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PhD. Thesis Summary

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Modelling of pollutant transport in rivers: process engineering approach

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Abstract

This thesis addresses the important problem of river pollution and pollutant propagation, which has to be attended with the help of predictive tools (pollutant transport models) in order to develop pollution assessment and counteracting systems and to take correct management decisions. This research field is having a lot of progress, mainly in the latest 15 years: the monitoring benefits from better technological support; data processing tools are able to deal with impressive quantity of data; new parameter calculation methods with improved accuracy have been proposed; and modelling methods have been improved. Even though, there still are important issues requiring attention, for instance the parameter estimation techniques; the wider applicability and transferability of mathematical models or the use of new software. On the other hand there is a possibility to develop the current approach on water quality modelling by using knowledge and experience from the process engineering field. The present thesis is aimed to address questions of this kind.

The thesis main objective is to develop a comprehensive process engineering approach on pollutant transport modelling by means of methods and tools from different fields.

The thesis main contribution could be summarized as consisting of several support tools and techniques to be used in the modelling of pollutant transport in rivers.

- Analytical and numerical models for pollutant transport prediction are developed for case studies where: very little water quality related research has been carried out (Someş River); no detailed mathematical models were available to predict pollutant transport (Swale River); or only short river reaches were investigated (Murray Burn). The advection-dispersion models have increasing level of complexity: from the simple conservative models for a short stream (540 m) representing one pollutant, to a complicated non-conservative model for a bigger river stretch (50.4 km) including multiple pollutants with inter-dependent transformations. Models for pollutant transport are able to simulate accidents and also customary pollution.

- Two novel techniques which enable the use of variable parameters along rivers in analytical models are implemented. They allow the inclusion of influences at the real location along the river; the representation of river non-uniformities and further application of already validated models to other river stretches.

- The development of models for the estimation of pollutant transport characteristic parameters (velocity, dispersion coefficient and nutrient transformation rates) as a function of the water flow, channel characteristics and/or seasonality are also a main result of this thesis. They bring additional knowledge for investigated case studies because no similar detailed investigations were carried out for the three river stretches.
- Moreover the existing knowledge and results are comprised in a comprehensive process engineering approach on pollutant transport modelling.

Main contributions along with the analysis of water quality modelling literature are presented along three thesis sections, comprising altogether 13 chapters, plus an additional section on conclusions and personal contributions. References are listed at the end along with the nomenclature. Findings offered in this PhD Thesis, along with other work related to pollutant transport modelling (e.g. the use of knowledge management techniques) have been presented in nineteen publications also listed in the thesis.

Keywords: river pollutant transport modelling; advection-dispersion parameters; dispersion coefficient; convective-dispersive transport; nutrient transformations.

Thesis table of content

SECTION 1. OVERVIEW

Thesis general presentation

Problem addressed

In recent years general interest in preserving the quality of environment has considerably increased. This is due to a need of ensuring the availability of resources for next generations, trough sustainable development. In the field of surface waters many problems are caused by pollutant release. Many rivers and especially those crossing inhabited areas are subjected to pollutant discharge. Therefore managers need reliable support tools for water quality assessment and to predict consequences of their decisions. This issue can be addressed with the use of tools for computational estimation of in-stream pollutant concentration. They are the main concern of this thesis.

This research field is having a lot of progress, mainly in the latest 15 years: the monitoring benefits from better technological support; data processing tools are able to deal with impressive quantity of data; new parameter calculation methods with improved accuracy have been proposed; and modelling methods have been enhanced.

Even though, there still are important issues requiring attention, for instance the parameter estimation techniques; the wider applicability and transferability of mathematical models or the use of new software. On the other hand there is a possibility to develop the current approach on water quality modelling by using knowledge and experience from the process engineering field. The present thesis is aimed to address questions of this kind.

Thesis objectives and structure

The main objective of this thesis is to develop a comprehensive process engineering approach on pollutant transport modelling by means of methods and tools from different fields.

The sub-objectives to serve this goal were organized as described further.

- O 1. To develop, calibrate and validate mathematical models for pollutant transport in river stretches.
- O 2. To offer modelling support for a wide range of cases (e.g. methods to describe river stretches; models for parameters).
- O 3. To comprise existing knowledge and results in a comprehensive process engineering approach on pollutant transport modelling.

This thesis is organized in three sections, comprising altogether 13 chapters, plus an additional section on conclusions and main contributions. References are listed at the end along with the nomenclature.

- The first section is an overview consisting of a general thesis presentation (Chapter 1); a short glossary of terms (Chapter 2); and the presentation of investigated river stretches (Chapter 3). A list of publications related to this PhD thesis, presented by its author, is also included in this section.
- The second section concerns the analysis of water quality modelling literature. Pollutant transport phenomena and its modelling means are described taking into account process engineering aspects (Chapter 4). The accomplishments and needs of this research field are presented (Chapter 5), including a close look on the three case studies (Chapter 6).
- The third section consists of personal contributions. Its first chapter (7) shows this thesis main contributions and novelty compared to previous research. The next six chapters describe one category of results: the employed parameterization techniques (Chapter 8); the analytical and numerical modelling of pollutant transport in Murray Burn using classical means (Chapter 9); the process engineering approach on Murray Burn (Chapter 10); the use of these results along with new findings to model pollutant transport in River Swale (Chapter 11) and River Someş (Chapter 12); followed by wider discussions on the process engineering approach to pollutant transport modelling (Chapter 13).

Publications related to the PhD Thesis

ISI Journal Papers

1. **Ani, E.C.**, Avramenko, Y., Kraslawski, A., Agachi, P.Ş., 2010. Identification of pollution sources in Romanian Someş River using graphical analysis of concentration profiles. *Asia-Pacific Journal of Chemical Engineering,* in press**.**
2. **Ani, E.C.**, Hutchins, M.G., Kraslawski, A., Agachi, P.Ş., 2010. Mathematical model to identify nitrogen variability in large rivers. *River Research and Applications,* 26, 1-21.
3. **Ani, E.C.**, Cristea, V.M., Agachi, P.Ş., Kraslawski, A., 2010. Dynamic Simulation of Someş River Pollution Using MATLAB and COMSOL Models. *Revista de Chimie,* 61.
4. **Ani, E.C.**, Hutchins, M.G., Kraslawski, A., Agachi, P.Ş., 2010. Assessment of pollutant transport and river water quality using mathematical models. *Revue Roumanie de Chimie,* 55, 4, 285-291.

5. **Ani, E.C.**, Wallis, S.G., Kraslawski, A., Agachi, P.Ş., 2009. Development, calibration and evaluation of two mathematical models for pollutant transport in a small river. *Environmental Modelling and Software,* 24, 10, 1139-1152.
6. Avramenko Y., **Ani, E.C.**, Kraslawski A., Agachi P.Ş., 2009. Mining of graphics for information and knowledge retrieval. *Computers and Chemical Engineering,* 33, 3, 618-627.

Conference papers – ISI proceedings

7. **Ani, E.C.**, Wallis, G., Kraslawski, A., Agachi, P.Ş., 2009b. Detailed mathematical model for pollutants transport in a natural stream. *Computer Aided Chemical Engineering,* 26, 731-736. (ISSN 1570-7946, 19th European Symposium on Computer Aided Process Engineering (ESCAPE 19), June 2009, Cracow, Poland).
8. **Ani, E.C.**, Avramenko, Y., Kraslawski, A., Agachi, P.Ş., 2009c. Selection of models for pollutants transport in river reaches using case based reasoning. *Computer Aided Chemical Engineering,* 27, 537-542. (ISSN 1570-7946, 10th International Symposium on Process Systems Engineering (PSE 2009), August 2009, Salvador, Bahia, Brazil).

Books

9. **Ani, E.C.**, 2009. *Minimization of the experimental workload for the prediction of pollutants propagation in rivers. Mathematical modelling and knowledge re-use.* Acta Universitatis Lappeenrantaensis 355, Lappeenrannan teknillinen yliopisto, Digipaino, Lappeenranta, Finland, ISBN 978-952-214-829-2, pp. 189.

