



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

M. Van der Perk and M.F.A. Vogels

Utrecht University, Department of Physical Geography, Utrecht, Netherlands (m.vanderperk@geo.uu.nl)

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 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.

Here, we present a supply-based concentration rating curve for total phosphorus 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 phosphorus concentration [ $M L^{-3}$ ],  $Q$  is the river discharge [ $L T^{-1}$ ], and  $a$  and  $b$  are constants [-];
- 2) A long-term linear trend;
- 3) A seasonal trend of the form  $C(t) = A \cos [2\pi(t - T_k)/T]$  where  $A$  is the concentration amplitude [ $M L^{-3}$ ],  $t$  is the time ( $T$ ),  $T_k$  is the phase shift ( $T$ ), and  $T$  is the period [ $T$ ] (365.25 d).
- 4) A discharge dependent supply or loss term of the form  $C = -\Delta S / (Q \Delta t)$ , where  $S$  is the phosphorus stock [ $M$ ]. The phosphorus stock was assumed to increase linearly during periods of deposition, i.e. the discharge is below a critical discharge. If the discharge is greater than the critical discharge during a sufficiently long period ( $> 16$  days), the decrease in phosphorus stock was assumed to be proportional to the excess discharge above the critical discharge.

For model parameterization and calibration, we used the daily Aqualarm data of total phosphorus concentrations and the Waterbase data of water discharge measured daily by *Rijkswaterstaat* (Dutch Ministry of Infrastructure and the Environment) at the Lobith-Bimmen monitoring station at the German-Dutch border between 1 April 2004 and 20 July 2010. 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).

The total phosphorus concentrations show a long-term linear decrease of  $1.0 \times 10^{-5} \text{ mg l}^{-1} \text{ d}^{-1}$ . The amplitude of the seasonal fluctuation in phosphorus concentration was estimated to be  $0.03 \text{ mg l}^{-1}$ . The critical discharge for erosion and deposition was estimated to be  $1900 \text{ m}^3 \text{ s}^{-1}$ , the increase in phosphorus stock during deposition periods  $9300 \text{ kg d}^{-1}$ , and the supply from the phosphorus stock to the river water  $32 \text{ kg d}^{-1} \text{ per m}^3 \text{ s}$  excess discharge.

The squared Pearson's correlation coefficient between the observed and predicted total phosphorus increased from 0.16 for the traditional power-law concentration rating curve (Nash's efficiency coefficient = 0.13) to 0.36 for the supply-based rating curve (Nash's efficiency coefficient = 0.34). This implies that inclusion of the long-term and seasonal trends and a discharge dependent supply and loss term considerably 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.