text{ALG} \) and \( \text{ALG}_{\text{benth}} \) represent carbon in suspended and stream-bed attached primary producers, respectively. Primary producer biomass increases through fixation of \( \text{DIC} \) and decreases via respiration (to \( \text{DIC} \)), mortality (to \( \text{POC}_{\text{auto}} \)) or excretion (to \( \text{DOC} \)).

\[
d\text{ALG}/dt = \text{ALG}_{\text{PRIMARY \_PRODUCTION}} - \text{ALG}_{\text{RESPIRATION}} - \text{ALG}_{\text{MORTALITY}} - \text{ALG}_{\text{EXCRETION}} \tag{24}
\]
\[
d\text{ALG}_{\text{benth}}/dt = \text{ALG}_{\text{benth \_PRIMARY \_PRODUCTION}} - \text{ALG}_{\text{benth \_RESPIRATION}} - \text{ALG}_{\text{benth \_MORTALITY}} - \text{ALG}_{\text{benth \_EXCRETION}} \tag{25}
\]

Primary production depends on the biomass of the producers, their maximal growth rates, temperature, and light and \( \text{DIC} \) availability. Similarly, respiration and excretion are modelled as a fraction of primary producer biomass and depend on temperature (standard Q10 functions, see Eq. (22)).

\[
\text{ALG}_{\text{PRIMARY \_PRODUCTION}} = f_{\text{ALG}_{\text{pp}}}(T) \ast \text{ALG}_{\text{lim}} \ast \text{ALG}_{\text{DIC \_lim}} \ast k_{\text{ALG}_{\text{pp}}} \ast \text{ALG} \tag{26}
\]
\[
\text{ALG}_{\text{benth \_PRIMARY \_PRODUCTION}} = f_{\text{ALG}_{\text{benth pp}}}(T) \ast \text{ALG}_{\text{benth lim}} \ast \text{ALG}_{\text{benth DIC \_lim}} \ast k_{\text{ALG}_{\text{benth pp}}} \ast \text{ALG}_{\text{benth}} \tag{27}
\]
\[
\text{ALG}_{\text{RESPIRATION}} = f_{\text{ALG}_{\text{resp}}}(T) \ast k_{\text{ALG}_{\text{resp}}} \ast \text{ALG}_{\text{C}} \tag{28}
\]
\[
\text{ALG}_{\text{benth \_RESPIRATION}} = f_{\text{ALG}_{\text{benth resp}}}(T) \ast k_{\text{ALG}_{\text{benth resp}}} \ast \text{ALG}_{\text{benth}} \tag{29}
\]
\[
\text{ALG}_{\text{EXCRETION}} = f_{\text{ALG}_{\text{excr}}}(T) \ast k_{\text{ALG}_{\text{excr}}} \ast \text{ALG} \tag{30}
\]
\[
\text{ALG}_{\text{benth \_EXCRETION}} = f_{\text{ALG}_{\text{benth excr}}}(T) \ast k_{\text{ALG}_{\text{benth excr}}} \ast \text{ALG}_{\text{benth}} \tag{31}
\]

Mortality of \( \text{ALG} \) and \( \text{ALG}_{\text{benth}} \) is attributed to viral lysis and modelled with a parasitic lysis factor (\( vf \)) of 20 when a threshold concentration of \( \text{ALG} \) and \( \text{ALG}_{\text{benth}} \) of 19 μmol C L⁻¹ (≈65 μg L⁻¹ Chl a (Garnier et al., 2000)) is exceeded.

\[
\text{ALG}_{\text{MORTALITY}} = (f_{\text{ALG}_{\text{mord}}}(T) \ast k_{\text{ALG}_{\text{mord}}}) + (f_{\text{ALG}_{\text{mord}}}(T) \ast k_{\text{ALG}_{\text{mord}}}) \ast (1 + vf) \ast \text{ALG} \tag{32}
\]
\[
\text{ALG}_{\text{benth \_MORTALITY}} = (f_{\text{ALG}_{\text{benth mord}}}(T) \ast k_{\text{ALG}_{\text{benth mord}}}) + (f_{\text{ALG}_{\text{benth mord}}}(T) \ast k_{\text{ALG}_{\text{benth mord}}}) \ast (1 + vf) \ast \text{ALG}_{\text{benth}} \tag{33}
\]
Primary production of ALG and ALG\textsubscript{benth} includes a DIC limitation (DIC\textsubscript{lim}) term that is calculated with a Michaelis-Menten function as follows:

\[
ALG_{DIC,lim} = \frac{[DIC]}{k\_DIC + [DIC]}
\]  

