Supplement of

Complex interactions of in-stream dissolved organic matter and nutrient spiralling unravelled by Bayesian regression analysis

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S1 Mathematical details on the INSBIRE approach

In-stream samples were taken in a longitudinal series which is formally identical to a time series problem. We re-arranged the equations of the nutrient spiralling concept (Stream Solute Workshop, 1990) so that differences are replaced by current (e.g. \( C_x \)) and past (e.g. \( C_{x-1} \)) values of series. These equations conform to a time series including past values of the same variable as well as current and past values of other variables and are a form of non-linear autoregressive exogenous models (NARX; e.g. Billings, 2013). Several studies used the original equations of the Stream Solute Workshop protocol (1990) and solved them via variable transformation. Still, the results from a linear regression using transformed data and those of a direct non-linear fit differ (e.g. Stedmon et al., 2000). Therefore, we regard a non-linear solving algorithm superior in terms of accuracy. We proceeded differently, transforming all equations into a NARX form. Additionally, we extended the equations to incorporate interactions (Eqs. S7 and S8).

For the parameter determination we used a non-linear Bayesian fitting algorithm from the R package brms (Bürkner, 2017). We choose priors to approximately fit knowledge from other studies (e.g. Mineau et al., 2016) while keeping them broad, so they do not dominate the results. Priors and especially their limits were also adjusted to deliver converging models.

During a plateau addition experiment, concentration changes in a conservative tracer due to dilution effects. This was transformed into a NARX form (Eq. S1). We used this equation to determine the dilution factors and to correct measured DOC and nutrient concentrations as well as DOM components by the measured changes in conductivity.

\[
C_{x,t} = C_{amb,x,t} + \left( C_{x-1,t} - C_{amb,x,t} \right) \frac{dil_x}{dil_{x-1}} 
\]

(S1)

\( x \) … index of longitudinal sampling points

\( t \) … index of addition date

\( C_{x,t} \) … concentration at point \( x \) and date \( t \)(variable)

\( C_{amb,x,t} \) … ambient concentration at point \( x \) and date \( t \)(variable)

\( dil_x \) … dilution factor at point \( x \) (once calculated fixed values)

A reactive substance can be modelled using Eq. (S2). Variable \( x \) from the original equation (Stream Solute Workshop, 1990) was replaced by \( (d_{x-1} - d_x) \) to address a case with several sampling points with different distances from the addition point.

\[
C_{x,t} = C_{amb,x,t} + \left( C_{x-1,t} - C_{amb,x,t} \right) \frac{dil_x}{dil_{x-1}} e^{\frac{d_{x-1} - d_x}{s_w}} 
\]

(S2)

\( s_w \) … nutrient uptake length (parameter)

prior: \( s_w \sim Lognormal(400, 200), s_w \in [0.01, 10000] \)

\( d_x \) … distance of point \( x \) from origin (fixed)
Using the flow velocity and the water depth, the nutrient uptake velocity can be calculated from \( s_w \) (Eq. S3). This is useful to reduce flow-dependent effects.

\[
\frac{1}{s_w} = v_f [uz]^{-1} \tag{S3}
\]

\[
C_{x,t} = C_{amb,x,t} + \left( C_{x-1,t} - C_{amb,x,t} \right) \frac{dil_x}{dil_{x-1}} e^{\left( d_{x-1} - d_x \right) [uz]^{-1}} \tag{S4}
\]

\( v_f \) … nutrient uptake velocity (parameter)

prior: \( v_f \sim \text{Lognormal}[0.7,3], v_f \in [0.01,35] \)

\( u \) … flow velocity (calculated by Hec-RAS, then fixed)

\( z \) … water depth (calculated by Hec-RAS, then fixed)

The areal uptake rate can then be modelled using Eqs. 5 and 6:

\[
v_f = U C_{x,t}^{-1} \tag{S5}
\]

\[
C_{x,t} = C_{amb,x,t} + \left( C_{x-1,t} - C_{amb,x,t} \right) \frac{dil_x}{dil_{x-1}} e^{\left( d_{x-1} - d_x \right) U C_{x,t}^{-1}} \tag{S6}
\]

