



## ASSESSMENT OF POLLUTANT TRANSPORT AND RIVER WATER QUALITY USING MATHEMATICAL MODELS

Elisabeta-Cristina ANI<sup>a,b,\*</sup>, Michael George HUTCHINS<sup>c</sup>, Andrzej KRASLAWSKI<sup>a</sup> and Paul Serban AGACHI<sup>b</sup>

<sup>a</sup> Department of Chemical Technology, Lappeenranta University of Technology, Skinnarilankatu, 34, FIN-53851, Lappeenranta, Finland

<sup>b</sup> Faculty of Chemistry and Chemical Engineering, "Babes-Bolyai" University Cluj-Napoca, No. 11, Arany Janos Street, 400028, Cluj-Napoca, Roumania

<sup>c</sup> Centre for Ecology and Hydrology Wallingford, Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire, OX10 8BB, UK

Received September 22, 2009

This paper presents (1) general considerations related to the development of two mathematical models for non-conservative transport of nitrate and ammonium under unsteady water flow conditions; (2) their application to predict the transport of pollutant in both customary and accidental pollutant release circumstances; and (3) a discussion related to models use in water quality management. The studied river stretch is part of the River Swale in England, where pollutants are discharged by multiple point sources and also by tributaries. Experimental data was used for model development and verification. The models are useful to (i) assess the downstream river distance affected by pollutant release; (ii) estimate environmental damage; (iii) support decisions on where and how to counteract pollutant discharge; and (iv) also to support the further development of more refined water quality simulation tools.

### INTRODUCTION

During the past years there was major public interest concerning the management of water resources. A hot spot of this field is the availability of water of acceptable quality under circumstances of pollutant discharge in rivers. The water quality management in such situations requires fast decisions based on knowledge related to the distribution of pollutant concentration along the river downstream of the releasing source. This information can be facilitated by computer tools such as mathematical models for pollutant transport in rivers.

The pollutant transport modelling literature is rich in information regarding the transport and transformations of nitrate (NO<sub>3</sub>) and ammonium (NH<sub>4</sub>), often published along with other nutrients (e.g. phosphorus compounds). This information regards: (1) in-stream models for the prediction of pollutant concentration;<sup>11,6</sup> (2) software for water

quality modelling in large river networks;<sup>4,7</sup> (3) water quality assessment studies;<sup>12</sup> or (4) the transport of nutrient fluxes in catchments.<sup>9,10</sup> Some of these studies consider River Swale,<sup>4,7,9,10</sup> but none of them is focused on the prediction of pollutant transport at small time steps (less than one hour) in short river stretches (few kilometres) or after accidental release. This is the added value of the present paper compared to previous work.

This paper presents the application of two mathematical models for the transport of nitrate and ammonium along a river stretch. The models are capable to predict pollutant concentration along the river at small time steps (minutes) under customary pollutant discharge (model I) and also in the case of accidental release (model II). Experimental data regarding river channel characteristics and concentration measurements in normal pollution conditions was used for model development and verification.

\* Corresponding author: [eani@chem.ubbcluj.ro](mailto:eani@chem.ubbcluj.ro)

**THE EXPERIMENTAL DATA**

The experimental data (measurements of concentration, flow rate and hydraulic parameters) used for model building, calibration and verification were collected from River Swale in England during five sampling campaigns with the river in low flow, normal flow and storm conditions. Detailed description of the study area and monitoring campaigns (hereafter referred to as campaigns 1 to 5) is provided elsewhere.<sup>9,10</sup> The sampling was done along a river stretch of 50.4 km at four monitoring sites (hereafter referred to as M1

to M4) in the main channel and at three other sites in the main tributaries (rivers Bedale Beck, Wiske and Cod Beck).

Available concentration data concerns the unsteady state of the river in normal pollution conditions. Time series of water flow, nutrient concentration and sometimes of water depth are provided at monitoring points. The water flow, river width and water depth time series corresponding to M1 to M4 during campaign 3 are presented in Fig. 1 and Fig. 2. Observed concentration time series for the same campaign can be seen in Fig. 6.

