Integrated modelling of conventional pollutants and organic contaminant fate in rivers: a microcosm study

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Abstract A new conceptual dynamic integrated model is presented which can be used to describe both conventional pollutants and organic contaminant fate in rivers. The model is designed to assess the short-term fate of organic contaminants in two compartments (bulk water and benthic sediment), taking into account the effect of nutrient dynamics. The biodegradation submodel was refined using a microcosm (artificial river) study and Linear Alkylbenzene Sulphonate (LAS) as an example. Based on data generated during the microcosm study, the model was calibrated and validated in both steady state (continuous constant load) and dynamic (pulse load) conditions. The results show that the simulated data set agrees well with the measured data set. Furthermore, thorough investigation of the model output sensitivity to the model inputs was made, and the results show that the fate of LAS is sensitive to the following model input variables: ammonia nitrogen, dissolved oxygen, microbial biomass and readily biodegradable soluble COD, and the model parameters mainly related to the biodegradation submodel. The model provides good understanding of the interaction between conventional pollutants and organic contaminants fate in rivers.

Keywords Artificial river; integrated modelling; river water quality; sensitivity analysis

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Introduction

The consequence of conventional pollutants, nutrient enrichment and contamination by toxic organic compounds are the main water quality problems in surface waters, and hence they have been subject to extensive research and modelling. Despite the fact that these two water quality problems interact in various ways, linking these two problems is not a common practice. However, knowledge of interaction between conventional pollutants and organic contaminants is required for various purposes. Among them two are particularly important: (1) it assists the water quality manager to make decisions on the method of handling the contaminated sediments (e.g. dredging, capping, etc.), and (2) it helps to evaluate and predict the bioavailability, fate and effect of contaminants in the aquatic environment (Gunnarsson *et al.*, 1996).

Nutrient enrichment can influence the in-stream fate and toxicity of organic contaminants in various ways. In comparison to oligotrophic systems, high biomass production in an eutrophic system can result in a lower contaminant level in each individual organism. The higher concentrations of dissolved and particulate organic carbon can result in low contaminant concentrations of the truly dissolved fraction (e.g. Gunnarsson *et al.*, 1996). Chemical sorbed to Particulate Organic Carbon (POC) can also be removed from the bulk water by sedimentation (e.g. Millard *et al.*, 1993). In oligotrophic systems on the other hand, the limiting inorganic substrates/nutrients, e.g. nitrogen and phosphorus sources, can limit microbial growth, and thereby influence the biodegradation of organic contaminants (e.g. Greer *et al.*, 2003). A recent experimental study also confirmed that the concentration dynamics of basic water quality variables such as dissolved oxygen, ammonia nitrogen and readily biodegradable Chemical Oxygen Demand (COD) can influence the fate of organic contaminants (Linear Alkylbenzene Sulphonate (LAS)) in an artificial river (Deksissa and Vanrolleghem, 2003a). To take into account these interactions in the river water quality model, an attempt was made to develop a new dynamic integrated model (Deksissa and Vanrolleghem, 2003b) that needs to be validated and refined.

The goal of this study is therefore to refine/validate the integrated river water quality model on the basis of a microcosm study. The biodegradation submodel was refined such that it includes bulk water and benthic sediment/biofilm degradation, Dissolved Oxygen (DO) and other nutrient limitations. The performance of the model was evaluated by comparing a simulated data set with a measured data set. On the basis of a sensitivity analysis, the relative importance of the model parameters and input variables was also examined.

Material and methods

Experimentation set-up

Figure 1 shows the river set-up and its schematic representation. The river was constructed as a cascade of 5 U-shaped gutters each 2 m long. The total river length and volume are 10 m and 36.84 L respectively. Two air diffusers were placed in each gutter to provide oxygen and to counteract sedimentation. The design Total Hydraulic Residence Time (HRT) was chosen such that it corresponds to the half-life of the chemical of concern, in this case LAS that has a half-life of approximately 3 h as calculated from the reported first order degradation rate constant in small natural streams (Shröder, 1996; Fox *et al.*, 2000). For the chosen river size, the average flow rate was set to 0.2 L min^{-1} in all LAS degradation experiments so as to achieve the average hydraulic residence time of 3 h. Two types of organic contaminant load were applied: steady state (continuous constant load) and dynamic (pulse load) conditions.

