

PREDICTION OF THE FATE OF POLLUTANTS IN RIVERS BY MEANS OF NONLINEAR VOLTERRA SERIES

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ABSTRACT: The transport of a conservative soluble pollutant along a uniform channel is usually described by means of the well-known Advection-Dispersion Equation. To apply this equation to a practical scenario, the dispersion coefficient value for the reach is required. Since dispersion coefficients cannot be measured in-situ directly from a simple individual measurement, they have to be estimated from available experimental data. In this paper an alternative modelling approach is presented in which the transport of a conservative soluble pollutant in rivers is modelled by means of a non-linear Volterra series. The description of the system by the Volterra series is a generalization of the concept of the linear transfer function, which is of great importance in the analysis of linear systems. Data for this study were derived from a programme of 18 tracer experiments undertaken in the Murray Burn, which is a stream that flows through the Heriot-Watt University Campus at Riccarton in Edinburgh. A two-term nonlinear model was first fitted to the records of breakthrough curves from 10 randomly chosen experiments. Then the performance of the method was assessed by making predictions for the remaining 8 experiments. Predictions from a cascade of continuously stirred tank reactors and from Fischer's routing procedure were also obtained. The results obtained indicate that generally the simple nonlinear model gives better results than those obtained by the routing procedure and that it gives marginally better results than the cascade model.

1 INTRODUCTION

Models describing the geophysical processes contributing to the hydrological cycle were developed in non-linear form in the nineteenth century. From their physical basis such models can simulate the complete runoff regime, providing such outputs as: river discharge, groundwater head and evaporation losses. Furthermore, transfer of mass, momentum and energy can be calculated directly from governing partial differential equations which are solved using numerical methods, for example the St. Venant equations for surface flow and river flow, the Richards equation for flow in the unsaturated zone and the Boussinesq equation for ground water flow. An accurate application to rivers of this hydraulic approach requires a detailed topographical survey and the determination of roughness parameters. In order to avoid these

difficulties, alternative non-linear approaches were developed, namely conceptual and black box models. Conceptual hydrological models are designed to approximate within their structure the general internal sub-processes and physical mechanisms that govern the hydrological cycle. Such models usually incorporate simplified forms of physical laws. Until recently, for practical reasons most conceptual models were lumped. In the second approach, known as black-box analysis, an attempt is made to extract, from the past records of input-output events of the system under examination, enough knowledge of the dynamics of the system, to provide a basis for predicting its output from other specified inputs (Dooge and O'Kane, 2003).

In this paper, alternative approaches to describing the transport of a conservative soluble pollutant along a channel are compared, namely a conceptual model of a cascade of continuously stirred tank reactors, a black-box

nonlinear Volterra series model in the form of a sum of convolution integrals, and a Fischer's routing procedure with dispersion coefficients determined by means of a Multi-Layer Perceptron Artificial Neural Network or via linear regression.

2 MURRAY BURN EXPERIMENTS

Between 1999 and 2001, 26 tracer experiments were performed on the Murray Burn, which is a small river that flows through the Heriot-Watt University Campus at Riccarton in Edinburgh. These experiments were undertaken at various flow rates in a 540m long reach. Each experiment consisted of the release of a tracer (Rhodamine WT) followed by the collection of tracer concentrations at up to 4 cross-sections. The tracer was injected to the river at the same place each time. In the first few experiments concentration measurements were collected only at the first two cross-sections, but in the later experiments three or four of the cross-sections were used. In a few cases, equipment or human failure led to data not being successfully collected. Further information on the experiments is available in Burke (2002), Wallis and Manson (2005) or Wallis et al (2007).

In the present paper models are used to predict the tracer concentration versus time profiles at the second cross-section using concentration measurements at the first cross-section. The distance between these two cross-sections is about 137 meters. The data come from 18 experiments, which were considered to contain reliable data.

3 LINEAR DISPERSION MODEL

A simple approach to modelling pollutant transport is a cascade of continuously stirred tank reactors as depicted in Fig. 1.