(34)

Light limitation for both pelagic and benthic primary producers is calculated using a spatial and temporal distribution of solar radiation reaching the surface of the water body and a water turbidity (\(\eta\text{\_tot}\)) that affects light penetration through the water column. Cloudless average solar radiation per month of the year (MOY) per latitude (lat) is calculated by dividing the month-integral solar radiation by the number of hours per month (HPM) as below:

\[
I_0(MOY, lat) = \frac{\int_{t_0}^{t} I_0(t, lat) dt}{HPM}
\]  

(35)

where I\(_0\), the solar radiation above the water surface, is integrated over time. Light limitation (\(I\text{\_lim}\)) is calculated separately for benthic primary producers (ALG\textsubscript{benth}) and for pelagic primary producers (ALG). For the pelagic primary producers, limitation by light is integrated over the water column from water surface to the water body bottom at depth \(z\), whereas for the benthic primary producers, production only takes place at the bottom, at depth \(z\), of the water body. This is formulated as follows:

\[
I\_lim(MOY, lat) = \begin{cases} 
\frac{I_z}{I_z + k_{scal} ALG\text{\_benth}} & \text{for ALG\textsubscript{benth}} \\
\frac{I_0(MOY, lat)}{I_0(MOY, lat) + k_{scal} ALG\text{\_c}} & \text{for ALG}
\end{cases}
\]  

(36)

with the light intensity \(I_z\) at depth \(z\) modelled using the Lambert-Beer equation:

\[
I_z = I_0(MOY, lat) \times e^{-\eta\text{\_tot} \times z}
\]  

(37)

The turbidity \(\eta\text{\_tot}\) is calculated by adding all contributions to light attenuation (Scheffer, 2004). The turbidity \(\eta\text{\_tot}\), with \(\eta\text{\_water}=0.8\) and \(\eta\text{\_PIM}=0.03\), is calculated according to:

\[
\eta\text{\_tot} = \eta\text{\_water} + \eta\text{\_POC\text{\_terre}} \times [POC\text{\_terre}] + \eta\text{\_POC\text{\_auto}} \times [POC\text{\_auto}] + \eta\text{\_ALG} \times [ALG] + \eta\text{\_DOC} \times [DOC] + \eta\text{\_PIM} \times [PIM]
\]  

(38)

\(I_0\), represents the solar radiation above the water surface and is calculated according to:

\[
I_0(t, lat) = \theta(t, lat) \times tt \times I\text{\_solar\_constant}
\]  

(39)

with \(\theta(t, lat)\) as the solar zenith angle. Zenith is the hemispheric point above the location of reference. Transmissivity (tt) is fixed at 0.8 [-] and the solar constant (I\text{\_solar\_constant}) fixed at 1367 W m\(^{-2}\).
The solar zenith angle is calculated from:

\[ \theta_s(t, \text{lat}) = \arccos(\sin(\text{lat}) \times \sin(\delta(t)) + \cos(\text{lat}) \times \cos(\delta(t)) \times \cos(h(t, \text{lat}))) \]  

with \( \delta \) as the solar declination angle. The solar declination angle is the angle the sun makes with the Earth’s equatorial plane. \( h \) is the hour angle, which is the radian angle the earth has turned around, since the previous midnight at the location of reference at time \( t \).

The solar declination is calculated as follows:

\[ \delta(t) = 23.45 \times \pi/180 \times \sin(2\pi*(284+\text{DOY}(t))/362.5) \]  

Figure 3: C forms, C sources and biogeochemical interactions in all simulated waterbodies. For clarity purposes, these schemes do not show the lateral influx and export. The numbers correspond to the equations in the text.