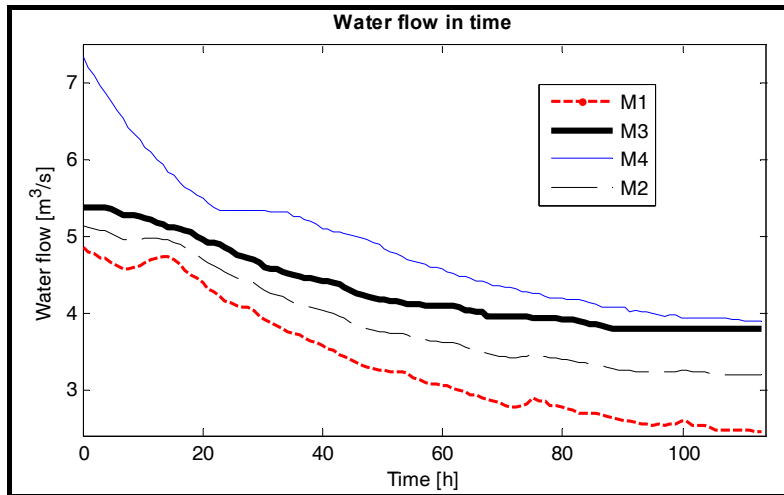


Fig. 1 – Dynamic water flow at the four monitoring sites during campaign 3.

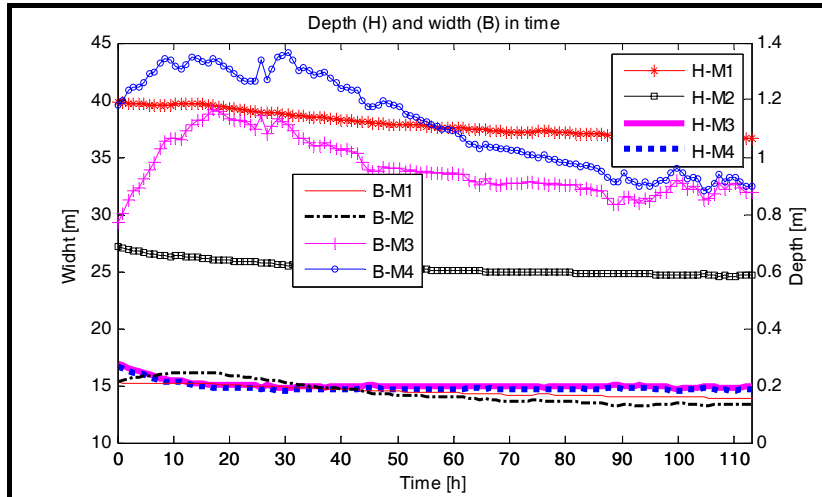


Fig. 2 – Dynamic river channel width and water depth during campaign 3.

**MATHEMATICAL MODELLING**

Existing information related to the river stretch enabled the development and verification of model I, which is further used for the development of model II.

The models are based on analytical solutions of the fundamental advection-dispersion equation (ADE) for mass transport in rivers:<sup>8,13</sup>

$$c(x,t) = \frac{M}{A\sqrt{4\pi D_x t}} \exp\left(-\frac{(x - V_x t)^2}{4D_x t}\right) \tag{1}$$

$$c(x, t) = c_0 + \frac{(c_s - c_0)}{2} \left[ \operatorname{erfc} \left( \frac{x - V_x t}{\sqrt{4D_x t}} \right) + \exp \left( -\frac{x V_x}{D_x} \right) \operatorname{erfc} \left( \frac{x + V_x t}{\sqrt{4D_x t}} \right) \right] \quad (2)$$

where  $x$  is the distance along the river stretch [m];  $t$  is the time [s];  $M$  is the mass of released tracer [g];  $A$  is the cross-sectional wetted area of the channel [ $\text{m}^2$ ];  $D_x$  is the dispersion coefficient [ $\text{m}^2/\text{s}$ ];  $V_x$  [m/s] is the water velocity [m/s];  $c_0$  [mg/L] is the initial concentration along the river stretch ( $x$  [m]), assuming nonzero initial condition throughout the river;  $c_s$  [mg/L] is the concentration at the source during the release ( $t$  [s]).

It is well known that each ADE analytical solution corresponds to a certain type of pollutant release: (1) bulk instantaneous discharge and (2) continuous variable discharge. Consequently in the present research each analytical solution is the core of a module able to simulate a certain type of discharge. The results of multiple modules are superposed in order to simulate the pollution from multiple sources of different type.<sup>2</sup>

The present models use two modules: (a) a module for bulk instantaneous discharge, based on

equation (1) and (b) a module for continuous variable discharge, based on equation (2).