This completely mixed system can be used to model pollutant concentration in sub-reaches of a natural watercourse. The mass balance equations for a conservative pollutant can be expressed in terms of concentrations (C), flows (Q) and volumes (V) as:

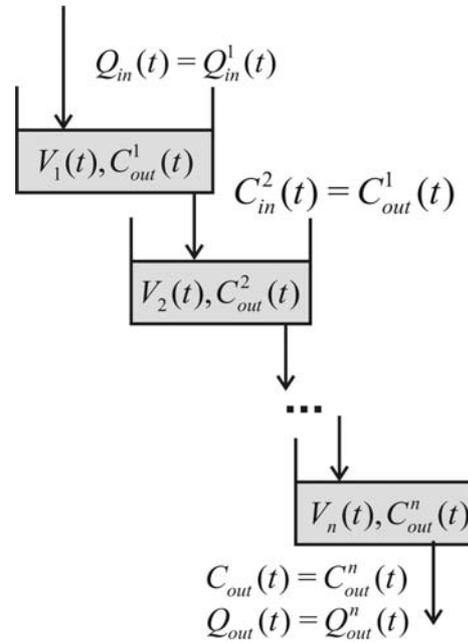


Fig. 1. Cascade of continuously stirred tank reactors

$$\begin{aligned} \frac{d}{dt} V_1(t) C_{out}^1(t) &= Q_{in}(t) C_{in}(t) - Q_{out}^1(t) C_{out}^1(t) \\ \frac{d}{dt} V_2(t) C_{out}^2(t) &= Q_{out}^1(t) C_{out}^1(t) - Q_{out}^2(t) C_{out}^2(t) \end{aligned} \quad (1)$$

$$\dots$$

$$\frac{d}{dt} V_n(t) C_{out}^n(t) = Q_{out}^{n-1}(t) C_{out}^{n-1}(t) - Q_{out}^n(t) C_{out}^n(t)$$

Let us denote the inverse of the hydraulic residence time as follows

$$a = Q/V \quad (2)$$

It may be readily shown that for an actual river reach a depends linearly on mean water velocity and nonlinearly on river flow. To solve the set of Equations (1) the Laplace transformation is applied (s is a complex variable).

$$\begin{aligned} C_{out}^1(s) &= \frac{1}{1+s/a} C_{in}(s) \\ C_{out}^2(s) &= \frac{1}{1+s/a} C_{out}^1(s) \end{aligned} \quad (3)$$

$$\dots$$

$$C_{out}^n(s) = \frac{1}{1+s/a} C_{out}^{n-1}(s)$$

One can see that for steady state flow conditions the input-output relation for the cascade of continuously stirred tank reactors in Laplace transform domain is given by

$$C_{out}(s) = \frac{1}{(1+s/a)^n} C_{in}(s) \quad (4)$$

The term

$$h(s) = \frac{1}{(1+s/a)^n} \quad (5)$$

is simply a transfer function and its inverse Laplace transform is given by

$$h(t) = a \frac{(at)^{n-1}}{(n-1)!} \exp(-at) \quad (6)$$

Hence taking the inverse Laplace transform of Equation (4) gives the Linear Dispersion Model (LDM)

$$C_{out}(t) = \int_0^t h(\tau) C_{in}(t-\tau) d\tau \quad (7)$$

Note that the LDM approach (determined by the kernel $h(t)$) has two parameters (n, a) that can be estimated based on input-output concentration data pairs.

4 VOLTERRA SERIES – NONLINEAR DISPERSION MODEL

The description of the spreading of a pollutant in a river reach for steady flow conditions by means of the Volterra series is a generalization of the concept of the transfer function described in the previous section, which is of great importance in the analysis and design of linear systems. The Volterra Series Nonlinear Dispersion Model (VDM) represents an explicit input-output relation for nonlinear systems and consists of an infinite series composed in the form of convolution integrals. The first term is the convolution integral of the first order kernel and the input function. The n -th order term is an n -fold convolution integral containing the n -th order kernel multiplied by an n -th order product of the input function:

$$C_{out}(t) = \int_0^t h_1(\tau_1) C_{in}(t-\tau_1) d\tau_1 + \int_0^t \int_0^t h_2(\tau_1, \tau_2) C_{in}(t-\tau_1) C_{in}(t-\tau_2) d\tau_1 d\tau_2 + \dots \quad (8)$$

where $C_{out}(t)$ is the concentration of pollutant at the downstream location, $C_{in}(t)$ is the concentration of pollutant at the upstream location, $h_1(\tau_1)$ is the first order kernel which reflects the linear properties of the system, $h_2(\tau_1, \tau_2)$ is the second order kernel which reflects the quadratic properties, and so on.