2.3 Model and sensitivity analysis

To analyse the performance of the full biology DISC model (Fig. 3), we present two other simplified in-stream C processing schemes:
1) the abiotic reference, with only POC, DOC and DIC external sources, transport, and atmospheric CO₂ exchange, and excluding any in-stream processing of DOC and production, mortality and mineralization of autochthonous C.

2) the respiration-only run, i.e. an extended abiotic system including respiration, but excluding autochthonous production. The numbers of the equations correspond with the numbers in Fig. 3.

Model parameter values and inputs are presented in Tables 2 and 3. The schemes of the abiotic and the respiration system respectively can be found in the supplementary material file.

Also, to further evaluate the model performance, we calculated the sensitivity of the modelled 5-year average (1995-2000) CO₂ emissions, total carbon export and POC retention to the variation of 45 parameters, 8 environmental constraints and 8 carbon sources using Latin Hypercube Sampling (Saltelli, 2000). The method allows to quantify sensitivity of model outcomes to varying parameters values with a relatively limited number of runs. We ran the model 750 times with a uniformly randomized combined set of all model parameters, external constraints and external inputs. In each run, each model parameter, constraint and input is randomly multiplied with a factor between 0.95 and 1.05 and combined into a setting for one run. For temperature, the randomization is applied between -1K and +1K of the default temperature. Values used for the parameters, constraints and inputs are presented in the supplementary material.

The contribution of each parameter (Xᵢ) to model outcome Y is assessed with linear regression (Saltelli, 2000: in Beusen et al 2015):

\[ Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 \ldots + \beta_n X_n + e \]  

with \( \beta_i \) as the ordinary regression coefficient of parameter \( i \) and \( e \) the error of the approximation of \( Y \). The linear regression model can be evaluated for parameter contribution analysis if the coefficient of determination (R²) is close to 1, i.e. when there is no variation of \( Y \) that is not explained with the linear regression model. A standardized regression coefficient (SRCᵢ) is used to scale \( \beta_i \) to the relative contribution of variation of \( Y \), by using the standard deviations of \( X_i \) and \( Y \) as follows:

\[ SRC_i = \beta_i \frac{\sigma_{X_i}}{\sigma_Y} \]  

\( SRC_i \) is independent of units and scale of parameters. The \( SRC_i \) has a value between -1 and 1. A positive \( SRC_i \) value indicates that an increased parameter value leads to an increased output \( Y \). A negative \( SRC_i \) indicates a decreased output \( Y \) with an increased parameter value. \( SRC_i^2 / R^2 \) yields the contribution of each parameter \( X_i \) to model outcome \( Y \).
3. Results

The DISC module has been developed for global application, but, in this paper, we apply the model to the stream network of the Rhine basin without parameter tuning. The river Rhine drains an important part of Western Europe with an area of 185620 km² and a length of 1250 km (van der Weijden and Middelburg, 1989). The annual average discharge is 2300 m³/s. The hydrology of the Rhine is strongly impacted by dams. Furthermore, with a population of 58 million inhabitants, it drains strongly urbanized landscapes with intensive agricultural systems (Uehlinger et al., 2009). The river Rhine has been monitored over decades for a range of monitoring stations. We present the IMAGE-DGNM results for the period 1950-2000, with estimates of the carbon delivery, retention, biogeochemical transformation, export and emission to the atmosphere for the entire watershed.