\( U \) … areal uptake rate (parameter)

prior: \( U \sim \text{Lognormal}[2,3], U \in [0.01,40] \)

A linear relation between uptake velocity and concentration is needed to properly calculate \( U \). In other cases, uptake functions such as the Michaelis-Menten formulation can be used to describe the observed uptake-concentration relation (Stream Solute Workshop, 1990). An uptake efficiency loss, mathematically described by a power function, was shown in experiments with N-NO3 (Dodds et al., 2002; O’Brien et al., 2007). We additionally tested a linear function, an asymptotic regression function and an exponential function. A mechanistic argumentation for either of these functions is difficult (Stream Solute Workshop, 1990), but testing the suitability with the Bayes factor (BF) leads to good empirical fits.

To include interactions, we added a product of power functions for relevant compounds and nutrients (Eqs. S7 and S8). Where beneficial, the wetted width \( w \) was added to analyse influences of the stream bed surface on retention processes. The added value \( l \) was added as a degree of freedom to allow curves, that do not go through the origin. The relevance of these effects was tested in the modelling process by comparing different combinations of compounds in models using the BF, which can also be a measurement of variable importance.

\[
v_f = kw \left( l + \prod_{i} C_{i,x,t}^{mil} \right) \tag{S7}
\]
\[ C_{x,t} = C_{amb,t} + \left| C_{x-1,t} - C_{amb,t} \right| \cdot \frac{\text{dil}_x}{\text{dil}_{x-1}} e^{(d_{x-1} - dx)kW(t+\prod C_i^{m_i}) uz^{-1}} \]  

(S8)

\( k \) … uptake rate factor (parameter)

prior: \( k \sim \text{Lognormal}(0.7,3), k \in [0.01,35] \)

\( w \) … wetted width, constant 1 to represent no influence (calculated by Hec-RAS, then fixed)

\( l \) … additive value (parameter)

\( i \) … index of nutrient or DOM component

\( C_{i,x,t} \) … concentration of compound i at point x and date t (variable)

\( m_i \) … exponent determining the strength of the relations (parameter)

prior: \( m_i \sim \text{Normal}(-0.2,0.4), m_i \in [-1,1] \) if a dampening influence was assumed from literature

prior: \( m_i \sim \text{Normal}(0.2,0.4), m_i \in [-1,1] \) if a stimulating influence was assumed

Since we had no prior information for \( m_i \) from previous studies, it was important to test the influence of the prior on the final results by using a uniform distribution and normal distributions with different parameters. In the presented models, the priors for any parameters did not dominate the results, but were important to ensure a convergent of the fitting algorithm. Due to the double-exponential structure of Eq. (S8) in \( m_i \), the limits were essential.

To set up the models, we used the difference of concentrations (Eq. S9) as the dependent variable and restructured the equations above accordingly. We assumed a normal error distribution for the differences of concentrations and the differences of fluorescence. The nature of the measurements would also allow a log-normal error distribution, but our data clearly deviated from that assumption, so we used a normal error distribution.

\[ D_{x,t} = C_{x,t} - C_{amb,t} \]  

(S9)

\( D_{x,t} \) … concentrations (DOC, SRP, N-NO\(_3\)) or fluorescence (DOM PARAFAC components) deviation from ambient conditions

model error assumptions: \( D_{x,t} \sim \text{Normal}(\mu_{x,t}, \sigma^2) \)

\( \mu_{x,t} \) … calculated difference from Eqs. (S2), (S4) and (S8) restructured to suffice Eq. (S9)

The accuracy of the model can be compared to expected measurement errors (e.g. lab instrument errors, errors from sampling procedure) and show the point where no additional information can be expected from the data (for proper error propagation analysis see Haefner, 2012, chapter 9). Using the simulated probability density of the residuals, which is in the same units as the measured values, we get an impression if further information can be expected from the data. The 95% probability interval of the residuals can be a meaningful metric of the model accuracy. This approach makes it easier to distinguish between signal and noise compared to an approach where Eqs. (S2), (S4) and (S8) are applied step-wise
and error propagation is not considered. It can also help in planning the experimental scheme to improve the signal-to-noise ratio because amongst others, the error depends on the instruments, sample handling, concentrations and concentration difference of consecutive samples.