This type of series was applied for the first time by Volterra and Frechet in 1910 on functional equations (Volterra, 1959). It was used by Wiener (1958) in cybernetics. In hydrology, to model rainfall-runoff or flood routing, it was applied by Amorocho and Brandstetter (1971), Napiórkowski and O’Kane (1984), Napiórkowski and Kundzewicz (1986).

The identification of the kernels of the Volterra series was discussed in detail by Napiórkowski and Strupczewski (1984). It was shown that in general the identification of the kernels is a typical example of an ill-posed problem in the sense of Tichonov (1963), so very good fitting of the output from the model to the observed data may be completely misleading, as far as identification of the system is concerned (see example in Napiórkowski and Strupczewski, 1984).

The Volterra series is suitable for representing conservative systems mainly due to necessary and sufficient conditions for mass conservation, which were introduced by Boneh (1972) and are given for symmetric kernels by

$$\int_0^\infty h_1(\tau) d\tau = 1 \quad h_1(\tau) \geq 0 \quad (9)$$

$$\int_0^\infty h_2(\tau, \tau + \vartheta) d\tau = 0 \quad \vartheta \geq 0 \quad (10)$$

The condition (9) means that the nonlinear component affects only the distribution of the predicted pollution ordinates and the total value of it is zero.

To overcome the problem of ill-posedness of identification of the kernels, Napiórkowski and Strupczewski (1979, 1981) reduced the class of functions in which the solution is sought. They analytically derived the first two kernels of the Volterra series for the model that is a nonlinear analogy of Equation (3). For that model the structure of the kernels was shown to be

$$h_1(t_1) = a H_n(t_1) \quad (11)$$

$$h_2(t_1, t_2) = b \{ H_n(t_1) \sum_{i=1}^n H_i(t_2) + H_n(t_2) \sum_{i=1}^n H_i(t_1) - H_n[\max(t_1, t_2)] \} \quad (12)$$

where

$$H_i(t) = \frac{(at)^{i-1}}{(i-1)!} \exp(-at) \quad (13)$$

The two Equations (11) and (12) are linked through the fact that two parameters, a and n ,

appear in the equations of both kernels. One can see that $h_1(t_1)$ in Equation (11) is a transfer function for a cascade of linear continuously stirred tank reactors in steady flow conditions. The second-order kernel described by Equation (12) meets the conditions specified for conservative systems. It is worth mentioning that the shape of the second-order kernel is determined by parameter a , and that parameter b can be treated as a measure of nonlinearity.

The VDM determined by two kernels $h_1(t_1)$ and $h_2(t_1, t_2)$ has three parameters (n, a, b) that can be estimated from input-output concentration data pairs.

The optimization problem:

$$J(n, a, b) = \int_0^T [C_{obs}^i(t) - C_{out}^i(t)]^2 dt \quad (14)$$

where $i \in [1, I]$ and I is the number of input-output pairs, $C_{out}^i(t)$ is output from the model, $C_{obs}^i(t)$ is the observed concentration at the downstream cross-section and T is the measurement duration, can be reduced to optimization with respect to one variable only. Let us denote by $\delta C_{out}^i(t)$ the linear response of the VDM, and by $\delta^2 C_{out}^i(t)$ the quadratic response for $b=1$. Then due to the linearity of the second term with respect to b the objective function takes the form:

$$J(n, a, b) = \int_0^T [C_{obs}^i(t) - \delta C_{out}^i(t) - b\delta^2 C_{out}^i(t)]^2 dt \quad (15)$$

Note that the functions $\delta C_{out}^i(t)$ and $\delta^2 C_{out}^i(t)$ depend on parameters n and a but do not depend on the parameter b . Hence b can be determined from the necessary condition for an extreme, $\partial J / \partial b = 0$.

$$b = \frac{\int_0^T [C_{obs}^i(t) - \delta C_{out}^i(t)] \delta^2 C_{out}^i(t) dt}{\int_0^T [\delta^2 C_{out}^i(t)]^2 dt} \quad (16)$$

The following steps are therefore required in the overall optimization of the VDM:

- assuming $b=0$ compute the initial values of the parameters n^* and a^* as in linear analysis, e.g. by moment matching;
- assuming an integral value of the parameter n (close to n^*) compute the functions $\delta C_{out}^i(t)$ and $\delta^2 C_{out}^i(t)$;
- compute directly b from Eq. (16);
- maintaining the same value of n and varying the parameter a determine the

optimal set of values of (a, b) for assumed value of n ; and

- assuming a range of values of n repeat the procedure for each n to determine the optimal set of three parameters (n, a, b) .