Technical reports in books

10. **Ani, E.C.**, 2009. Research report: I. The identification of pollution sources from long term monitoring data. II. The reuse of knowledge in modelling pollutant transport in rivers. In: Ljung, M. (Ed.), *Yearbook 2009, Graduate School in Chemical Engineering.* Abo Akademi University, Turku, Finland, ISSN 1238-2647, 23-32.
11. **Ani, E.C.**, 2008. Research report: Propagation of pollutants and availability of high quality water in a river basin - case of Someş Basin Rivers. In: Ljung, M. (Ed.), *Yearbook 2008, Graduate School in Chemical Engineering.* Abo Akademi University, Turku, Finland, ISSN 1238-2647, 21-30.
12. **Ani, E.C.**, 2007. Research report: Propagation of pollutants and availability of high quality water in a river basin as supply chain management - case of Someş Basin rivers. In: Ljung, M. (Ed.), *Yearbook 2007, Graduate School in Chemical Engineering.* Abo Akademi University, Turku, Finland, ISSN 1238-2647, 19-27.

Conference Proceedings Books

13. **Ani, E.C.**, Hutchins, M.G., Agachi, P.Ş., 2010. Advection-dispersion model for nutrient dynamics in River Swale. In: Carrera, J., Sanchez-Vila, X., Fernandez-Garcia, D., Bolster, D. (Eds.), *Programme and Proceedings of the XVIII Conference on Computational Methods in Water Resources (CMWR 2010),* June, 21-24, 2010, Barcelona, Spain, Dsignum Estudi Grafic, ISBN 978-84-96736-93-1, http://congress.cimne.com/CMWR2010, p. 39, paper 276.
14. **Ani, E.C.**, Agachi, P.Ş., 2007. Numerical models to simulate pollution scenarios in Someş River. Paper 2029 in: Gani R. and Johannsen D.J, *6th European Congress of Chemical Engineering (ECCE-6) Proceedings book*, September, 16-21, Copenhagen, Denmark, ISBN 978-87-91435-57-9, http://www.ecce6.kt.dtu.dk/, Vol. 1, 985.

Other conferences

15. Avramenko Y., **Ani, E.C.**, Kraslawski A., Agachi P.Ş., 2010. Identification of pollution sources in rivers using the graphical analysis of concentration profiles. 19 International Congress of Chemical and Process Engineering *CHISA 2010* and the 7 European Congress of Chemical Engineering *ECCE-7*. August 28 – September 1, Prague, Czech Republic, http://www.chisa.cz/2010/Default.aspx, no. 1392.
16. Avramenko Y., **Ani, E.C.**, Kraslawski A., Agachi P.Ş., 2009b. Mining of graphics for the assessment of pollution sources along the river. *Computer Aided Process Engineering Forum* (*CAPE Forum) 2009*, March, 27-28, Limerick, Ireland.
17. **Ani, E.C.**, Kraslawski, A., Hutchins, M.G., Agachi, P.Ş., 2009. The models for pollutant transport in rivers as decision support tools for the rational management of the river water quality. *International Forum-Competition of Young Researchers. Topical Issues of subsoil usage. WG 8*, April, St. Petersburg State Mining Institute, Russia.
18. **Ani, E.C.**, Kraslawski, A., Agachi, P.Ş., 2008. Pollutant transport characterization as a function of river characteristics and pollutant release type. OP. 3.5., *Computer Aided Process Engineering Forum* (*CAPE Forum) 2008*, February, 7-8, Thessaloniki, Greece.
19. **Ani, E.C.**, Cristea, V.M., Agachi, P.Ş., 2007. Dynamic simulation of Someş river pollution using MATLAB and COMSOL models. *10th Edition of Academic Days of Timişoara*, May, 24-25, Timişoara, Romania.

Investigated river stretches and field data

Comprehensive pollutant transport modelling, especially when relying on the fundamental advection equation for mass transport in rivers (ADE), requires a lot of experimental data from different rivers. In order to meet this requirement the present thesis is based on field data from three river stretches of different magnitude, shortly described in Table 1.

Table 1. Characteristics of the investigated rivers stretches and available field data.

River	**Murray Burn Stream**	**River Swale**	**River Someş**
Location	Edinburgh, UK	Yorkshire, UK	Transylvania, RO
Investigated length [km]	0.54	50.4	421
Width [m]	2.4 – 3.9	26 – 43	4 – 115
Channel aspect	Natural aspect	Combined natural and man-made	
Pollution	Water infiltration from soil	Pollution sources and tributaries	
Monitoring campaigns	26 experiments (bulk point release)	10 campaigns in normal pollution	60 months in normal pollution
Monitoring sites	4 - main channel	4 - main channel 3 – tributaries	12 - main channel
Monitored features	Rhodamine WT	4 nutrients; water flow depth (some campaigns)	25 water quality parameters water flow
Sampling resolution	High resolution (seconds)	Hourly resolution	Monthly average
Field data provider	Heriot Watt University, Edinburgh, Scotland	Centre for Ecology and Hydrology, Wallingford, England	Romanian National Waters Administration, Someş-Tisa Water Department (DAST)

Employed field data consists of: (1) time or/and space series of data measured for water quality parameters (e.g. concentration, water pH, dissolved oxygen, concentration of certain chemical species); and (2) channel characteristics measurements, including channel parameters (e.g. hydraulic parameters: water flow, river bed slope, river width) which are employed to represent the channel configuration (river channel profile).

SECTION 2. LITERATURE SUPPORT AND THESIS CONTRIBUTIONS

The Fickian advection-dispersion approach employed in the present thesis is based on the convective-diffusive mass transport in running waters. The employed mathematical tool is the fundamental advection-dispersion equation (ADE) for pollutant transport in running waters. ADE is a partial differential equation (PDE) derived from the mass balance applied to a mass volume unit in the river (Socolofsky and Jirka, 2005). Pollutant transport models developed in the framework of this thesis are based on the one-dimensional (1D) form of ADE for longitudinal direction (equation 1), which takes into account pollutant sources and sinks along with its transport.

1) $$\frac{\partial c}{\partial t} = -\frac{\partial (cV_x)}{\partial x} + \frac{\partial}{\partial x}\left(D_x \frac{\partial c}{\partial x} \right) + S_s \pm S_t$$

The evolution of pollutant concentration (c [mg/L]) in time (t [s]) along the river (x [m]) is influenced by the convective velocity of water (V_x [m/s]), which carries the pollutant downstream, and by the longitudinal dispersion coefficient (D_x [m^2/s], hereafter referred to as dispersion coefficient), which is responsible for the pollutant spreading all over the river channel. S_s ([mg/L]) represents pollutant sources (e.g. industrial sites, sewage treatment works); and S_t ([mg/L]) stands for pollutant transformations during transport.

This 1D form of ADE holds only after the Fickian period is reached: chemical species are uniformly mixed in cross-sectional profile of the channel. D_x stands here for the combined effect of diffusion (mixing produced by Brownian motion and turbulences), dispersion (mixing enhanced by variations of velocity across the stream) and differential longitudinal advection (Wallis and Manson, 2004; Liu, 1977).

Mathematical models proposed in this thesis (chapters 8 to 11) have different complexity levels, and are able to simulate releases from different types of pollution sources. Models are of two kinds: (1) numerical models, employing the PDE itself (1D ADE), implemented in COMSOL Multiphysics; and (2) analytical models, employing the analytical solutions of ADE (explicit solutions from literature, e.g. Chin, 2006; Socolofsky and Jirka, 2005; Pujol and Sanchez-Cabeza, 2000), implemented in MATLAB. For exemplifications equation **3** shows the analytical solution (Fischer et al., 1979) of ADE for an instantaneous injection of a mass of tracer.

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

where c is the tracer concentration [mg/L]; x is the distance along the river [m]; t is the time from the tracer release [s]; M is the mass of released tracer [g]; A is the cross-sectional wetted area of the channel [m^2], D_x is the dispersion coefficient [m^2/s], V_x is the velocity of the water [m/s], x_s is the location of the source [m], and k is the first order transformation rate constant [1/s].

This thesis section (2) deals with fundamental aspects related to pollutant transport in rivers; their modelling support and published studies. The phenomenology, along with basic equations and parameters to describe it are shortly presented in the first chapter, while the last two chapters cover its presence in the scientific literature: accomplishments and needs related to pollutant transport modelling and studies related to the three case studies. The literature study had to be extensive due to the concern this thesis has towards mathematical modelling using ADE and to the focus on three different river stretches, where different pollutants are taken into account. Chapters also offer a short view on the present thesis achievements compared to existing research, opening the way for the next thesis section which contains more details on achievements and novelty.