Analytical methods

Samples were taken at distances of 0.5, 2, 4, 6, 8 and 10 m and analysed for total (unfiltered) LAS concentration in the bulk water using a non-specific Azure A analytical method (de Tonkelaar and Bergshoef, 1969) knowing that there is no other type of

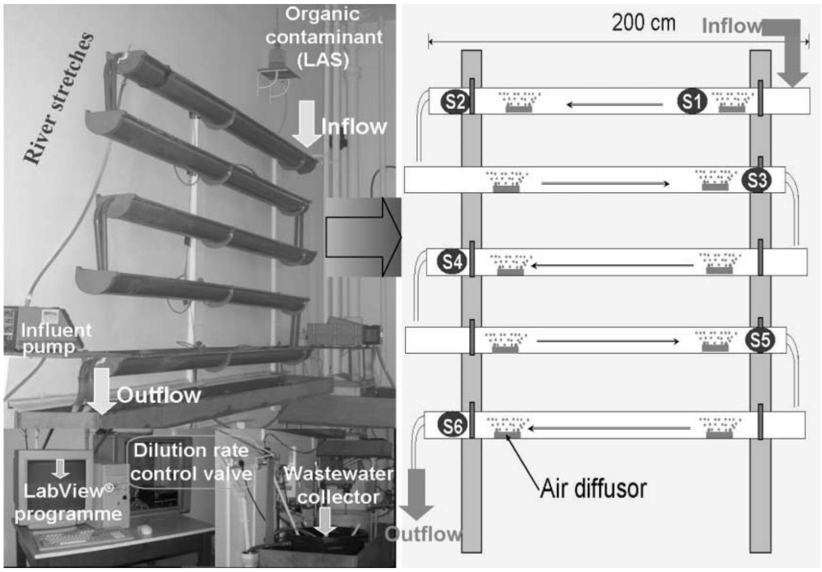

Figure 1 River set-up (left) and schematic illustration of the artificial river set-up (right): S1 to S6 are monitoring locations

anionic surfactants except LAS in the river system. Samples of the same location were analysed for the other water quality variables: Dissolved Oxygen (DO) with a standard DO electrode; soluble Chemical Oxygen Demand (COD), NH_4-N and NO_3-N with Dr. Lange analysis kits. Furthermore, the microbial biomass (both in suspension and in the benthic sediment) was determined based on measuring the dry weight (24 h at 105°C) of a known volume of water sample.

Model formulation

Integrated model. Details of the model description for the dynamic integrated model of conventional pollutants (nutrient enrichment or eutrophication) and organic contaminant fate in rivers are presented elsewhere (Deksissa and Vanrolleghem, 2003b). As the goal of this study is to refine the biodegradation submodel of this model, only a short summary of the model description is given below. The proposed integrated model has two main submodels: a basic water quality (conventional pollutants) submodel and an organic contaminant fate submodel. In the basic water quality submodel, a simplified version of IWA River Water Quality Model No. 1, RWQM1 (Reichert *et al.*, 2001) was applied. The RWQM1 is a comprehensive basic river water quality model in which microbial biomass, inorganic nutrients (N and P), dissolved and particulate organic carbon are considered explicitly as state variables. The microbial growth and carbon cycle are the link between the conventional pollution (eutrophication) and contamination by toxic organic compounds. As RWQM1 contains such important linking processes, it is very suitable to study such integrated river water quality problems in which conventional pollutants and organic contaminants interact.

In the organic contaminant fate submodel, the process rates included in the model are biodegradation (both by suspended and attached microbial biomass), sedimentation, resuspension and mass transfer (diffusion) between benthic sediment and the overlying water. Using a cascade of Completely Stirred Tank Reactors in Series (CSTRS), a general mass balance in the bulk water of each tank is expressed as follows:

$$\frac{d(VC_T)}{dt} = Q_{in}C_{Tin} - Q_{out}C_T - k_{bio\mathrm{deg}}C_T V - r_{sed}\cdot A + r_{resusp}\cdot A + r_{diffu}\cdot A \tag{1}$$

where V is the bulk water volume [m^3]; C_{Tin} and C_T are the total unfiltered LAS concentration in the inflow and outflow respectively [mg L^{-1}]; Q_{in} and Q_{out} are the inflow and outflow rates [m^3 d^{-1}]; k_{biodeg} is the overall pseudo first-order biodegradation coefficient [d^{-1}]; r_{sed}, r_{resusp} and r_{diffu} are the rates of sedimentation, resuspension, and mass transfer (diffusion) respectively [mg $L^{-1}d^{-1}$], which are respectively a function of the average sedimentation velocity (u_{sed}), resuspension velocity (u_{resusp}) and mass transfer velocity (K_L) [m d^{-1}]; A is the surface area at the river bed [m^{-2}].