3.1 Carbon flows in the Rhine basin

Irrespective of the complexity of the biological processing, the river Rhine represents a source of CO₂ to the atmosphere (Fig. 4). In the abiotic scheme (Fig. 4(a)), CO₂ emissions are very low (0.02 Tg C/yr), while emissions in the respiration-only scheme (Fig. 4(b)) and in the biological scheme (Fig. 4(c)) are 118 (2.36 Tg C/yr or 41% of total C inputs) and 93 times higher (1.85 Tg C/yr or 32% of total C inputs), respectively. This indicates that outgassing of delivered CO₂ from external sources is very limited compared to within system generation of CO₂ by respiration. Furthermore, the difference between the respiration-only and biology scheme with respect to the basin CO₂ emissions suggests that in-stream biological processing is an important aspect in regulating CO₂ emissions from the aquatic continuum. The export of DIC is only 7% and 6% higher in the respiration-only (1.35 Tg/yr or +0.9 Tg/yr) and biology scheme (1.33 Tg/yr or +0.7 Tg/yr) respectively, than in the abiotic scheme (1.26 Tg /yr), while in-stream production of DIC is 2.42 and 3.71 Tg C/yr for respectively the respiration and the biology scheme versus 0 Tg C/yr in the abiotic scheme (Fig. 5). Nearly all CO₂ that is produced and consumed through in-stream biogeochemistry is emitted to the atmosphere in both the respiration-only and the biology schemes.
In the abiotic scheme, about 3.25 Tg C/yr (57%) is retained in the Rhine basin, while total C retention in the respiration-only and biological schemes is 1.66 Tg/yr (29% of total C input) and 2.07 Tg/yr (36% of total C input), respectively (Fig. 5). The difference in C retention between the respiration-only and the biology scheme implies that in-stream biological processing is a necessary element to consider when quantifying basin retention of carbon. Total carbon delivery is 5.8 Tg/yr in all schemes, but total C export to the ocean in the abiotic scheme is 2.48 Tg/yr (43% of total C input), and 1.78 Tg/yr (31% of total C input) and 1.88 Tg/yr (32% of total C input) in the respiration and biology schemes, respectively.

DIC, DOC and POC terrestrial average inputs into freshwaters of the Rhine basin are 1.3, 0.96 and 3.51 Tg/yr, or 23, 17 and 60% of the total C input, respectively (Fig. 5). In the abiotic scheme, DOC delivery is fully balanced by export. In the respiration-only and biology schemes, DOC delivered to the aquatic system is partly exported (0.27 Tg/yr, 28% DOC of input, and 0.34 Tg/yr, 35% DOC of input, respectively). In-stream removal of DOC through mineralization is 0.69 Tg/yr (72% of DOC input) and 0.82 Tg/yr (85% of input). In the biology scheme, an additional 0.2 Tg/yr (21% of DOC input) of DOC is produced in-stream by algal excretion. Export of DOC for the abiotic, respiration-only and biology schemes is 0.96, 0.27 and 0.34 Tg/yr, respectively.

About 0.26 Tg/yr (7% of POC input) of the POC delivered to the freshwater system (3.51 Tg/yr) is exported in the abiotic scheme. In the respiration-only and biology scheme, export of POC is 0.16 Tg/yr (5% of POC input) and 0.2 Tg/yr (6% of POC input), respectively. For the biology scheme, POC includes POCterrestrial and POCautotrophic. POC removal is 3.25 Tg/yr (93% of total POC input) in the abiotic scheme, and 3.35 Tg/yr (95% of POC input) and 4.69 Tg/yr (134% of POC input) in the respiration-only and full biology respectively. In-stream production of POC (1.38 Tg/yr) in the biology scheme through primary production results in a higher POC removal rate than POC input.
3.2 Validation

Basin average DIC concentrations are higher by a few mg/L in the respiration and biology scheme compared to the abiotic one, as an effect of in-stream production of DIC by respiration. Alkalinity concentrations are identical among the different schemes, since the imported bicarbonate is not biogeochemically active during its transport through the aquatic continuum. Simulated DIC and alkalinity concentrations in the biology scheme are on average respectively 46% and 43% lower than
observations (Fig. 6(b) and 6(e)) and are also weakly correlated with measurements (bicarbonate $r^2=0.01$; DIC abiotic: $r^2=0.05$; DIC respiration: $r^2=0.07$; DIC biology: $r^2=0.07$). The weak correlation is likely related to the parameterization of the riverine alkalinity flux (Jansen, 2010), which depends on the coarse spatial distribution of the lithology and riverine discharge. The lithological data (Dürr et al., 2005) used here show only the dominant lithological class in 0.5 by 0.5-degree resolution. Furthermore, runoff calculated by PCR-GLOBWB is prone to uncertainty and may be systematically underestimated in source areas of alkalinity.