SECTION 3. PERSONAL CONTRIBUTIONS

Novelty in describing study sites

This chapter presents the answer to several challenges regarding analytical models: (1) river non-uniformity representation; (2) inclusion of influences; and (3) applying existing models to other rivers. In order to take into account non-uniformities of the study area the most analytical models for pollutant transport use a classical approach to describe a study site. This implies splitting the river into independent reaches characterised by constant average parameter values (Fig. 1).

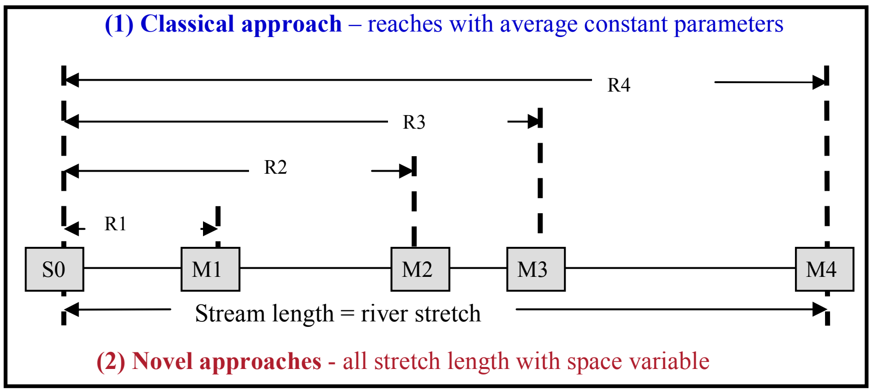

Fig. 1. River length parameterization options for analytical models (S0 = pollution source; M1 to M4 = monitoring sites; R1 to R4 = river reach): exemplification for Murray Burn.

In contrast with previous models an important feature of analytical models presented in this thesis is that river characteristic parameters are variable along the modelled river stretch, due to the application of two novel approaches used to parameterize the study area. The new approaches work with variable parameters along the river stretch, as illustrated in Fig. 1. They allow the location of influences at the real distance along the river and open the possibility of implementing non-point pollution sources using models already validated for point sources. This is an important advance in analytical modelling, since field data related to point sources are much easier to collect compared to distributed sources data.

Modelling and simulation of pollutant transport in Murray Burn

The objectives of this chapter are: (1) the development, calibration and evaluation of two kinds of mathematical models for an instantaneous pollutant release in Murray Burn; and (2) the development of models for the evaluation of velocity and dispersion coefficients. The two mathematical models are: an analytical model in Matlab and a numerical model in COMSOL.

Both models were calibrated and evaluated following the methodology presented in Fig. 2.

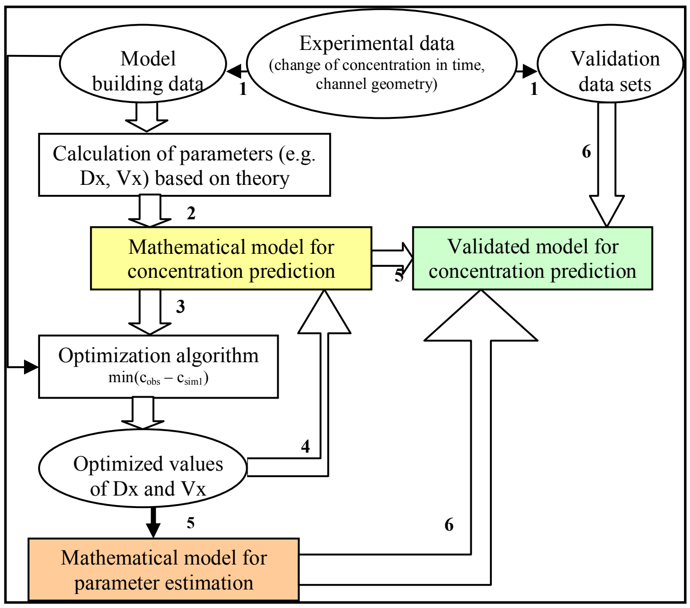

Fig. 2. Modelling methodology.

In this work a lot of attention was given to the methodology for the estimation of velocity and the dispersion coefficients because good prediction of concentrations in streams relies heavily on the ability to estimate both parameters well. Optimised values of parameters obtained in the calibration phase of model development, however, were quite robust and showed well defined increasing trends with increasing flow rate.

Parameter estimation models give the possibility to obtain the velocity and dispersion coefficient values independently of tracer experiments. The proposed non-linear model for velocity and dispersion coefficient (Whitehead et al., 1986) proved to make satisfactory estimations (see Fig. 3 and Fig. 4) for the first three reaches, but the fourth reach was not as well catered for. There was little evidence that a more sophisticated model (e.g. Fischer et al., 1979) for estimating dispersion coefficients provided significantly better predictions of solute concentrations.

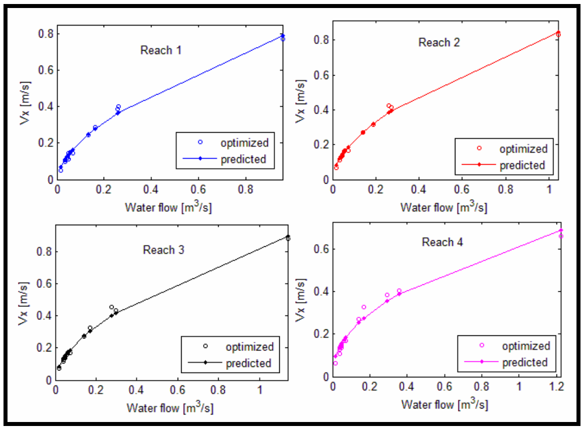

Fig. 3. Velocity estimation with the simple non-linear model for the analytical reaches.

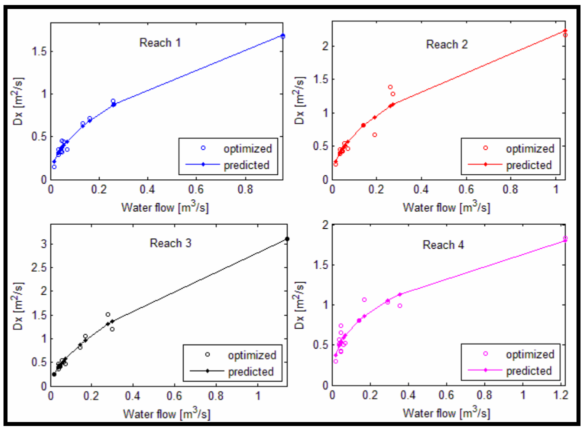

Fig. 4. Dispersion coefficient estimation with the simple non-linear model for the analytical reaches.

Results of model calibration and evaluation runs showed that both models were able to capture the main features of observed concentration-time profiles (e.g. Fig. 5 and Fig. 6).

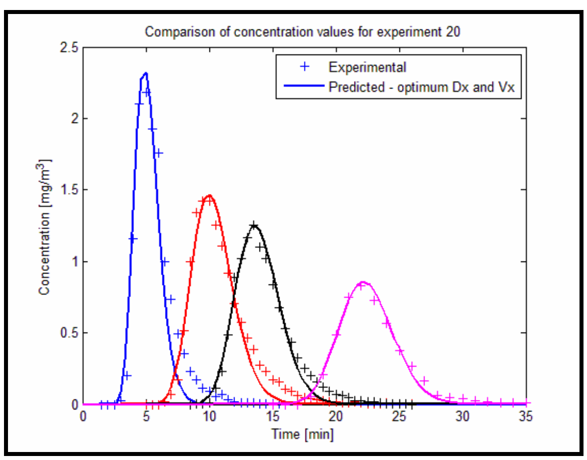

Fig. 5. Calibration results of analytical model for medium flow experiment (Q = 261 L/s).

Concerning the usual discussion on weather a model should focus on peaks or on trails it should be mentioned that models developed for Murray Burn are able to make good predictions of the peak value and also of the time of exposure to medium and low concentration values, i.e. the width of the predicted concentration profiles are well simulated (Fig. 5 and Fig. 6).