Note that for $b=0$ the two-term model reduces to the LDM, described by Equation (7), so the optimization is even simpler for this case.

5 FISCHER'S ROUTING PROCEDURE

The third technique used to predict the tracer concentration versus time profiles is the so-called frozen cloud method, or Fisher's Routing Procedure. It allows estimation of a concentration-versus-distance profile from a concentration-versus-time profile, routes it downstream from one cross-section to another and transforms it back to a concentration-versus-time profile at the new site. Here we present just the outline of the method proposed by Fischer, the details may be found, for example, in Rutherford (1994). If it is possible to assume, that

$$x_i = U_i t_i \quad (17)$$

where x_i is the i -th cross section location, U_i is the averaged cross-sectional velocity and t_i represents the time at which the spatial variance is evaluated for cross section x_i , then the relation

$$C(x, t_i) = C\left(x_i, t_i + \frac{x_i - x}{U_i}\right) \quad (18)$$

is valid. Using centroids (\bar{t}_i) instead of times t_i one obtains the following frozen cloud formula

$$C(x_{i+1}, t) = \int_{-\infty}^{\infty} \frac{C(x_i, \tau) U_i}{\sqrt{4\pi D_L (\bar{t}_{i+1} - \bar{t}_i)}} \times \exp\left(-\frac{U_i^2 (\bar{t}_{i+1} - \bar{t}_i - t + \tau)^2}{4D_L (\bar{t}_{i+1} - \bar{t}_i)}\right) d\tau \quad (19)$$

with the relation between two centroids

$$\bar{t}_{i+1} = \bar{t}_i + \frac{x_{i+1} - x_i}{U_i} \quad (20)$$

where τ is a dummy integration variable.

The method may be used to evaluate the concentration-versus-time profile at cross-section $i+1$, assuming that the centroid \bar{t}_{i+1} and longitudinal dispersion coefficient (D_L) are

known. In the present paper D_L is evaluated by two different methods: a simple linear regression (RPL) and a Multi-Layer Perceptron Artificial Neural Network (RPN).

Multi-Layer Perceptron Artificial Neural Networks have been successfully applied for the evaluation of dispersion coefficients (Kashefipour et al., 2002; Rowinski et al., 2005). In the current work the neural network model described in Wallis et al. (2007) is used. This model was optimized using morphometric and hydraulic data – namely reach mean values of channel width, channel depth, flow velocity, shear velocity and river sinuosity index – collected for many different small rivers, excluding the Murray Burn. A database composed of measured dispersion coefficients and various bulk flow hydraulic parameters from 81 river reaches published in Deng et al. (2001) and Sukhodolov et al. (1997) was available. All details of the neural network structure and optimization may be found in Wallis et al. (2007). Since the Murray Burn tracer measurements had not been used during the training of the network, this use of the network was a truly independent test of its ability to predict dispersion coefficients.

6. COMPARISON OF THE MODELS

Four models were applied to transform the breakthrough curves from cross-section 1 to cross-section 2 – LDM, VDM, RPN and RPL. The data obtained during 18 tracer experiments, performed under different flow conditions, were divided randomly into training (10 experiments) and validation (8 experiments) sets.

In case of the LDM and VDM approach for each experiment separately, parameter a , or parameters a and b , accordingly, were optimized to the data collected. Note, that the values of parameter a of the LDM and VDM models differ. Then using only the 10 training experiments (see Fig. 1 for LDM and Fig. 2 for VDM case) the linear dependence of parameter a on water velocity (U) was found. Clearly, the result is in accordance with our expectation.

From these relations the values of parameters a of the LDM and VDM models for all experiments were computed.