Simulated average values of pCO$_2$ in the respiration-only and biology schemes are high (Fig. 6(d): 1399 and 1183 ppm, respectively), but much lower than average values of 5261 ppm from the GLORICH database. This underestimation can be partly attributed to underestimated DIC and alkalinity, but values based on indirect measurements may also be strongly biased (Abril et al., 2015). Moreover, direct pCO$_2$ measurement in the Rhine using an equilibrator device vary from 545 to 1990 ppm (Frankignoule et al., 1998).

The average simulated abiotic (8.0), respiration-only (7.6) and biology (7.7) pH values (Fig. 6(a))] show a fairly good agreement with average measurements (pH=7.6), with a low $r^2$ for the abiotic run ($r^2=0.04$), and higher ones for the respiration and biology schemes ($r^2=0.31$ and $r^2=0.29$ respectively). The simulated DOC (Fig. 6(f)) and TOC (Fig. 6(c)) concentrations compare well with measurements (DOC [abiotic: $r^2=0.73$; respiration: $r^2=0.79$; biology: $r^2=0.81$]; TOC [abiotic: $r^2=0.88$; respiration: $r^2=0.95$; biology: $r^2=0.95$]), with the abiotic scheme leading to overestimated TOC and DOC compared to measurements (DOC_measurements: 2.8 mg/L and DOC_abiotic: 7.4 mg/L [> 159%]; TOC_measurements: 3.6 mg/L and TOC_abiotic: 14.3 mg/L [>297%]) and the respiration and biology scheme underestimating DOC and TOC (DOC_respiration: 3.6 mg/L [>29%] and DOC_biology: 3.7 mg/L [>31%]; TOC_respiration: 8.8 mg/L [>144%] and TOC_biology: 9.0 mg/L [<150%]).
Figure 6: Comparison between average measurements (x-axis) and average simulations (biology scheme) for all available stations in the Rhine basin. Measurements are from the GLORICH database (Hartmann et al., 2014). Figure 7 shows a 50-year simulation (for the abiotic, respiration-only and biology schemes) and measurement time series for station Bimmen/Lobith at the German/Dutch border. Differences among simulation results of the different schemes are most apparent for the organic forms of carbon (DOC and TOC). In the abiotic simulations all delivered organic C remains organic and concentrations are high, whereas in the other two schemes, organic forms are mineralized to DIC, resulting in lower concentrations of organic forms and elevated pCO₂. Time series of all other available measurement locations are found in the supplementary material section E (validation data).
3.3 Sensitivity analysis

The influence of a range of parameters on simulated CO$_2$ emissions, C export and C retention was investigated, but we discuss only those parameters that have an influence of more than 20% on the variation of simulated CO$_2$ emissions, C export or C retention. Table 4 shows the most important outcomes of the sensitivity analysis. The entire table, containing all assessed parameters and SRC results is available in the supplementary materials section F (sensitivity analysis).

Simulated total basin CO$_2$ emissions are strongly influenced by many model parameters. Total basin CO$_2$ exchange is positively influenced by litter input in floodplains (SRC = 0.45), DIC fluxes from groundwater (SRC = 0.43), the organic sediment mineralization rate (SRC = 0.28) and temperature (SRC = 0.27). The CO$_2$ exchange is negatively influenced by alkalinity flux from groundwater (SRC= -0.42), global radiation (SRC = -0.24) and burial rate (SRC = -0.22). Except for the floodplains, CO$_2$ emissions are largely governed by DIC and ALK inputs that originate from groundwater. CO$_2$ emissions from floodplains are predominantly sensitive to temperature, global radiation, organic sediment mineralization rate, burial rate, minimum sediment thickness and most dominantly by input of POC from terrestrial vegetation.

Figure 7: Timeseries of measurements and simulations at Bimmen/Lobith, Germany. Measurements are from the GLORICH database (Hartmann et al., 2014)
The sensitivity analysis shows that variability of total C export (of which DIC is the dominant C species) is almost entirely governed by variability of alkalinity delivery from groundwater, i.e. weathering (SRC = 0.9). Almost all other carbon eventually escapes to the atmosphere.