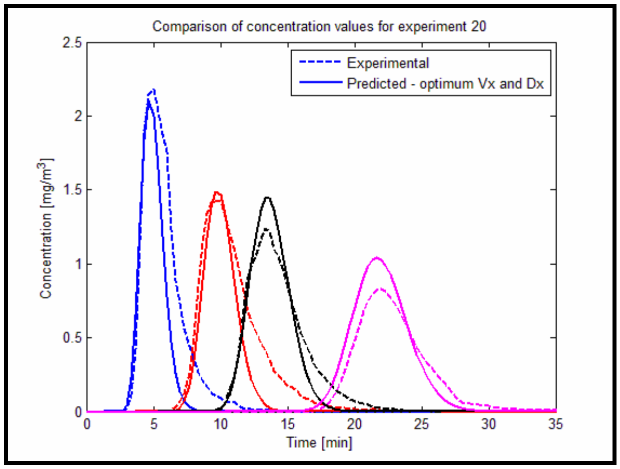

Fig. 6. Calibration results of the numerical model for a medium flow experiment (Q = 261 L/s).

Considering the simulation of all experiments by both models, the peaks are the best predicted feature and the trailing edges are the least well predicted feature. Furthermore, reaches 1 and 2 are the best simulated reaches, while reach 4 is generally the worst. The quality of concentration prediction for the last site could be related to the long distance between the source and this last site along which the channel is non-uniform. Also the real or apparent spatial variation in the flow rate might have an influence.

Process engineering approach applied to pollutant transport modelling in Murray Burn

The objectives of this study are:

1. to improve concentration prediction by modifying the optimization algorithm;
2. to test the novel approach I for river parameterization of Murray Burn;
3. to investigate the possibility of using a travel time dependent model for the evaluation of velocity;
4. to find if travel time dependent models for dispersion coefficient help improving its estimation; and
5. to compare results of the two parameterization approaches with respect to improvements in parameter estimation and concentration prediction.

This study employs the analytical model for pollutant transport in Murray Burn developed, calibrated and evaluated before. In that research step the classical approach of parameterisation was applied to develop the analytical model. In this research step is intended to use both, the classical and the novel approach 1 in order to describe the modelled river stretch.

The modelling methodology employed for the initial development and calibration of the analytical model was used in this study also. Few modifications were required in order to fulfil above presented objectives. They are mentioned below along with important specifications regarding the methodology.

1. The parameter calculation, model calibration and evaluation were carried out separately for each approach.
2. A*b-initio* parameter calculation for the novel approach was carried out using numerical reaches of Murray Burn, as they are suitable in representing the river as a continuous computational domain with variable parameters. Reaches are not characterised by average values of parameters. *Ab-initio* parameter values at monitoring sites (M1 to M4) are the ones for numerical reaches are used to apply the novel approach 1; while the ones for analytical reaches are used to apply the classical approach.
3. The original optimization algorithm was modified. The weighted sum of squared differences (Rode et al., 2007) was employed to attach importance weights to data points (Ng and Perera, 2005) in order to predict trails more accurately, and to improve the overall model prediction. Several sets of weights were proposed and an optimization problem was formulated and solved in order to avoid subjectivity while associating weights to concentration data. Results presented hereafter reveal improvement of prediction accuracy at M4.
4. D_x and V_x optimum values resulted employing the new algorithm are further used to develop models for parameter estimation. Models have the same form for each parameterisation approach, but different values for model features (e.g. coefficients C_{1V} and C_{2V} take different values for each approach at M1 to M4).
5. The parameter estimation models were introduced in the concentration model in order to finish its calibration, and to make predictions of D_x and V_x for the experiments in the evaluation data set. The evaluation was made by comparing predicted against measured concentration profiles. The prediction accuracy was measured by calculating R-squared for each concentration profile.

Results show that: (1) velocity estimation is more precise than dispersion coefficient estimation; and (2) generally the novel parameterization approach improves parameter prediction. The advance is visible especially for the estimation of D_x at M4. Velocity is estimated better by the simple non-linear model compared to the travel time dependent formula, even if differences between the performances of the two models is relatively small at first three sites. Dispersion coefficient benefits the most from the use of the novel approach for parameterization. The best estimates at all sites in both approaches are given by the non-linear model, followed by the modified Fischer using non-linear velocity; with the specification that estimation is improved in the novel approach I. Regarding errors associated to these two model options it is observed that D_x is mostly overestimated at medium flows and slightly underestimated at high flows.

Some comparative results of the model evaluation when using the two approaches are presented in Fig. 7 (for a low flow experiment) and Fig. 8 (for a high flow experiment).

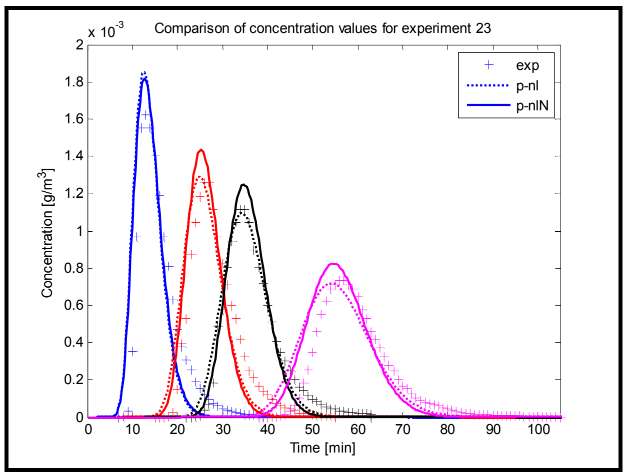

Fig. 7. Evaluation results for a low flow experiment (62.1 L/s).

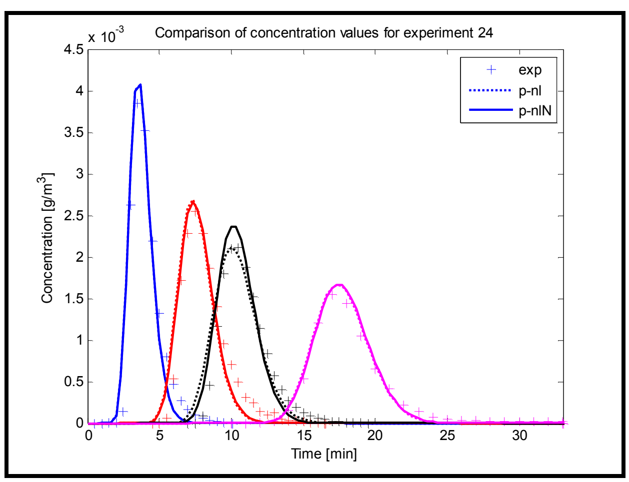

Fig. 8. Evaluation results for a high flow experiment (535.4 L/s).

Even though calibration results for the novel approach are sometimes lower compared to classical approach, evaluation results show improvements when using the novel approach.

Interestingly, in evaluation runs the novel approach of describing the study site brings improvements in the concentration prediction at all the monitoring sites.

The overall results show that (1) the novel approach for study area parameterisation improves model's prediction performance; (2) the modification of the optimization algorithm with respect to attention given to trails also improves the overall prediction accuracy; (3) making the model efficient for the simulation of pollutant transport in Murray Burn. Clearly, such prediction tools are very important in the field of environmental modelling, and their prediction accuracy depends very much on the ability to make good estimations of V_x and D_x.

Modelling and simulation of pollutant transport in Swale River

The objectives of the present case study (presented in Ani et al., 2010a) are:

(1) to develop a new tool for the prediction of nutrient (nitrate, ammonium, soluble reactive phosphorus - SRP and organic phosphorus - OP) transport along a short stretch (50.4 km) of Swale River under unsteady flow conditions;

(2) to make the developed model consistent with QUESTOR; in order

(3) to compare ADModel results when using QUESTOR transformation rates against the use of newly estimated parameters;

(4) to relate nutrient dynamics in the river stretch to variability in nutrient transformation rates; and

(5) to illustrate the benefits gained in terms of model skill with the new ADModel approach.

Extensive field and literature studies motivated the development of modelling of nitrate, ammonium, SRP and OP, as they are very important nutrients for river Swale. ADModel relies on ADE analytical solution for point continuous release (Pujol and Sanchez-Cabeza, 2000) and was developed using experimental data from lower river Swale. Model results are discussed in relation to QUESTOR (Eatherall et al., 1998), well known modelling software, developed at the Centre for Ecology and Hydrology (CEH) Wallingford, UK. QUESTOR has been applied to river Swale by researchers at CEH.