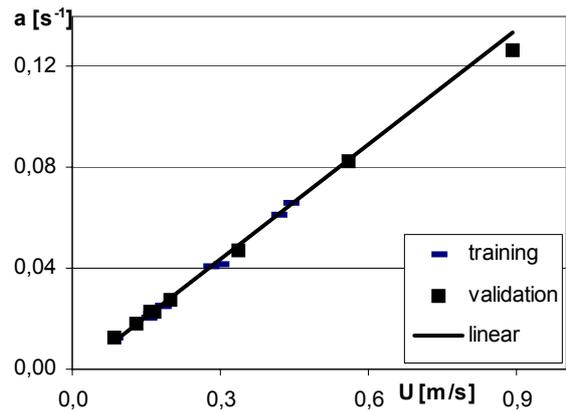


Fig. 1 Linear dependence of LDM parameter a on water velocity [U].

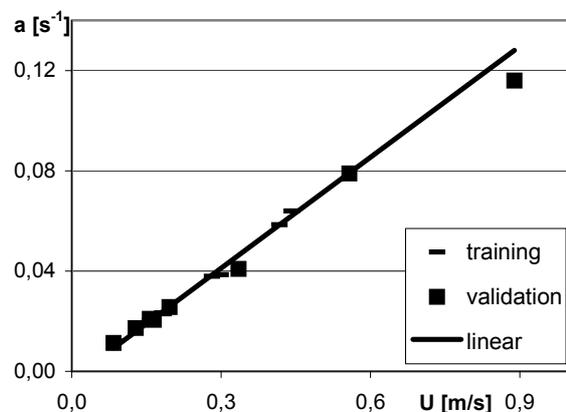


Fig. 2 Linear dependence of VDM parameter a on water velocity [U].

Table 1. Optimized and evaluated parameter a of LDM for each experiment; t – training set; v – validation set.

| Exp. | Data | n | a optimal | a evaluated | Flow (l/s) |
|------|------|----|-----------|-------------|------------|
| 2 | v | 18 | 0.0279 | 0.0278 | 72.1 |
| 4 | t | 18 | 0.0222 | 0.0218 | 45.5 |
| 5 | v | 18 | 0.0226 | 0.0218 | 47.5 |
| 6 | t | 18 | 0.0408 | 0.0408 | 129.8 |
| 7 | t | 18 | 0.0418 | 0.0435 | 142.3 |
| 8 | v | 18 | 0.0225 | 0.0229 | 45.8 |
| 9 | t | 18 | 0.0205 | 0.0213 | 38.2 |
| 10 | t | 18 | 0.0254 | 0.0255 | 59.5 |
| 15 | t | 18 | 0.0254 | 0.0259 | 55.2 |
| 16 | v | 18 | 0.0122 | 0.0107 | 16.4 |
| 17 | t | 18 | 0.0123 | 0.0108 | 13.8 |
| 18 | v | 18 | 0.0183 | 0.0174 | 35.5 |
| 20 | t | 18 | 0.0664 | 0.0652 | 261.6 |
| 21 | v | 18 | 0.0472 | 0.0490 | 190.0 |
| 22 | t | 18 | 0.0617 | 0.0616 | 273.1 |
| 23 | t | 18 | 0.0253 | 0.0255 | 61.4 |
| 24 | v | 18 | 0.0827 | 0.0831 | 524.1 |
| 26 | v | 18 | 0.1263 | 0.1337 | 1041.2 |

In Tab. 1 flow values noted during the experiments are presented. Tab. 1 and 2 clearly show that computed a parameters are very

close to the optimized ones, not only for training, but also for validation data.

It was more difficult to find any relation between b parameter – governing the nonlinear behaviour of the VDM approach – and river flow or water velocity. The fluctuations of optimal b values seem to be random from experiment to experiment, however they are not very big (see Tab. 2b). Because of that, using the mean value of b parameter optimized for 10 training experiments, was found to be a reliable estimate of this parameter's value.