The most important controlling factor of the modelled retention of POCterre is the mineralization rate of SEDOCterre, \( k_{\text{SEDOCterre.min}} \), which is governed by temperature. More mineralization enables more C to escape from the system as DIC. As expected, the burial rate also strongly affects POC retention. Furthermore, an increased input of POCterre from litterfall leads to an increased total retention fraction.

Many regression models use discharge as a driver of river C export at the river basin scale (Beusen et al., 2005; Mayorga et al., 2010; Kroeze et al., 2012; Strokal et al., 2016), our sensitivity analysis suggests that discharge has a minor direct influence on the C biogeochemistry, retention and emissions and only total C export was strongly influenced by discharge (SRC=0.34). This concerns the river Rhine, and analysis of the results for other rivers is needed to assess if this is a general or local feature.

4. Conclusions

The DISC module of IMAGE-DGNM is a major step forward in basin scale modelling of river systems. For the first time, we are able to make an integral and systemic simulation of biogeochemical C processing on the river basin scale in fair agreement with observations. Results show that process-based modelling is essential to assess the fate of C in river basins. Biogeochemical production and consumption of C within its lifetime in the river basin are in the same order of magnitude as the inputs. The sensitivity analysis showed that in-stream chemistry and CO\(_2\) emissions are weakly correlated with discharge in contrast to recent regression approaches. The dominant driver of total C export, being mainly DIC export, is the weathering input from groundwater. CO\(_2\) emissions are strongly responsive to temperature variability and POC dynamics. The sensitivity analysis also suggests that if we want to understand CO\(_2\) emissions from river systems, floodplains are a pivotal component to consider, as increases in CO\(_2\) emissions originate for 45% from terrestrial vegetation litter delivery to floodplains/wetlands. This may be higher for tropical floodplains, as floodplains/wetlands contribute relatively much to the total water area of river basins.

Our results show that improvement in some model formulations could result in a better match of simulations with observations. Firstly, a better description of the hydrology in low-order streams to replace the current parameterization will improve our C cycle model in headwaters. The HydroSheds dataset (Lehner and Grill, 2013) is a good candidate to improve our PCR-GLOBWB model. The HydroLakes dataset (Messager et al., 2016) will improve the current data on lake and reservoir water volume. Secondly, C inputs are an important source of uncertainty in terms of their spatial distribution, organic/inorganic ratios and form (dissolved or particulate). For example, an improved estimate of terrestrial POC input from litterfall and its variation between headwaters to wider mainstreams is necessary to provide a more robust quantification and spatial estimate of CO\(_2\).
emissions from freshwaters. Similarly, alkalinity input from groundwater is important but uncertain and can be improved by a better model for weathering and DOC input to aquifers and transformation to DIC. Finally, the modelled primary production is limited by light and carbon. A future major challenge to be tackled in global biogeochemical modelling frameworks is to introduce limitations to primary production imposed by nutrients (nitrogen, phosphorus and silicium) and oxygen availability.

**Code and data availability**

The presented version of CARBON-DISC is archived on Zenodo (van Hoek et al., 2019) under the Gnu Public License, GPL v3, in the form of input data and scripts to run the model and the raw output data for all the simulations presented in this study. Python scripts containing the source code of CARBON-DISC 1.0 are available in section A (source code). All used input data is found in section B (model input). Raw output data for the model runs shown in the results section are found in section C (raw output data). Data specifically to reproduce the figures are found in section D (data for figures). For further information about the IMAGE-DGNM framework and the data used to produce the presented results, please contact Alexander F. Bouwman ([alex.bouwman@pbl.nl](mailto:alex.bouwman@pbl.nl)).

**Author contributions**

W.J. van Hoek prepared the original draft, developed the CARBON-DISC module and ran the model simulations. A.H.W. Beusen and J.M. Mogollón integrated the IMAGE-GNM and PCR-GLOBWB to construct the IMAGE-DGNM framework in which the CARBON-DISC was developed. J.J. Middelburg, A.F. Bouwman, L. Vilmin, X. Liu and J.J. Langeveld contributed to formulate concepts and research aims.