Similar equations were used to establish mass balances for nutrients, dissolved and particulate organic carbon in both compartments (benthic sediment and bulk water). In all compartments, both a truly dissolved and a sorbed phase of the organic contaminant can be simulated (see details in Deksissa *et al.*, 2003c). As the three phases of chemical partitioning are included in the model, the model can predict the concentration of phases that are sorbed to the Particulate Organic Carbon (POC) and to the Dissolved Organic Carbon (DOC) in both bulk water and benthic sediment.

Refining the biodegradation submodel. The aerobic degradation of organic contaminant (LAS) is determined not only by dissolved oxygen but also by other substrates like inorganic nitrogen. Indeed, the aerobic microbial growth on the organic contaminants requires a nitrogen source. The overall pseudo first order biodegradation coefficient (k_{biodeg}) that includes both bulk water and biofilm can be expressed conceptually as follows:

$$k_{biodeg} = k_{bulk} + k_{biofilm} \tag{2}$$

$$k_{bulk} = k_{b1} \cdot F_T \cdot \frac{S_{NH}}{K_{NH} + S_{NH}} \cdot \frac{S_{O2}}{K_{O2} + S_{O2}} \cdot S_{GC} \cdot X_H \tag{3}$$

$$k_{biofilm} = f(k_{b2}, S_{O2}, S_{NH}, K_L, L_f, S_{GC}, X_f, d_{bed}) \tag{4}$$

where k_{biodeg} is the overall pseudo first-order biodegradation rate constant [d^{-1}]; k_{bulk} and k_{biof} are respectively, the pseudo first-order biodegradation rate constant in the bulk water [d^{-1}] and in the biofilm [d^{-1}]; k_{b1} and k_{b2} are the second-order biodegradation rate constant in the bulk water and in the biofilm respectively [L mg^{-1} d^{-1}]; F_T is the temperature correction factor (Thomann and Mueller, 1987) [$-$]; S_{O2} is the dissolved oxygen concentration [mg L^{-1}]; K_{O2} is the half saturation constant for oxygen [mg L^{-1}]; S_{NH} is the ammonia nitrogen concentration [mg L^{-1}]; K_{NH} is the half saturation constant for ammonia [mg L^{-1}]; S_{GC} is the generic organic contaminant concentration (LAS) [mg L^{-1}]; X_H is the suspended microbial biomass concentration [mg L^{-1}]; k_{b2} is the second-order biodegradation rate constant in the biofilm [L mg^{-1} d^{-1}]; L_f is the biofilm thickness [m]; X_f is the biofilm density [g m^{-3}]; d_{bed} is the active sediment depth [m].

In the benthic sediment compartment, two biofilm modelling approaches were applied: half-order kinetics (Rauch and Vanrolleghem, 1998) and second-order kinetics (Melcer *et al.*, 1995). The former was applied for DO, whereas the latter was used for the other substrates (nutrients and organic contaminants). Nitrogen and oxygen limitations are not explicitly included in the model of Melcer and his co-workers. Therefore, an attempt has been made to consider both oxygen and nitrogen limitation in the model using a logistic function e.g. if $S_{NH} > S_{NH,minimum}$ and $S_{O2} > S_{O2,minimum}$ then, biofilm degradation of the organic contaminant will take place. Of course, this method will result in a discontinuous function, but at least the effect of nutrients and dissolved oxygen is included.

Sensitivity analysis. The sensitivity analysis is an investigation of the influence of changes in model parameters on simulated results. The most widely used sensitivity function is the relative sensitivity function. In this method, model parameters or inputs are changed by a small positive or negative percentage, and then the resulted effect on the change of the model prediction is examined. Based on the results of such analysis, the relative importance of the model input parameters can be analysed. Such information will be used for the model calibration.

For a dynamic (time dependent) analysis, the relative sensitivity function (S_R) is calculated as follows:

$$S_R(t) = \frac{\Delta C / C(t)}{\Delta P / P} = \frac{\Delta C}{\Delta P} \cdot \frac{P}{C(t)} \tag{5}$$

$$\overline{S_R} = \frac{\sum_{i=1}^{n} |S_{R,i}|}{n} \tag{6}$$

where S_R(t) is the relative sensitivity at a time t, $C(t)$ is the predicted model output or concentration C at time t, P is the model parameters or inputs, $\overline{S_R}$ is the average relative sensitivity, $|S_{R,i}|$ is the absolute value of $S_{R,i}$, and n is number of data points.