ADModel is developed, calibrated and evaluated by considering the transport parameters and associated nutrient transformations, according to the methodology in Fig. 9. Calibration was carried out using an original methodology, in two steps: calibration I, when dispersion coefficients were optimized; and calibration II, when reference transformation rates were optimized. In each step an original optimization algorithm in two steps, using different objective functions, was employed. Calibration I has been carried out using both nitrogen and phosphorus compounds, while calibration II was carried out just for nitrogen compounds.

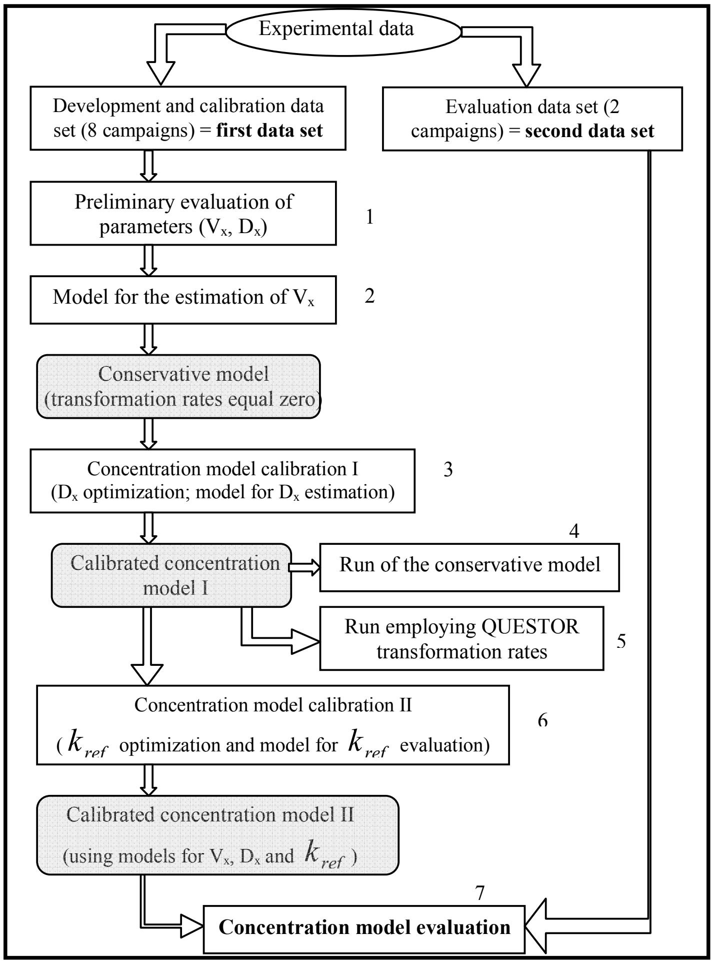

Fig. 9. Methodology used for ADModel building, calibration and evaluation.

Results after calibration I, using conservative model and non-conservative model with QUESTOR calibrated reference transformation rate constants, show that ADModel is able to represent the main trend of measurements for all four nutrients; and reveal the need to improve the representation of transformations variability.

A model to predict the reference transformation rate constants as a function of seasonality and/or water flow was formulated during calibration II (see Table 2) using optimum values of reference transformations (e.g. Fig. 10).

Table 2. Transformation processes dependence on influencing factors.

Process	Nitrification	Denitrification	Mineralization	Sedimen-tation	Re-suspension
Transformed amount [mg/L]	k_{ref_nit}, T, c_{NH_4}	k_{ref_den}, T, c_{NO_3}	k_{ref_min}, T, c_{OP}	k_{ref_sed}	k_{ref_res}
Factors influencing k_{ref}	Q, seasonality	Q, seasonality	Q, seasonality	Q	Q

T is the measured water temperature [ºC]; Q is the water flow [m^3/s]; c_{NH_4}, c_{NO_3}, c_{SRP} and c_{OP} [mg/L] are the concentrations of NO_3, NH_4, SRP and OP; k_{ref_nit}, k_{ref_den} and k_{ref_min} [1/day] are reference rate constants for nitrification, denitrification and mineralization; k_{ref_sed} and k_{ref_res} [mg/L] are reference rate constants for sedimentation and re-suspension.

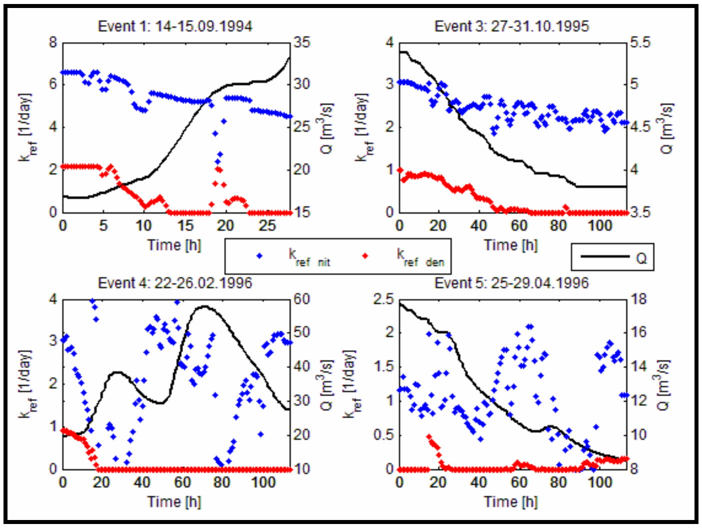

Fig. 10. Optimum reference transformation constants (k_{ref}) and water flow (Q) values during calibration campaigns.

This transformation model improved the representation of dynamics between campaigns and to some extent within campaigns, although the procedure for estimating variability in transformation rates needs further development. At four sites along the Swale, ADModel reproduced the main trend of hourly resolution ammonium and nitrate concentrations (see Fig. 6), showing predictive capability for simulation of accidental discharges and detailed study of pollutant transport along the river stretch. This capability is absent in an existing model applied to the Swale (QUESTOR) which is designed for prediction of water quality over long periods in daily steps and is more appropriate for larger river networks (hundreds of kilometres).

Although giving generally better results than a conservative model, the nitrification, denitrification and mineralization rates calibrated using QUESTOR over long-time periods from fortnightly monitoring proved not optimal for the simulation of short-term changes. Modelling river nutrient response to season-specific short-term changes in flow is far more demanding of model structure than applications spanning many years where periodic datasets capture little information beyond average status. Yet, in doing the former, ADModel yields goodness-of-fit statistics broadly similar to what QUESTOR achieves in doing the latter.

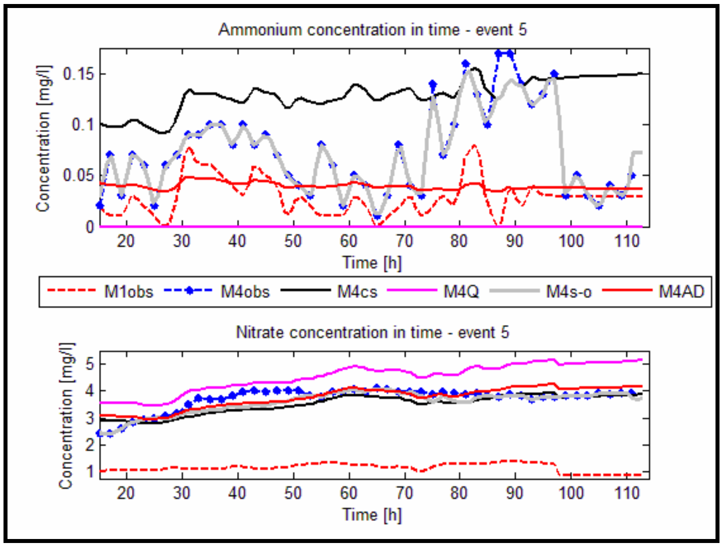

Fig. 11. Comparative results of ADModel for conservative and non-conservative transport during campaign 5 (normal flow conditions) (obs = observations; cs = simulation using conservative model; Q = simulation using non-conservative model with kref from QUESTOR; s-o = simulation using optimum kref; AD = simulation using non-conservative model with kref from the model developed during calibration II).