**Competing interests**

The authors declare that they have no conflict of interest.

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Table 1: Sources of C to surface waters as shown in fig. 03 and description of their calculation

<table>
<thead>
<tr>
<th>Source</th>
<th>Description</th>
</tr>
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<tr>
<td>DOC input from waste water (WAS$_{DOC}$)</td>
<td>Global organic carbon from waste is obtained from estimates by (Prairie and Duarte, 2006) is combined with the spatio-temporal estimates of P in wastewater from Vilmin et al. (2018) to obtain DOC in waste water from (Vilmin et al., 2018). All organic carbon in waste water is assumed to be in dissolved form.</td>
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<tr>
<td>DOC input from surface runoff (SRO$_{DOC}$)</td>
<td>DOC in soil moisture is transported to the oceans via rivers ((Mcdowell et al., 1984; Aitkenhead and McDowell, 2000; Lobbes et al., 2000; Hernes et al., 2017). DOC in soil moisture enters surface freshwaters via surface runoff. DOC in soil moisture is related to the soil organic carbon (fSOC) (Liu et al., 2013). The dissolved fraction of the total soil organic carbon is here assumed to 1%. A spatial distribution of SOC is obtained from (Batjes, 2016). SOC [%] is multiplied with bulk density [kg/dm$^3$] ((Batjes, 2002), which gives the mass density of soil organic carbon [kg/dm$^3$]. Multiplication of the soil organic carbon mass density with monthly surface runoff from (Van Beek et al., 2011)</td>
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<td>POC$<em>{terre}$ input from soil loss (SOI$</em>{POC}$)</td>
<td>Soil erosion delivers terrestrial POC in freshwaters parallel to an approach proposed by (Cerdan et al., 2010) based on slope, soil texture and land cover type. Country aggregated soil loss rates for arable land, grassland and natural vegetation were applied to all grid cells with each their own areal fraction of arable land, grassland and natural vegetation. The soil loss enters the surface...</td>
</tr>
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</table>
waters as SPM. To account for the POC$_{\text{terre}}$, SPM input is multiplied with f$_{\text{SOC}}$ from (Batjes, 2016) to obtain the fPOC in eroded soil.

$POC_{\text{terre}}$ input from litterfall

Terrestrial $POC$ input from litterfall is based on IMAGE estimates of C production with NPP for wetlands and floodplains from the LPJ model (Sitch et al., 2003). In the DISC module, $POC_{\text{terre}}$ from litterfall enters surface waters in two ways. 1: via riparian zones of small streams 50% of total NPP within the areal fraction of riparian zones (of 1 meter wide) is assumed to end in the stream. 2: via floodplains along the mainstream 100% of total NPP within the floodplain area is considered to end up in the floodplain surface waters.

$DIC$/Alkalinity input from weathering

Lithology and discharge are the strongest controllers for annual bicarbonate fluxes for 338 catchments basin across North America. (Jansen, 2010; Moosdorf et al., 2011; Lauerwald et al., 2013). Here we apply the empirical parameterization for annual bicarbonate fluxes from (Jansen, 2010). We use lithological data from (Dürr et al., 2005). All the $DIC$ input from this source is assumed to be bicarbonate.

Table 2: Parameters, units, values and literature references

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<td>day$^{-1}$</td>
<td>0.072</td>
<td>(Garnier et al., 2000)</td>
</tr>
<tr>
<td>$k_{ALG_benth_mort}$</td>
<td>day$^{-1}$</td>
<td>0.096</td>
<td>(Garnier et al., 2000)</td>
</tr>
</tbody>
</table>
Table 3: Model parameters and units