Model I is based on module (b), for customary pollution. During its calibration models for the estimation of pollutant transport characteristic parameters are developed. They are further used to verify model I.

Model II is developed relying on the validated model I and the models for parameter estimation, to which module (a) is added. The model is capable to simulate the transport of pollutant during accidental release, along with customary pollution conditions.

The implementation of these modules enables the development of model II based on the structure of the already verified model I. Consequently model II can be applied to River Swale with no further validation. The methodology presented in Fig. 3.

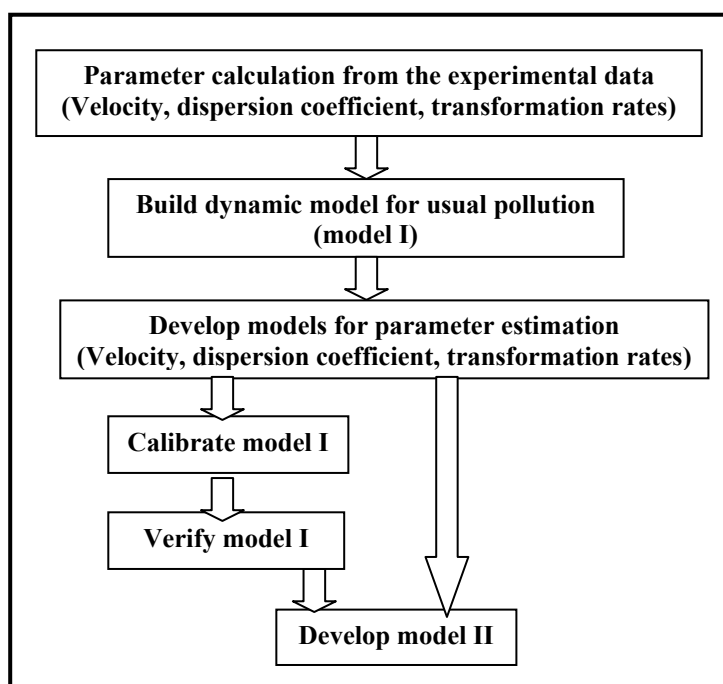


Fig. 3 – The methodology followed during the development of models.

Both models rely on the same river channel parameters and pollutant transport characteristic parameters (e.g. velocity, dispersion coefficient, and transformation rates). They take into account the variability of channel parameters along the river, pollutant transformations during transport

(sources and sinks), unsteady water flow, unsteady tributary and point pollution source influences.

The main pollutant transformations affecting nitrate and ammonium during the transport are nitrification (sink of ammonium and source of nitrate) and denitrification (sink of nitrate). They

are considered to have first order kinetics, and for each monitoring campaign they are characterised by variable transformation rates along the river, depending on temperature.

## RESULTS AND DISCUSSION

River water velocity and dispersion coefficient are key parameters of the ADE type mathematical models. In this research the velocity is calculated

from available experimental data regarding water flow time series and channel characteristics. Resulting time series in the case of campaign 3 are shown in Fig. 4.

The dispersion coefficient is first calculated from experimental data, using well known formulae, and further optimized during the calibration of model I.<sup>1</sup> Optimum values during campaign 3 are available in Fig. 5.

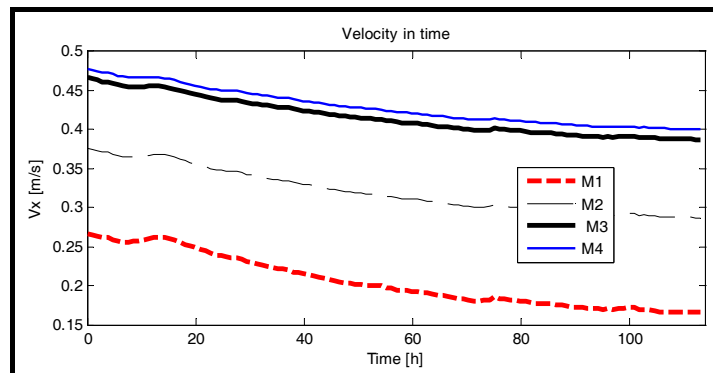


Fig. 4 – Water velocity at the four monitoring sites during campaign 3.