**S2 Additional resources**

**Table S1: Samplings, dates, discharge, concentrations of nutrients and fluorences (additionally in %) of DOM PARAFAC components. Additionally introduced amounts are calculated from expected ambient and measured values at the listed dates.**

| source | date     | code | discharge | DOC  | P-PO₄ | N-NO₃ | N-NO₂ | N-NH₄ | Hum-mic (C1) | Hum-ter (C2) | Hum-micter (C3) | Qui (C4) | Trp (C5) | Tyr (C6) |
|--------|----------|------|-----------|------|-------|-------|-------|-------|--------------|--------------|----------------|----------|----------|----------|
|        |          |      |           |      | µg l⁻¹ | µg l⁻¹ | µg l⁻¹ | µg l⁻¹ | Fmax RU | % | Fmax RU | % | Fmax RU | % | Fmax RU | % | Fmax RU | % |
| none   | 2018-07-16 | A    | 0.93      | 1301 | 9.4   | 2548  | 11.1  | 10.9  | 0.53  | 44 | 0.21 | 17 | 0.24  | 20 | 0.08  | 6 | 0.13  | 10 | 0.02  | 2 |
| none   | 2018-07-23 | C    | 0.73      | 1459 | 13.9  | 1890  | 12.9  | 10.2  | 0.56  | 42 | 0.26 | 20 | 0.27  | 20 | 0.09  | 7 | 0.11  | 8 | 0.03  | 2 |
| none   | 2018-07-30 | F    | 0.69      | 1279 | 11.2  | 1963  | 10.4  | 9.5   | 0.54  | 44 | 0.23 | 19 | 0.26  | 21 | 0.09  | 7 | 0.11  | 9 | 0.01  | 0 |
| none   | 2018-08-06 | I    | 0.67      | 1420 | 18.8  | 2194  | 11.3  | 13.4  | 0.57  | 43 | 0.25 | 19 | 0.27  | 20 | 0.10  | 7 | 0.13  | 10 | 0.01  | 1 |
| none   | 2018-08-13 | L    | 0.47      | 1257 | 11.3  | 1893  | 7.8   | 10.5  | 0.54  | 43 | 0.23 | 18 | 0.25  | 20 | 0.09  | 7 | 0.13  | 10 | 0.01  | 1 |
| none   | 2018-08-20 | O    | 0.41      | 1229 | 3.3   | 1640  | 5.4   | 0.9   | 0.51  | 44 | 0.21 | 18 | 0.24  | 20 | 0.08  | 7 | 0.12  | 10 | 0.01  | 1 |
|        |          |      |           |      | µg l⁻¹ | µg l⁻¹ | µg l⁻¹ | µg l⁻¹ | Fmax RU | % | Fmax RU | % | Fmax RU | % | Fmax RU | % | Fmax RU | % |
| corn   | 2018-08-07 | J    | 0.58      | 403  | 4.9   | 75    | 0.2   | 0.0   | 0.00  | 0 | 0.00 | 0 | 0.00  | 0 | 0.00  | 0 | 0.00  | 0 | 0.07  | 59 | 0.05  | 41 |
| corn   | 2018-08-14 | M    | 0.82      | 1534 | 19.5  | 25    | 0.8   | 0.0   | 0.03  | 19 | 0.01 | 9 | 0.01  | 4 | 0.02  | 12 | 0.04  | 25 | 0.05  | 31 |
| cow dung | 2018-07-19 | B    | 0.80      | 2284 | 62.0  | 0     | 5.9   | 60.4  | 0.20  | 28 | 0.09 | 12 | 0.08  | 11 | 0.11  | 16 | 0.12  | 17 | 0.12  | 16 |
| cow dung | 2018-07-26 | E    | 0.64      | 1235 | 31.5  | 710   | 1.1   | 0.0   | 0.15  | 19 | 0.02 | 3 | 0.02  | 3 | 0.04  | 5 | 0.12  | 15 | 0.45  | 56 |
| leaves | 2018-07-24 | D    | 0.60      | 272  | 2.6   | 193   | 3.8   | 1.5   | 0.28  | 26 | 0.00 | 0 | 0.00  | 0 | 0.03  | 3 | 0.07  | 54 | 0.18  | 17 |
| leaves | 2018-07-31 | G    | 0.41      | 1225 | 25.2  | 707   | 0.0   | 0.4   | 0.59  | 67 | 0.00 | 0 | 0.00  | 0 | 0.08  | 9 | 0.03  | 4 | 0.17  | 20 |
| nettles | 2018-08-16 | N    | 0.44      | 148  | 2.3   | 92    | 51.4  | 23.0  | 0.00  | 0 | 0.00 | 0 | 0.00  | 0 | 0.01  | 15 | 0.01  | 35 | 0.02  | 49 |
| nettles | 2018-08-21 | Q    | 0.38      | 188  | 8.5   | 252   | 33.8  | 26.9  | 0.04  | 18 | 0.01 | 5 | 0.01  | 3 | 0.02  | 10 | 0.05  | 26 | 0.07  | 37 |
| pig dung | 2018-08-02 | H    | 0.46      | 469  | 37.6  | 157   | 5.5   | 45.1  | 0.09  | 25 | 0.06 | 16 | 0.03  | 9 | 0.01  | 3 | 0.06  | 17 | 0.11  | 2 |
| pig dung | 2018-08-09 | K    | 0.72      | 251  | 49.0  | 193   | 5.0   | 62.3  | 0.05  | 25 | 0.02 | 10 | 0.02  | 9 | 0.05  | 27 | 0.03  | 1 |