Table 2a. Optimized and evaluated parameter a of VDM, with optimized n , for each experiment; t – training set; v – validation set.

| Exp. | Data | n | a optimal | a evaluated |
|------|------|----|-------------|---------------|
| 2 | v | 18 | 0.0256 | 0.0259 |
| 4 | t | 18 | 0.0203 | 0.0200 |
| 5 | v | 18 | 0.0209 | 0.0200 |
| 6 | t | 18 | 0.0380 | 0.0383 |
| 7 | t | 18 | 0.0386 | 0.0409 |
| 8 | v | 18 | 0.0206 | 0.0211 |
| 9 | t | 18 | 0.0190 | 0.0195 |
| 10 | t | 18 | 0.0230 | 0.0236 |
| 15 | t | 18 | 0.0230 | 0.0240 |
| 16 | v | 18 | 0.0113 | 0.0093 |
| 17 | t | 18 | 0.0120 | 0.0094 |
| 18 | v | 18 | 0.0172 | 0.0158 |
| 20 | t | 18 | 0.0640 | 0.0620 |
| 21 | v | 18 | 0.0409 | 0.0463 |
| 22 | t | 18 | 0.0585 | 0.0584 |
| 23 | t | 18 | 0.0233 | 0.0236 |
| 24 | v | 18 | 0.0789 | 0.0792 |
| 26 | v | 18 | 0.1160 | 0.1280 |

Table 2b. Optimized and evaluated parameter b of VDM for each experiment; t – training set; v – validation set.

| Exp. | Data | $(b \cdot 10^6)$ optimal | $(b \cdot 10^6)$ evaluated |
|------|------|-----------------------------|-------------------------------|
| 2 | v | 0.6773 | 0.4905 |
| 4 | t | 0.5850 | 0.4905 |
| 5 | v | 0.5117 | 0.4905 |
| 6 | t | 0.8102 | 0.4905 |
| 7 | t | 0.4471 | 0.4905 |
| 8 | v | 0.5838 | 0.4905 |
| 9 | t | 0.4706 | 0.4905 |
| 10 | t | 0.3395 | 0.4905 |
| 15 | t | 0.7765 | 0.4905 |
| 16 | v | 0.3180 | 0.4905 |
| 17 | t | 0.1038 | 0.4905 |
| 18 | v | 0.1870 | 0.4905 |
| 20 | t | 0.3558 | 0.4905 |
| 21 | v | 0.9340 | 0.4905 |
| 22 | t | 0.4304 | 0.4905 |
| 23 | t | 0.5860 | 0.4905 |
| 24 | v | 0.2003 | 0.4905 |
| 26 | v | 0.1729 | 0.4905 |

In the case of the RPL, D_L was estimated from a linear regression to the flow based on the training data set only. This was a similar technique to that used for the LDM model in which the a parameter was obtained from a linear regression to velocity, also based only on the training data set.

Table 3. Root mean square error (RMSE) and maximum error (MAX) evaluated for LDM, VDM, RPN and RPL. In case of the last method, no data obtained from Murray Burn was used during optimization (t), hence all experiments compose validation set (v).

| Exp. | Set | Measure | LDM | VDM | RPN | RPL |
|------|-----|---------|-------|-------|-------|-------|
| 2 | v | RMSE | 0,036 | 0,025 | 0,062 | 0,063 |
| | | MAX | 0,118 | 0,103 | 0,176 | 0,182 |
| 4 | t | RMSE | 0,048 | 0,036 | 0,080 | 0,081 |
| | | MAX | 0,146 | 0,127 | 0,197 | 0,198 |
| 5 | v | RMSE | 0,050 | 0,051 | 0,083 | 0,084 |
| | | MAX | 0,141 | 0,185 | 0,241 | 0,244 |
| 6 | t | RMSE | 0,019 | 0,019 | 0,043 | 0,045 |
| | | MAX | 0,071 | 0,092 | 0,170 | 0,180 |
| 7 | t | RMSE | 0,071 | 0,074 | 0,085 | 0,088 |
| | | MAX | 0,446 | 0,398 | 0,338 | 0,353 |
| 8 | v | RMSE | 0,048 | 0,028 | 0,063 | 0,063 |
| | | MAX | 0,151 | 0,076 | 0,196 | 0,196 |
| 9 | t | RMSE | 0,061 | 0,043 | 0,063 | 0,061 |
| | | MAX | 0,213 | 0,115 | 0,182 | 0,167 |
| 10 | t | RMSE | 0,072 | 0,120 | 0,137 | 0,137 |
| | | MAX | 0,266 | 0,390 | 0,411 | 0,411 |
| 15 | t | RMSE | 0,041 | 0,027 | 0,056 | 0,055 |
| | | MAX | 0,035 | 0,031 | 0,169 | 0,170 |
| 16 | v | RMSE | 0,180 | 0,209 | 0,125 | 0,125 |
| | | MAX | 0,458 | 0,560 | 0,330 | 0,307 |
| 17 | t | RMSE | 0,170 | 0,223 | 0,116 | 0,115 |
| | | MAX | 0,536 | 0,727 | 0,348 | 0,345 |
| 18 | v | RMSE | 0,125 | 0,186 | 0,195 | 0,194 |
| | | MAX | 0,324 | 0,549 | 0,466 | 0,454 |
| 20 | t | RMSE | 0,061 | 0,057 | 0,127 | 0,119 |
| | | MAX | 0,214 | 0,220 | 0,389 | 0,397 |
| 21 | v | RMSE | 0,136 | 0,130 | 0,154 | 0,161 |
| | | MAX | 0,465 | 0,457 | 0,467 | 0,439 |
| 22 | t | RMSE | 0,044 | 0,036 | 0,121 | 0,116 |
| | | MAX | 0,148 | 0,114 | 0,342 | 0,334 |
| 23 | t | RMSE | 0,033 | 0,021 | 0,053 | 0,056 |
| | | MAX | 0,102 | 0,061 | 0,161 | 0,162 |
| 24 | v | RMSE | 0,085 | 0,165 | 0,194 | 0,185 |
| | | MAX | 0,259 | 0,466 | 0,664 | 0,577 |
| 26 | v | RMSE | 0,408 | 1,161 | 0,403 | 0,382 |
| | | MAX | 1,499 | 3,020 | 1,616 | 1,247 |