From both long-term (QUESTOR) and shorter-term modelling (ADModel) improvement in concentration prediction accuracy is suggested. Some possibilities are considered in detail, providing a general focus for future investigation regarding: e.g. representation of existing concepts (microbially-mediated transformations); representation of sources; additional sources and in-river processes; improvements with respect to field data.

Modelling and simulation of pollutant transport in Someş River

The modelling of pollutant transport in Someş River has been carried out in several steps.

(1) First hydraulic parameters of the river stretch were analysed and processed for the division of the stretch in five reaches of different length.

(2) A study on river pollution was carried out. Its results show that nutrients and heavy metals are amongst the most important pollutants, discharged by a wide range of pollution sources. The river reach between upstream Cluj-Napoca and downstream Dej was identified as critical river reach to be further subjected to modelling.

(3) River channel features and pollutant transport parameters were estimated for this river reach. Field data and mathematical models have been employed.

(4) Further, three analytical models have been implemented in order to simulate pollutant transport. The models are able to make concentration prediction after accidental and

routine pollutant releases from (1) continuous point sources; (2) instantaneous point sources; and (3) instantaneous non-point sources.

(5) Results of analytical models for constant and variable parameters are shown. The employment of variable model parameters is possible with the help of a novel technique for river parameterization.

(6) The analytical model comparison with a numerical model (developed elsewhere, not in the present thesis) in order to test the novel approach.

Models employ variable parameters along the river, as measurements reveal non-uniform channel features and water flow. Parameters have been estimated, as appropriate, using field data and/or models or values proposed in literature. River channel features (slope, width, depth) and water flow have been computed on the basis of river measured data. Velocity is estimated as function of water flow and cross-sectional profile. Longitudinal dispersion coefficient was estimated using two models:

(1) McQuivey-Keefer (1974) formula chosen with the help of the knowledge reuse software described by Avramenko et al. (2009). The empirical coefficient value (0.058) may vary between river reaches in order to account for non-uniformity.

(2) Iwasa and Aya (1991) formula proposed by Chendrean (2009) with the help of the developed methodology for the identification of dispersion coefficients.

Transformation rates are expressed trough first order kinetics, which takes into account biological, chemical, physical transformations and any other processes leading to the change of pollutant concentration during transport. The employed value of the total transformations constant (k) is 10^{-5} s^{-1} and represents a pollutant sink. This parameter is assumed to be independent of water parameters (e.g. temperature, BOD, DO, pH).

Pollution sources data: location; discharged pollutant; flow and concentration; were also specified. The models were used to simulate the transport of pollutant discharged by sources identified by Ani et al. (2010b) along Someş with the graphical analysis method.

The below exemplified pollution scenario regards a non-point source located between km 95 and km 100 along one bank of Someş River. Fig. 12 and Fig. 13 show simulation results of the same model using constant and variable parameters. The total simulation time is 15 hours, and the river distance represented in the figure starts at the upstream boundary, where the source is located (km 95) and is extended 80 km downstream.

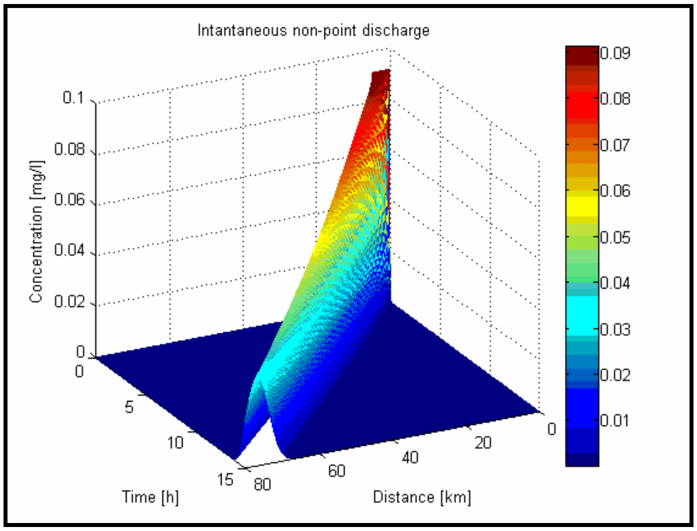

Fig. 12. Transport of pollutant discharged through non-point release: constant parameters.

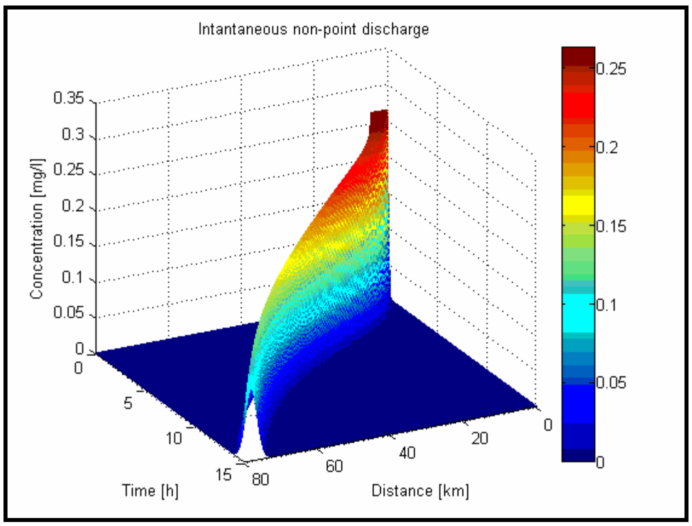

Fig. 13. Transport of pollutant discharged through non-point release: variable parameters.

Even if the same discharged quantity of pollutant is employed in both simulations, concentration profile has different shape and values. Simulation results obtained when using constant and variable parameters show substantially different values of concentration, profile shape and affected river length. This reveals that the variability of parameters has to be correctly represented in models. Models employing variable parameters made good concentration predictions during the modelling exercises presented below and behaved well during the evaluation process for both Murray Burn and Swale. The use of variable parameters would be recommended taking into account these considerations and also the fact that constant parameters transform the river into an idealised study area, and simplify the hydraulics of the channel.

The analytical model developed in this thesis for the point continuous release, employing variable parameters, was further evaluated against a numerical model, developed outside of the frameworks of this thesis. The purpose of this evaluation is (1) to test the novel approach 2 and (2) to compare aspects related to the development and utility of analytical and numerical models.

Both models (1) account for the same river parameters; (2) present the same pollution scenario; (3) have been developed on the same assumptions for the initial conditions; boundary conditions; and transformation kinetics; and (4) take into account the combined effects of the convective-dispersive transport together with transformation driving forces on the pollutant distribution along the river length in time. The source is located in the industrial site of the Cluj-Napoca city at 90 km downstream the river spring. The release, of 5g/s of non-conservative pollutant is originating from a discharge pipe and it is assumed to be instantly distributed over the cross section of the river.

The evaluation of the river distance affected by pollutant at certain moments of time after the release start is presented in Fig. 14 and Fig. 15, which reveal similar results of the two models.

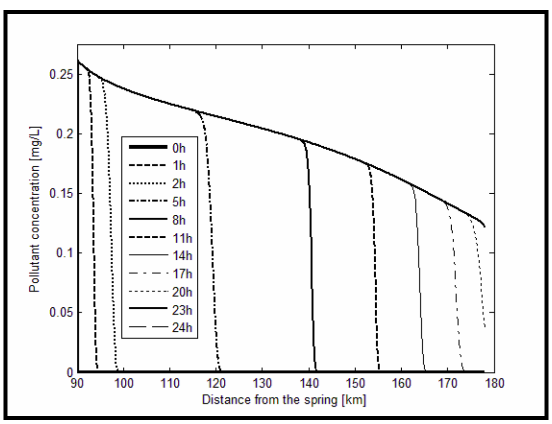

Fig. 14. Simulation results of the analytical model.

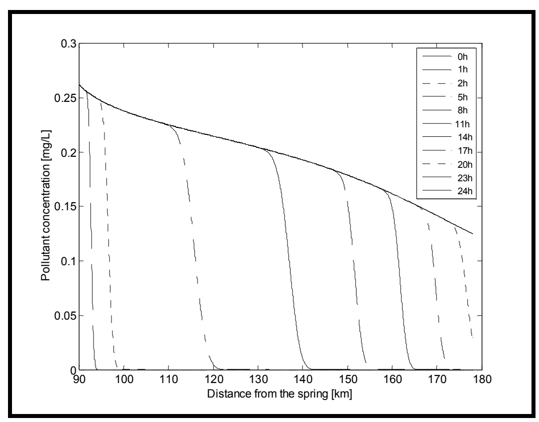

Fig. 15. Simulation results of the numerical solution.