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Table S2: Correlation of nutrient and DOM fraction uptake velocity $v_f$; Bayes factor in brackets; only shown, if Bayes factor > 1.

|                | Hum-micter (C3) | Qui (C4) | Tyr (C6) |
|----------------|-----------------|----------|----------|
| Trp (C5)       | 0.78 (2.98)     | 0.50 (1.31) |          |
| Tyr (C6)       |                 | 0.66 (6.10) |          |
| DOC            |                 | 0.58 (4.63) | 0.41 (1.36) |

Table S3: Model comparison $v_f$ with and without random effects (mixed models, MM) of source and addition date. The Bayes $R^2$ shows the absolute model performance and the BF indicates whether the addition of the random effects leads to a model improvement.

| model          | Original model | Source effects | Date effects | comment                                           |
|----------------|----------------|----------------|--------------|---------------------------------------------------|
|                | Bayes $R^2$    | Bayes $R^2$    | BF           |                                                   |
| Hum-mic (C1)   | 0.51           | 0.48           | 0.17         | 0.50 | 4.61 | The date has a substantial impact on $v_f$. |
| Hum-ter (C2)   | 0.34           | 0.49           | 0.7          | 0.49 | 0.65 | Neither date nor source improved the model. |
| Hum-micter (C3)| 0.52           | 0.51           | 0.21         | 0.54 | 0.22 | Neither date nor source improved the model. |
| Qui (C4)       | 0.46           | 0.46           | 0.09         | 0.45 | 0.12 | Neither date nor source improved the model. |
| Trp (C5)       | 0.29           | 0.29           | 1.39         | 0.48 | 134.23 | The date has a decisive influence on $v_f$. |
| Tyr (C6)       | 0.29           | 0.34           | 10.68        | 0.70 | 1.2e8 | Both, source and date improved the model, but the effects of date were stronger. |
| DOC            | 0.26           | 0.46           | 1563         | 0.46 | 146  | Both, source and date improved the model, but the effects of source were stronger. |
| NO₃            | 0.16           | 0.29           | 0.41         | 0.29 | 0.65 | Neither addition nor source improved the model. |
| SRP            | 0.56           | 0.57           | 0.17         | 0.56 | 0.11 | Neither addition nor source improved the model. |
Table S4: BF for inclusion of model parameters and probability intervals of the parameter estimates. The Table provides additional information to Table 7. $v_f$: uptake velocity, $k$: uptake rate factor, $w$: wetted width, $C_i$: fluorescence of PARAFAC components, $m_i$: exponent of relation, $l$: additive parameter