Results for four representative experiments – to allow visual comparison – are presented in Fig. 3-6. One of them was numbered among the training set (experiment 23, Fig. 5) and shows an almost perfect fit, especially by

means of the VDM approach. The other three were selected from the more important validation set. These include the very good prediction for experiment 8 (Fig. 3), a case for which all the methods used have “truncated” the peak (experiment 21, Fig. 4) and one of the most difficult cases – with much higher flow conditions than noted during other experiments – experiment 24 (Fig. 6). Note, that the mean value of b parameter turned out to be not appropriate for much bigger flow conditions (see Tab. 2b), which results in a poorer performance of the VDM model for experiment 24, compared with the other methods.

Two measures were used to compare the results – the root mean square error between the predicted and measured concentration values (RMSE) and the maximum difference between measured and computed concentrations for each experiment (MAX). It must be mentioned, that the maximum difference was not always noted at the peak – see for example, RPN method in case of experiment 21 (Fig. 4). Tab. 3 presents the RMSE and MAX measures for all experiments. The grey highlight indicates the best model for a particular experiment, according to RMSE and MAX separately.

It can be seen that in 10 out of 18 experiments, the VDM model turns out to be the best one according to RMSE, however only 3 of them were included in the validation set. The RPL or RPN models are the best for 3 experiments only – 2 of them were contained in the validation set, including the case with the highest flow recorded (experiment 26). For both experiments with higher flows (24 and 26) choosing the mean value of b parameter cannot be recommended. This is clear from Tab. 2b, which shows that optimal b value is much smaller.

Although the RPN model is rarely among the best methods, its ability to still make good forecasts should be highlighted, as this method does not use any of the tracer concentration measurements from the Murray Burn to evaluate the rate of dispersion (the model was optimized on data sets collected from different rivers, see Wallis et al., 2007).

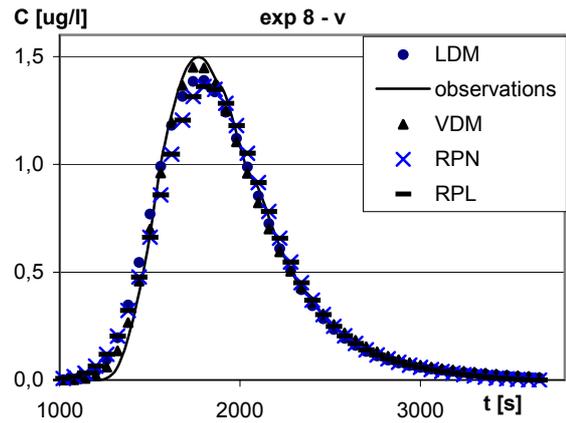


Fig. 3 Prediction of concentration versus time profile for cross-section 2 by means of LDM, VDM, RPL and RPN approaches. Experiment 8, validation data set.