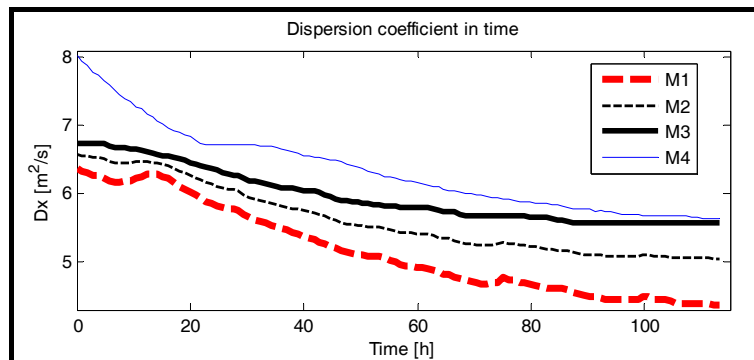


Fig. 5 – Dispersion coefficient at the four monitoring sites during campaign 3.

The model for customary pollution circumstances was developed, calibrated and verified using experimental data. Fig. 6 shows results of the calibrated model I for the 3<sup>rd</sup> monitoring campaign. The model inputs in terms of concentration are represented by measurements at M1, the upstream boundary of the river stretch: the dashed tick line (starting at 0.8 mg/L), for NO<sub>3</sub>, and the point markers (starting at 0 mg/L) for NH<sub>4</sub>. The model outputs are the simulated concentrations at M3: the dash-dot thin line (starting at 2.2 mg/L) for NO<sub>3</sub> and the continuous line (starting at 0.3 mg/L) for NH<sub>4</sub>.

Generally results reveal a big increase of NH<sub>4</sub> and NO<sub>3</sub> concentration along the investigated river

stretch. In the case of campaign 3, the increase of NO<sub>3</sub> along the stretch is clearly visible, while the increase of NH<sub>4</sub> is obvious just sometimes. The higher pollutant concentration at M3 compared to M1 is caused by pollution sources and tributaries discharging into the main channel of River Swale.

Most of the simulations show that model I was capable to cope with this concentration increase along the river and to reproduce the main trend of NO<sub>3</sub> and NH<sub>4</sub> observations. At times the predicted concentration does not fit very well to specific measurements. In the case of campaign 3, during the first 45 hours of simulation, the NO<sub>3</sub> concentration predicted at M3 is higher than the measured concentration, while during the last

25 hours of simulation the predicted concentration is lower than the measured one. This behaviour could be related to the pollutant transformation model which doesn't take into account the dynamic variation of transformation rate constants,

but just their variation in space. The values corresponding to campaign 3 for the two processes are listed in Table 1.

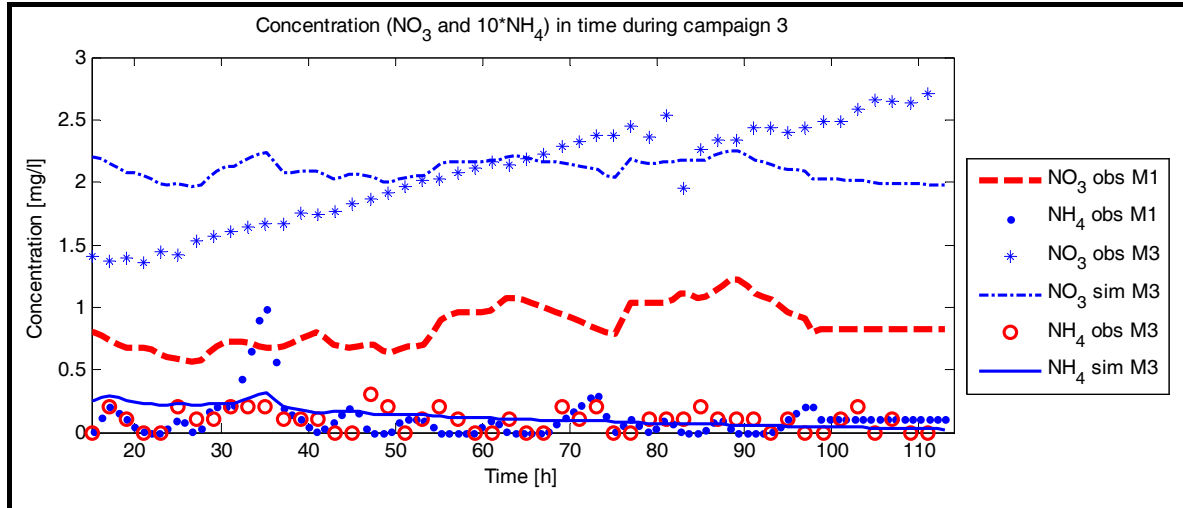


Fig. 6 – The evolution of nitrate and ammonium concentration at M3 during the 3<sup>rd</sup> monitoring campaign (obs = experimental data; sim = simulated concentration).