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{ALG_benth_excr}$</td>
<td>day$^{-1}$ 0.072 (Garnier et al., 2000)</td>
</tr>
<tr>
<td>$\nu_{ALG_benth}$</td>
<td>- 20 (Garnier et al., 2000)</td>
</tr>
<tr>
<td>(parasitic lysis amplification)</td>
<td></td>
</tr>
<tr>
<td>$p_{\text{threshold}}_{ALG_benth}$</td>
<td>mmol C L$^{-1}$ 0.019 (Garnier et al., 2000)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAS$_{DOC}$</td>
<td>dissolved organic carbon in waste water [Mmol yr$^{-1}$]</td>
</tr>
<tr>
<td>LIT$_{POC_terre}$</td>
<td>particulate organic carbon in litterfall [Mmol yr$^{-1}$]</td>
</tr>
<tr>
<td>WEADIC</td>
<td>dissolved organic carbon in weathering [Mmol yr$^{-1}$]</td>
</tr>
<tr>
<td>SOI$_{POC_terre}$</td>
<td>particulate organic carbon in soil loss [Mmol yr$^{-1}$]</td>
</tr>
<tr>
<td>LEA$_{DOC}$</td>
<td>dissolved organic carbon in soil leaching water [Mmol yr$^{-1}$]</td>
</tr>
<tr>
<td>WAS$_{DOC}$</td>
<td>dissolved organic carbon in waste water [Mmol yr$^{-1}$]</td>
</tr>
<tr>
<td>f$_{DOC}$</td>
<td>mass fraction of dissolved organic carbon [-]</td>
</tr>
<tr>
<td>f$_{SOC}$</td>
<td>mass fraction of soil organic carbon [-]</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>soil dry bulk density [kg dm$^{-3}$]</td>
</tr>
<tr>
<td>soil$_{ro}$</td>
<td>soil runoff [mm yr$^{-1}$]</td>
</tr>
<tr>
<td>TSS</td>
<td>total suspended solids [Mmol]</td>
</tr>
<tr>
<td>NPP</td>
<td>net primary production [Mmol yr$^{-1}$]</td>
</tr>
<tr>
<td>$f_{\text{wetlands}}$</td>
<td>areal fraction of wetlands [-]</td>
</tr>
<tr>
<td>$f_{\text{floodplains}}$</td>
<td>areal fraction of floodplains [-]</td>
</tr>
<tr>
<td>$b_0$</td>
<td>empirical parameter used to calculate alkalinity discharge</td>
</tr>
<tr>
<td>$A_L$</td>
<td>area with lithological class L [km$^2$]</td>
</tr>
<tr>
<td>Q</td>
<td>discharge [km$^3$ yr$^{-1}$]</td>
</tr>
<tr>
<td>$b_L$</td>
<td>empirical parameter accounting for effect of lithological class L on alkalinity discharge</td>
</tr>
<tr>
<td>v</td>
<td>flow velocity in order I [cm s$^{-1}$]</td>
</tr>
</tbody>
</table>
### Table 4: SRC values of most relevant parameters and results obtained from the sensitivity analysis. In green the most important positive SRC’s, in red the most important negative SRC’s.

<table>
<thead>
<tr>
<th>parameter</th>
<th>CO₂ exchange</th>
<th>TC</th>
<th>POC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>main</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>stream</td>
<td>lakes</td>
<td>reservoirs</td>
</tr>
<tr>
<td>Q</td>
<td>-0.01</td>
<td>-0.11</td>
<td>-0.18</td>
</tr>
<tr>
<td>T</td>
<td>0.27</td>
<td>0.04</td>
<td>0.11</td>
</tr>
<tr>
<td>I₀</td>
<td>-0.24</td>
<td>-0.08</td>
<td>-0.04</td>
</tr>
<tr>
<td>k₆₀₀</td>
<td>0.28</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>k₆₀₁₀_veg</td>
<td>-0.22</td>
<td>-0.02</td>
<td>-0.03</td>
</tr>
<tr>
<td>k₆⁰⁰_sed</td>
<td>0.16</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>WEA_DIC</td>
<td>0.43</td>
<td>0.72</td>
<td>0.71</td>
</tr>
<tr>
<td>WEA_ALK</td>
<td>-0.42</td>
<td>-0.70</td>
<td>-0.68</td>
</tr>
<tr>
<td>LIT_POC_floodplains</td>
<td>0.45</td>
<td>0.03</td>
<td>0.02</td>
</tr>
</tbody>
</table>