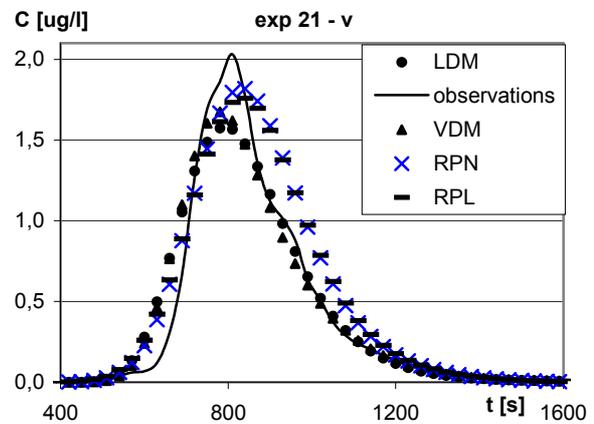


Fig. 4 Prediction of concentration versus time profile for cross-section 2 by means of LDM, VDM, RPL and RPN approaches. Experiment 21, validation data set.

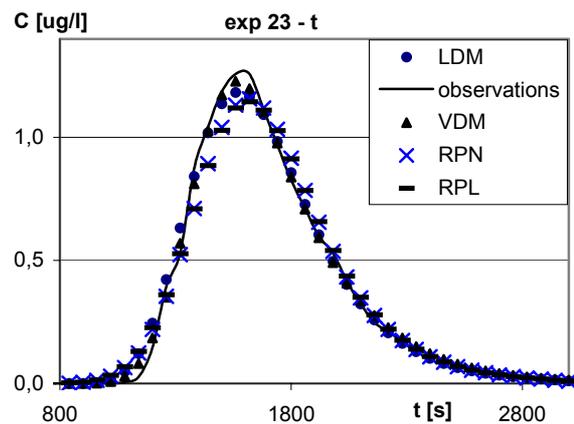


Fig. 5 Prediction of concentration versus time profile for cross-section 2 by means of LDM, VDM, RPL and RPN approaches. Experiment 23, training data set (with exception of RPN approach – see paper text).

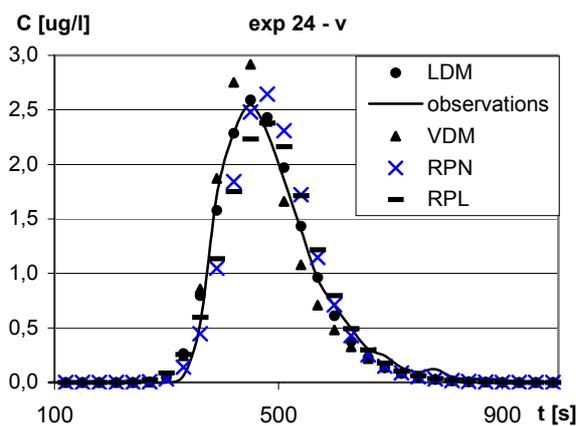


Fig. 6 Prediction of concentration versus time profile for cross-section 2 by means of LDM, VDM, RPL and RPN approaches. Experiment 24, validation data set.

Comparing MAX values, the difference in the performance between the LDM and VDM models is negligible, however both are better than the RPL or RPN approaches. Hence both error measures used in the paper show similar performance for the approaches used. In general, including the mean value of nonlinear b parameter improves the results obtained from the LDM model, with the exception of very different hydrological conditions to those included in the training set.

7. CONCLUSIONS

In the present paper the nonlinear Volterra series based dispersion model was introduced. Its ability to transform breakthrough curves of solute concentration from one cross-section to another has been verified, and results have been compared with predictions made by a linear cascade model and by Fischer's routing procedure using two different methods for evaluating the longitudinal dispersion coefficient. Concentration-time data sets obtained during several tracer tests performed in the Murray Burn under different hydrological conditions were used for evaluating model parameters, finding their dependence on water velocity and for testing the proposed approaches. The results obtained indicate that generally the nonlinear Volterra model gives better results than those obtained by the routing procedure and that it gives marginally better results than the cascade model.

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