A supply-based concentration rating curve to predict total phosphorus concentrations in the Rhine River

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1. Introduction

Concentration rating curves are useful for the analysis of the response of sediment or solute concentrations to changes in stream discharge or for the interpolation of infrequent concentration measurements in time with discharge as an auxiliary variable, for example to estimate annual sediment or solute loads.

A known limitation of rating curves is that their performance is generally poor, which can be partly attributed to the fact that rating curve methods neglect the hysteresis effects in the concentration response to changes in discharge. To enhance the performance of rating curve models, they should account for these hysteresis effects.

2. Supply-based rating curve

Here, we present a supply-based concentration rating curve for total phosphorus (P) concentrations in the Rhine River, the Netherlands, which does account for the above hysteresis effects. The supply-based concentration rating curve has four components:

1) The traditional power law rating curve of the form
   \[ C = a Q^b \]
   where \( C \) is the total P concentration [M L^{-3}], \( Q \) is the river discharge [L T^{-1}], and \( a \) and \( b \) are constants [-] (Fig 1b);

2) A long-term linear trend (Fig. 2);

3) A seasonal trend of the form \( C(t) = A \cos \left[ \frac{2\pi(t - T)}{1} \right] \) where \( A \) is the concentration amplitude [M L^{-3}], \( t \) is the time (T), \( T \) is the phase shift (T), and \( T \) is the period (T) (365.25 d) (Fig. 2).

4) A discharge dependent supply or loss term of the form
   \[ C = \frac{\Delta S}{(Q - Q_{\text{crit}})} \]
   where \( S \) is the P stock [M].

The P stock was assumed to increase linearly during periods of deposition, i.e. when the discharge is below a critical discharge \( Q_{\text{crit}} \). If \( Q > Q_{\text{crit}} \) for more than 16 days, the P stock was assumed to decrease proportionally to the excess discharge above the critical discharge.

3. Model parameterization and calibration

The model parameters were calibrated by a step-wise procedure which involved in some steps visual calibration (e.g. concentration amplitude, critical discharge for erosion/ deposition) and in other steps regression analysis (e.g. long-term linear trend, power law rating curve).

4. Results

The total P concentrations show a long-term linear decrease of \( 1.0 \times 10^{-5} \) mg l^{-1} d^{-1}. The amplitude of the seasonal fluctuation in P concentrations was estimated to be 0.03 mg l^{-1}. The critical discharge for erosion and deposition was estimated to be 1900 m s^{-1}, the increase in phosphorus stock during deposition periods 9300 kg d^{-1}, and the supply from the phosphorus stock to the river water 32 kg d^{-1} per m^{2} s^{-1} excess discharge.

The \( R^2 \) between the observed and predicted total P increased from 0.19 for the traditional rating curve (Nash’s efficiency coefficient \( = 0.18 \)) to 0.35 for the supply-based rating curve (Nash’s e.c. = 0.34) (Fig. 3).

5. Conclusions

The results imply that inclusion of the long-term and seasonal trends and a discharge dependent supply and loss term substantially enhances the performance and predictive power of the concentration rating curve model. As the response to changes in discharge is different for dissolved and particulate total phosphorus, a further improvement of model performance can likely be achieved by deriving separate concentration rating curves for dissolved total phosphorus and sediment-associated phosphorus.