Model calibration and validation. The model has to be calibrated and validated prior to application as a tool in the water quality management. The hydraulic submodel was calibrated first and then by the calibration of the water quality submodel. A conceptual hydraulic model (a cascade of CSTRS) was applied in which the optimum number of CSTRS was determined using NaCl as a tracer (conservative substance). Using different number of CSTRS varying between 5 and 25, the optimum number of tanks was thus selected based on the best fits between the measured and simulated tracer data. The best fit was evaluated based on the Root Mean Square error (RMS) objective function as follows:

$$RMS = \left[\frac{\sum(C_{measured} - C_{simulated})^2}{n}\right]^{0.5} \tag{7}$$

where n is the number of measured data points, and $C_{measured}$ and $C_{simulated}$ are the measured and simulated concentration of NaCl.

The water quality submodel was calibrated by changing the values of important model parameters selected on the basis of the sensitivity analysis. To validate the model, the model was run on the basis of independent data, and then the model output was compared with the measured data set. The RMS (Equation 7) was used again to evaluate the agreement of the simulated data set with the measured data set. Both time series and steady-state data were used to evaluate the model performance.

Model implementation. The proposed model was implemented in the WEST® simulator (Vanhooren *et al.*, 2002; De Pauw and Vanrolleghem, 2003). Figure 2 shows the graphical representation (configuration) of the CSTRS model used in this study. In this configuration, the artificial river was divided into 5 main river stretches in series (river_1 to river_5) and each river stretch was further subdivided into the required equal number of tanks, depending on the results of the model calibration.

Results and discussion

To calibrate the hydraulic submodel, the optimum number of tanks was determined using an average flow rate of 0.2 L min^{-1} and NaCl as a tracer. Different numbers of CSTRS were used varying from 5 to 25. The results show that a series of 15 CSTRS gives the lowest RMS, and hence it is the optimum number of CSTRS (see Figure 3 left). Also, the simulated data set with 15 CSTRS agrees well with the measured data set (Figure 3

Figure 2 CSTRS model in the WEST® simulator

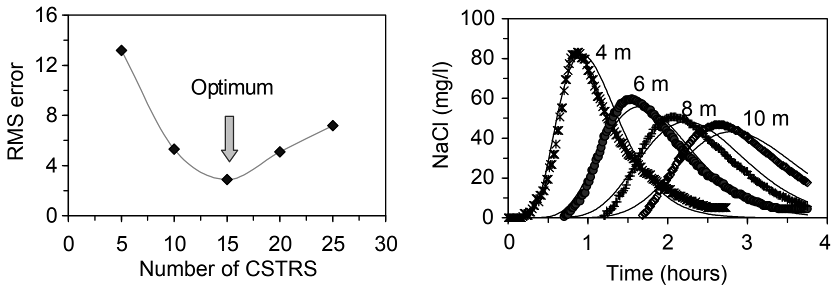

Figure 3 Determination of optimum number of tanks (left) and model fit with the measured values using the optimum number of tanks (right)

Table 1 Model parameter values applied in the model

	Parameter	Literature values	Calibrated
1	L_f	0.0001[a]	0.0001
2	X_f	40000[a]	40000
3	k_{b1}	3.8[b]	3
4	k_{b2}	0.024[c]	0.028
5	K_L	0.00365[d]	0.00365
6	K_{NH}	0.012[e]	0.012
7	K_{O2}	0.011[e]	0.011
8	d_{bed}	measured	measured
9	u_{sed}	0–0.25[f]	0.25
10	u_{resusp}	0.0–0.0008[g]	0.0005

[a]Melcer *et al.* (1995); [b]Schnoor (1996); [c]Boejie, 2001; [d]calculated based on the empirical formula given in Thomann and Mueller (1987); [e]Reichert *et al.* (2001); [f]Giri *et al.* (2001); [g]DiToro (1982)

right). This indicates that 15 CSTRS can adequately describe the pollution propagation (dispersion) of the artificial river.

To select important model parameters for the model calibration, a preliminary sensitivity analysis was carried out with the default parameter values (literature values) (see Table 1). Using data collected in January and May 2003, the model parameters were calibrated manually by trial and error. The results are given in Table 1. For both the dynamic and steady-state simulations, the calibration results (see Figure 4) show that the simulated data sets agree well with the measured data sets within 10 – 20% error.

To validate the model, the model was run on the basis of independent data without changing the calibrated values except for the forcing function parameters e.g. temperature and the active sediment layer. Using data collected on January 27, 2003, the dynamic simulation result shows that the predicted data set agrees well with the measured data set (see Figure 5).