The computation time needed for obtaining the numerical solution (24 hours of the real process time) is of 142 seconds, compared to 43 seconds simulation time requested by the analytical model. The analytical approach shows to be less expensive and able to provide simulation results in shorter computation time.

Models for the simulation of pollutant concentration in Someş River are a great achievement of the present thesis, especially in the present situation when very little similar research has been carried out (e.g. Cristea et al., 2010; Rosca-Bocancea and Agachi, 2001 and 2000). They are valuable due to their predictive capabilities, but also because they open up possibilities for the development of new and computation efficient computer tools for water quality management, in-stream pollution counteraction and waste water treatment in the Someş River Basin.

Process engineering approach: wider discussions

Analytical vs. numerical models

For the simulation of continuous point pollutant release in the Romanian Someş River two mathematical models were implemented, using Matlab (for the analytical model) and COMSOL (for the numerical model) (Ani et al., 2010c). Two mathematical models were also developed for the simulation of instantaneous point discharges in Murray Burn stream: analytical model in Matlab and numerical model in COMSOL (see Ani et al., 2009). For both rivers the two kinds of models were designed as systems with similar constituent elements which have the ability to predict both the space (along the river) and time evolution of conservative and non-conservative pollutants concentration.

In both individual cases the two model types use the same initial and boundary conditions and variable parameters along the investigated river segment. They provided similar results for predicting the time and space pollutant concentration evolution. The analytical approach shows to be less expensive and able to provide simulation results in shorter computation time.

A main advantage of numerical models is the ability to cater for a wide variety of initial and boundary conditions. This makes it possible to use for other kinds of releases of pollutants, such as the steady or unsteady releases over finite time intervals. These facts motivated the development of numerical models along with the interest to see how such numerical models behave since very few COMSOL-based models for solute transport in rivers have been published before (e.g. Cristea et al., 2010).

Numerical models are more flexible compared to the analytical ones. Adding, modifying or crossing out influences (e.g. a pollution source of any type) is possible and easy to implement at any time. The core of the numerical model (the PDE) remains the same, and the elements to be specified are: location of the source, space distribution of the source, release duration, nature of discharge, initial and boundary conditions. For the case of the analytical model, in order to simulate the pollutant release from another type of source it is needed to implement in the model the PDE solution corresponding to that specific type of pollutant release.

The use of reaches influences the model application on other rivers, requiring some additional changes. For example, the reaches of a new river to be investigated would have to be defined before adapting either model for that river. In COMSOL the number of numerical reaches could be changed easily by suppressing or adding internal boundaries in the computational domain. It is also easy to reduce or increase the number of reaches in the analytical model. However, this thesis is proposing novel techniques for parameterizing the study area in order to use variable parameters in the analytical models. The study area is represented as a single river stretch with influences at the real location along the river. Consequently the model is easier to implement for other rivers compared to analytical models using classical parameterization approach with reaches.

Model complexity and effectivity issues

The parameters characterizing pollutant transport in surface waters are variable along the space coordinates, represented by the length of the river, the channel width and the water depth. Trying to include all variables in 3D space would lead to very complex models arising difficulties related to the availability of experimental data for the models´ creation and evaluation. The alternative is the use of 1D and 2D models which are still able to represent the modelled system in a satisfactory manner.

Generally the 1D model is easier to use, and all necessary data to build it and evaluate it is accessible with lower experimental costs compared to 2D or 3D case. For the present case studies 1D concentration data was available at high monitoring resolution (up to two hours) for Murray Burn and Swale, and at lower resolution (monthly) for Someş River. The limits of a 1D model can also be investigated.

A 2D model represents more features of the system, but more data is needed. Some of this data is not available, for example dynamic cross-sectional profiles of the concentration field to calculate the transversal dispersion coefficients. The most often monitoring data is collected at only one place (middle of the stream) across the section on the assumption that tracer is well mixed (Wallis and Manson, 2004). An alternative option would be to use an empirical formula for these, but the values of the coefficients might not be very reliable, due to limitations of such methods, limitations which are similar to those for predicting the (longitudinal) dispersion coefficients.

Another argument for the use of simpler models is the fact that a 2D model is suitable within the advective zone, but beyond this distance the 1D model can be employed because the dominant mixing process is then longitudinal dispersion (Fischer et al., 1979; Chin, 2006; Wallis and Manson, 2005). In the case of rivers investigated in this thesis mixing is well done from the source till the first downstream monitoring site. In this distance mixing is done because its length is a lot larger compared to river width (more than 100 times).

The main features of concentration temporal profiles which have to be predicted by pollutant transport models are the peaks (the highest concentration value) and the leading and trailing edges of the profile (pollution wave arrival and leaving from a site). When working with pollutant transport models there is a discussion regarding the most important features of the concentration in time profiles to be predicted: leading and trailing edges vs. peak? From one point of view the peak is important to be predicted because it gives information about the magnitude of the event. On the other hand edges are important because they show for how long the pollutant is present. Any in-river flora and fauna could possibly resist a short exposure to a high concentration, but might be damaged very much when a longer exposure to a lower concentration occurs.

In this thesis the capacity of pollutant transport models to predict the peak and the edges is a mean of assessing model performance. This is a way to ensure that models are able to predict with accuracy the concentration of a pollutant along a river after its release. For all three case studies models were able to capture the main features of observed concentration in time profiles. Good predictions are made for the time of exposure to medium concentration values.

Many available pollutant transport models take into account pollutant release from a single source. In reality along a river there are multiple pollution sources. In such work the superposition of releases coming from each source is necessary, as explained by Socolofsky and Jirka, (2005). As example in this thesis is the development of a model for the simulation of multiple types of pollutant release based on the already validated ADModel for Swale River. The model is using two modules: (A) a module for continuous variable discharge and (B) a module for bulk instantaneous discharge; implemented in Matlab. The core is the already validated ADModel, which supports further development because models for transport parameter estimation were developed and verified. The pollutant concentration in the source and in the river at the source proximity (c_{S0} and c_S) have different values for each releasing source and for each modelled nutrient; initial and boundary conditions are also different depending on source and module; while V_x and D_x are common for both modules and for all nutrients, and depend on water flow rate, channel parameters and other hydraulic parameters. Consequently the new module can be applied to River Swale with no further validation, because it relies on the same river channel parameters and pollutant transport characteristic parameters (e.g. velocity, dispersion coefficient, and transformation rates). The employed methodology is presented in Fig. 16.

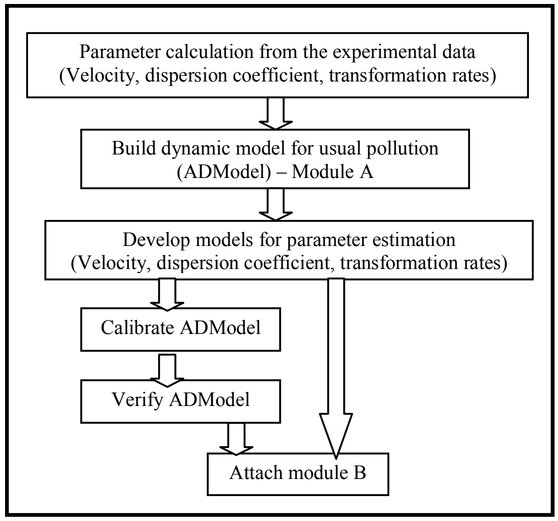

Fig. 16. The methodology followed during the development of module-based model.

The present module-based model is capable of simulating pollutant concentration in customary situations and under accidental release from multiple types of pollutant release. It is useful for understanding the propagation of pollutants along the river, to assess water quality, and also to carry out pollution management.

Parameter estimation related issues

In pollutant transport modelling the estimation of hydraulic and mass transport parameters could be carried out in two ways: using experimental data and using mathematical/ empirical models. Due to difficulties regarding data collection researchers tend to use models for parameter estimation, which have been developed and validated before (almost always on other rivers). Models are easy to use; provide results in shorter time compared to methods based on experimental data; and the most often they are not expensive estimation means, as they don't require detailed field data. At the same time they are very dangerous, because for some parameters there are multiple calculation options, giving different results. The use of inappropriate model can lead to inaccurate parameter estimation. Consequently the selection of the most appropriate model is very important and has been investigated outside of the frameworks of this thesis by the thesis author and colleagues (Avramenko et al., 2009; Chendrean, 2009): knowledge reuse software for the study of process mechanisms and a method for the identification of models to estimate parameters were developed. Their results have been employed in the present thesis for the Someş River.