| fraction/nutrient | most probable model (Eq. 1) | BF in favour of variable inclusion | estimates, [95% probability interval] |
|-------------------|-----------------------------|----------------------------------|-------------------------------------|
| Hum-mic (C1)      | $v_f = k \ w \ C_1^{m_1}$   | P($w \neq 1$): BF = 7.34         | $k = 2.11$, [1.65, 2.59]            |
|                   |                             | P($m_1 \neq 0$): BF = 1.4        | $m_1 = -0.38$, [-0.93, 0.28]        |
| Hum-ter (C2)      | $v_f = k (1 + DOC^{m_c})$   | P($l \neq 0$): BF = 2.36         | $k = 0.11$, [0.01, 0.61]            |
|                   |                             | P($m_c \neq 0$): BF = 7.69       | $l = 3.16$, [0.23, 8.01]            |
| Hum-micter (C3)   | $v_f = v_f$                 | -                                | -                                   |
| Qui (C4)          | $v_f = k C_1^{m_1} C_4^{m_4}$| P($m_1 \neq 0$): BF = 2.54      | $k = 0.71$, [0.14, 2.23]            |
|                   |                             | P($m_4 \neq 0$): BF = 2.44       | $m_1 = -0.25$, [-0.89, 0.39]        |
|                   |                             |                                   | $m_4 = -0.35$, [-1.05, 0.38]        |
| Trp (C5)          | $v_f = k C_2^{m_2} C_5^{m_5}$ | P($m_2 \neq 0$): BF = 2.71    | $k = 0.85$, [0.10, 3.20]            |
|                   |                             | P($m_5 \neq 0$): BF = 3.13       | $m_2 = -0.44$, [-1.23, 0.35]        |
|                   |                             |                                   | $m_5 = -0.55$, [-1.31, 0.22]        |
| Tyr (C6)          | $v_f = k C_2^{m_2} C_6^{m_6}$ | P($m_2 \neq 0$): BF = 2.34    | $k = 0.27$, [0.06, 0.76]            |
|                   |                             | P($m_6 \neq 0$): BF = 1.46e7   | $m_2 = -0.23$, [-0.98, 0.52]        |
|                   |                             |                                   | $m_6 = -0.96$, [-1.25, -0.69]       |
| DOC               | $v_f = k C_6^{m_6}$         | P($m_6 \neq 0$): BF = 10.50     | $k = 0.30$, [0.10, 0.75]            |
|                   |                             |                                   | $m_6 = -0.62$, [-0.95, -0.18]       |
| NO$_3$            | $v_f = v_f$                 | -                                | -                                   |
| SRP               | $v_f = k \ w \ SRP^{mp}$    | P($w \neq 1$): BF = 31.93       | $k = 26.18$, [10.17, 39.20]         |
|                   |                             | P($mp \neq 0$): BF = 6.21       | $mp = -0.31$, [-0.45, -0.07]        |
Figure S1: Probability density of the residuals for DOC, SRP and five of the six PARAFAC components. Comparison of two models: the simple model is according to Eq. (4), the complex one is the best performing model found, which is a mixed model including the leachate source (DOC), a mixed model including the sampling (Trp (C5) and Tyr (C6)) or the interaction models from table 5 (SRP, Hum-mic(C1), Hum-ter (C2), Qui (C4)). The dotted vertical lines are the boundaries of the 95% probability density interval. The probability density interval is smaller for better performing models.

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