Table 1

Transformation rate constants for nitrification and denitrification

Transformation rate constant / Monitoring site	M1	M2	M3	M4
Nitrification [1/s]	$4.35 \cdot 10^{-5}$	$1.83 \cdot 10^{-4}$	$2.00 \cdot 10^{-4}$	$2.00 \cdot 10^{-4}$
Denitrification [1/s]	0	$8.53 \cdot 10^{-6}$	0	0

In order to increase concentration prediction accuracy at M3 there is a need to consider: a higher consumption of  $\text{NO}_3$  during the first 45 hours and a lower consumption of  $\text{NO}_3$  during the last 25 hours (see Fig. 7). This requires further improvements of the transformations model, as discussed later in the paper.

Fig. 7 shows results of model II simulating accidental release (thin lines) and also normal pollution (tick lines). The combined effect of two different hypothetical accidents is shown: (1) a point bulk instantaneous discharge and (2) a continuous point discharge. The first accident takes place at the beginning of the monitoring when a point source situated 27 km upstream M3 discharges in the river a bulk of  $\text{NO}_3$  and  $\text{NH}_4$ . The bulk travels downstream and arrives at M3 several hours later. The second accident takes place in the second tributary, where  $\text{NO}_3$  and  $\text{NH}_4$  are discharged continuously from a point source during a whole day. The effects at M3 can be observed later, and the pollutant level in the

river is still high even after the release stop, due to the travel time of the pollutant between the source and M3.

It is well known that variations in nutrient concentration (increase or decrease) during their transport in rivers are caused by multiple processes that are difficult to represent and quantify, taking place in or outside the stream.<sup>10,5</sup> An example to illustrate this complex behaviour related to influencing factors is what happens with nitrate concentration in the river during a strong rainfall. A short and intense rainfall could greatly decrease the nitrate concentration due to a high amount of diluted water entering to the river, while a prolonged rainfall could cause an increase in concentration due to leaching of water through the soil (from where large quantities of nutrient are taken) before reaching the river. But in the case of very long wet periods (weeks) “system flushing” could take place, causing the nitrate concentration to decrease greatly along the stretch.<sup>9</sup>

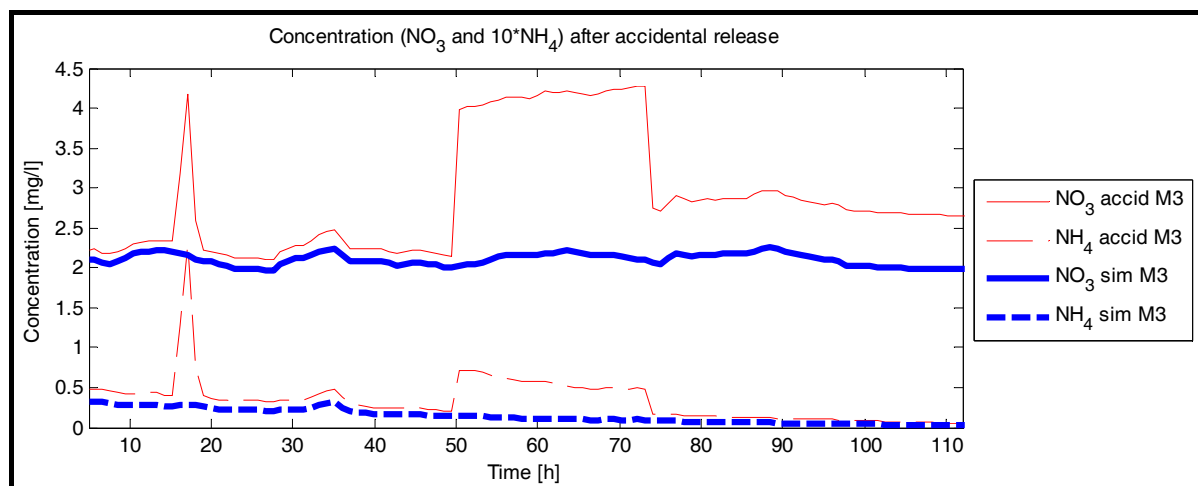


Fig. 7 – Evolution of nitrate and ammonium concentration at M3, during usual (sim) and accidental (accid) pollution.