It is worth discussing now the case of dispersion coefficient which is very difficult to estimate, even when experimental data is available (because problems in data series or data lack could affect seriously the results). This is the parameter with the highest number of mathematical/empirical models available for its estimation. The most of these models were developed using data from a high variety of river channels, water flows, longitudinal and transversal non-uniformities, with the intention to offer a widely applicable instrument (Wallis and Manson, 2004). Nevertheless the most often, as shown in this thesis also not all models are applicable to a certain river. Results show major differences between the application of models to rivers and even reaches of the same river. The longitudinal dispersion coefficient changes along a river (even dramatically some times), and varies even between similar rivers, or similar flow rates, as found in many studies (e.g. Wallis and Manson, 2004), and also confirmed by results in this thesis.

Therefore each river reach should be treated individually when choosing the proper model for D_x estimation, because more precise models associated to reaches are preferable to a single imprecise instrument associated to the whole river. For more complex and non-uniform cases even different hydrodynamic conditions of the same reach should be associated with a different parameter model.

In this thesis the approach was to test models and to choose the appropriate parameter estimation models. Proper models selected for a certain case ensure the accurate parameter estimation, while the use of any of the existing formulas could lead to inaccurate results.

Results use and perspectives

Thesis results are useful from academic point of view but also for the industry.

From the academic perspective the thesis offers several important techniques and tools to be used in pollutant transport modelling. Some techniques are novel (e.g. parameterisation of a river stretch) and could be the base for the development of new methods to be used in water quality modelling (e.g. the implementation of diffuse sources in models designed for point sources) or the application of models to other river stretches (e.g. parameter estimation models together with the novel parameterization techniques). The models are useful to study the phenomenology of pollutant transport, interdependencies of parameters, and could also represent the support for the development of new tools to predict and counteract the effects of pollutants released into rivers. In this respect numerical models can be used for building systems for active in-stream pollution neutralization.

In the water quality business sector models are able to help water quality managers when dealing with pollution scenarios, but also to take routine decisions regarding water quality. For example when an accidental pollution happens somewhere along the river the user has to specify the pollution source spatial coordinates, the quantity of pollutant, the type of release and other specific parameters. The program will display graphical information about pollutant concentration in the river enabling user to decide on monitoring and counteracting measures.

The impact of technological or demographical changes on river water quality could be assessed in a similar way, by using the models to predict pollutant distribution along the river when population increases, a new industrial site should be open, or an existing industry operates technological improvements leading to the modification of effluents. Critical zones along a river can also be identified, as well as the cause of unknown accidental pollutant releases.

The utilisation of models as decision making support tools, as learning or training tools represents a realistic achievement of the present thesis.

SECTION 4. CONCLUSIONS AND MAIN CONTRIBUTIONS

Conclusions

This thesis is focused on the development of a comprehensive process engineering approach on pollutant transport modelling by means of methods and tools from different fields. The research is based on large quantities of field data from three river stretches of different length and magnitude: Murray Burn, a short (0.54km) and small mountain-like stream from Edinburgh, Scotland; Someş River, a long (421km) and highly non-uniform Romanian river, starting in mountains as small stream and developing as large river; and Swale River (50.4km), a large and under human pressure river from North-East England. These rivers were chosen due to availability of experimental data, which enabled the development and evaluation (for Murray Burn and Swale) of pollutant transport models; and also due to their different hydraulics, which offered the possibility to apply different types of models.

Advection-dispersion models having increasing level of complexity were developed: from the simple conservative models for Murray Burn, representing one pollutant; to non-conservative models for a single pollutant in Someş River; and to a complicated non-conservative model for River Swale including four pollutants with inter-dependent transformations. Models for pollutant transport are able to simulate accidents and also customary pollution.

The investigation of three different river stretches and models development shows that studies related to water quality, and especially pollutant transport modelling, are very difficult to carry on, because they involve complex phenomena, require large amount of experimental data and need technical support. Even the simplest case in this thesis (Murray Burn bulk pollutant discharge from a conservative source) proved to be a very challenging pollutant transport modelling work that required large amount of time and experimental effort.

The develoment of models for very different cases was possible trough a systemic modelling approach and the use of process engineering specific methods and tools (e.g. original calibration approach using optimization algorithms developed for each case study) for modelling pollutant transport in rivers.

The interest was not just to have the best prediction tools for pollutant transport, but also to use reliable parameters, and to make models applicable for other similar case studies. This aim was achieved through extensive parameter studies and by presenting models for the estimation of transport characteristic parameters (dispersion coefficient, velocity, transformation rate constants) and also trough the use of novel parameterization approaches. Such findings improve predictive capabilities of developed models and also facilitate further model application to other rivers.

The design of specific pollutant transport modelling tools is of interest for economic agents, environmental agencies and universities. Such systems offer support and open up possibilities for new modelling methods, monitoring facilities, and for river water quality management tools (e.g. real time pollution counteraction systems). They are useful also for the estimation of the environmental impact of possible technological changes, as they can be applied in the pre-design stage and in practical use of processes as well, for scientific and economic reasons.

The utilisation of models as decision making support tools, as learning or training tools represents a realistic achievement of the present thesis.

Personal contributions

Three case studies were employed in order to fulfiel the above mentioned main goal. Water quality modelling literature is quite rich in studies regarding Murray Burn and Swale; while very little amount of such studies has been focused on Someş River. The achievements of this thesis related to each of the three rivers are presented in Table 3.

Table 3. Thesis contributions related to the three investigated river stretches.

River	Thesis contributions
Murray Burn	Comparative study of mathematical models for the evaluation of the longitudinal dispersion coefficient and velocity The development of models for the estimation of the two parameters for a wide range of flow rates Matlab analytical model for the transport of conservative pollutants from instantaneous point source COMSOL numerical model for point sources Calibration and validation of models Novel parameterization approach I to represent study area in analytical models in order to employ variable parameters Evaluation of the novel parameterization approach I with respect to prediction improvements
Swale River	Models for the estimation of velocity and longitudinal dispersion coefficient Models for the estimation of reference transformation rates for nutrients Matlab analytical model for the unsteady transport of nutrients pollutants from multiple continuous point sources and tributaries The implementation of influences at the real location along the river stretch, and not at reach boundaries as in existing models (e.g. QUESTOR) Calibration and validation of the model Original optimization algorithm employed during calibration
Someş River	Models for the estimation of river channel parameters Models for the estimation of transport parameters: velocity and longitudinal dispersion coefficient (employment of process engineering tools) Matlab analytical models for the transport of pollutants from: instantaneous point sources; instantaneous diffuse sources continuous point sources Novel parameterization approach II Pollution study

The main contributions of the present thesis presented above result in a process engineering approach on pollutant transport modelling, which contributes to the research field of pollutant transport modelling trough following main findings.

- The development, calibration and evaluation of pollutant transport models: detailed models working at small time steps (up to one hour), using analytical solutions of ADE, not employed previously in a similar way for the investigated case studies.

- The investigation of methods for the estimation of pollutant transport parameters (velocity, longitudinal dispersion coefficient and transformation rate constants).
- The identification of new techniques and methods useful for modelling pollutant transport in rivers with the use of analytical solutions of ADE: e.g. study area parameterization novel approaches are developed; original optimization algorithms to be used during model calibration.
- An important characteristic of this thesis results is the systemic process engineering approach employed during case studies investigation. This is related to issues discussed below: a systemic modelling methodology; accurate phenomena representation model flexibility, further development and wider use of results (e.g. application to other case studies). The accurate phenomena representation is done (1) tough the involvement of mass and momentum transport characteristic parameters in ADE modelling work (e.g. non-dimensional criteria employment); and (2) by using improved modelling techniques: e.g. enhanced representation of river characteristic parameters and influences, and good modelling of transport parameters.
- The level of detail in representing river features also brings added value to this research, compared to previous work on the three case studies.

The amount of case studies, their variety and also the important personal contributions make the present thesis valuable for the water quality research and practice.

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