The main  $\text{NO}_3$  and  $\text{NH}_4$  transformations (nitrification and denitrification) are controlled by factors such as: water temperature, water flow or seasonality. In the present research transformation rates are variable along the river, but constant in time. They are functions of temperature, but constant with respect to water flow and seasonality. The dynamic variation of transformation rates could be achieved through further investigation of their dependence on water flow and seasonality. This would enable a better representation of transformation processes and a more accurate prediction of nutrient concentration.

### THE UTILITY OF THE MODELS IN WATER QUALITY ASSESSMENT

The present models are capable of simulating pollutant concentration in customary situations and under accidental release. They are useful for understanding the propagation of pollutants along the river, to assess water quality, and also to carry out pollution management. For example when an accident happens somewhere along the river the model user has to specify: the pollution source spatial coordinates, flow level, discharge type and pollutant quantitative characteristics. The model will display graphical information on the concentration evolution in time and space. Based on predicted concentration distribution water quality professionals will be able to take the best decisions to counteract pollution. This knowledge is needed in normal situations, but especially in the case of accidental pollutant release, when the stakeholders have to be prepared for fast decision making. It also aids in the identification of critical zones along the river; of suitable points for siting

monitoring stations and of places to apply pollution counteraction measures.

In this respect mathematical modelling and simulation of the transport and transformation processes of chemicals in rivers could play a major role. The mathematical models and similar computer systems can be applied in pre-design and practical use of processes, and not only for economic reasons. They represent a support for the selection of scientifically justified and practically reasonable programs for long-term measures for a rational use of water resources. Also they open up possibilities for new monitoring facilities, for river water quality management tools and for the estimation of the environmental impact of possible technological improvements.<sup>3</sup> This brings them into the area of interest of economic agents, environmental agencies and also universities.

### CONCLUSIONS

This paper presents the application of two models for the non-conservative transport of nitrate and ammonium under unsteady flow conditions in River Swale, England. The models are useful for the prediction of pollutant concentration in case of customary and/or accidental chemicals release. They are intended to offer support in water quality management and water quality research.

### REFERENCES

1. E.C. Ani, S.G. Wallis, A. Kraslawski and P.Ş. Agachi, *Environ. Modell. Softw.*, **2009**, *24*, 1139-1152.
2. Y. Avramenko, E.C. Ani, A. Kraslawski and P.Ş. Agachi, *CAPE Forum 2009*, March, 27-28, Limerick, Ireland, **2009**.

3. F. Benkhaldoun, I. Elmahi and M. Seaid *J. Comput. Phys.*, **2007**, 226, 1, 180-203.
4. B. Boorman, *Sci. Total Environ.*, **2003**, 314-316, 379-395.
5. P.G. Whitehead, R.J. Williams and D.R. Lewis, *Sci. Total Environ.*, **1997**, 194/195, 447-456.
6. T. Deksissa, D. De Pauw and P.A. Vanrolleghem, *Environ. Toxicol. Chem.*, **2004**, 23, 9, 2267-2278.
7. A. Eatherall, D.B. Boorman, R.J. Williams and R. Kowe, *Sci. Total Environ.*, **1998**, 210/211, 499-517.
8. H.B. Fischer, E. Liet, C. Koh, J. Imberger and N. Brooks, "Mixing in Inland and Coastal Waters", Academic Press, New York, 1979, p. 104-147.
9. W.A. House and M.S. Warwick, *Sci. Total Environ.*, **1998**, 210/211, 111-137.
10. W.A. House and M.S. Warwick, *Sci. Total Environ.*, **1998**, 210/211, 139-152.
11. S. Marsili-Libelli and E. Giusti, *Environ. Model Softw.*, **2008**, 23, 451-463.
12. M. Neal, H. Davies, M. Neal, L. Hill and H. Wickham, *Sci. Total Environ.*, **2006**, 365, 15-32.
13. J.A. Sanchez-Cabeza and L. Pujol, *Wat. Res.* **1999**, 33, 10, 2345-2356.