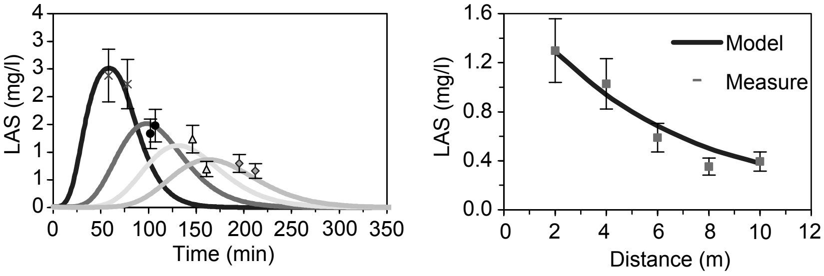

Figure 4 Model calibration: dynamic simulation (left) and steady-state simulation (right); the lines are the model predictions, the dot marks with error bar are the measured data

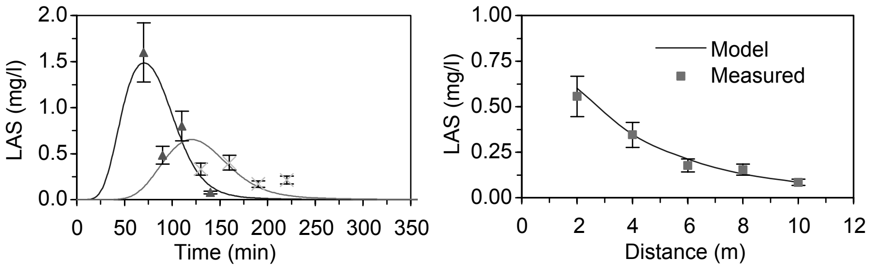

Figure 5 Model validation with a dynamic simulation (left) and steady state simulation (right)

Table 2 Sensitivity analysis for the model parameters

Rank	Parameters	Average $\lvert S_R \rvert$ (%)	Minimum $\lvert S_R \rvert$ (%)	Maximum $\lvert S_R \rvert$ (%)
1	k_{b1}	0.08219	0.01175	0.12885
2	K_L	0.02099	0.00226	0.03224
3	K_{NH}	0.01926	0.00275	0.03021
4	K_{O2}	0.01167	0.00009	0.01908
5	k_{b2}	0.01128	0.00154	0.01871
6	X_f	0.01125	0.00154	0.01867
7	L_f	0.01125	0.00154	0.01864
8	d_{bed}	0.00657	0.00010	0.01486
9	U_{sed}	0.00093	0.00001	0.00173
10	U_{resus}	0.00002	0.00000	0.00007

Sensitivity analysis

Using data collected in January 2003, the model output sensitivity was examined. In order to investigate the effect of model parameters and model inputs (conventional pollutants) on the fate of organic contaminant, the simulated concentration of LAS was used as the model output of interest. The results are given in Table 2 where the parameters are ranked on the basis of the average $|S_R|$ values. The results show that the biodegradation parameters are more influential than the physical parameters (U_{sed} and U_{resusp}). This indicates that these most sensitive parameters must be determined or measured accurately.

In addition to model parameters, the sensitivity to the model input variables was analysed too. Four model input variables were considered: readily biodegradable COD, NH_4-N, dissolved oxygen and suspended heterotrophic biomass concentrations. The results of this analysis are given in Table 3 where the average $|S_R|$ values are again used to rank the relative importance of the model input variables.

The results show that S_{NH} ranks first, followed by X_H, S_{O2} and S_S. Hence, LAS degradation is very sensitive to small changes in ammonia nitrogen, suspended microbial biomass, dissolved oxygen, and relatively less sensitive to the soluble readily biodegradable COD (S_S). This is due to the fact that S_{NH}, X_H and S_{O2} are explicitly incorporated in the organic contaminant fate submodel, while S_S only indirectly influences through X_H and S_{O2} by regulating the growth of X_H and increasing the S_{O2} consumption.

Consider an adequate COD concentration, but a low concentration of other inorganic nutrients such as dissolved oxygen, phosphorus, and nitrogen in the river system. As the bacterial growth depends on such multiple substrates, the limitation of one of the substrate reduces aerobic microbial activities. If there are adequate oxygen, phosphorus and nitrogen concentrations, an increase of the COD concentration will determine the growth of heterotrophic bacteria, which thereby will also enhance the LAS degradation. In contrast, for waters highly loaded with COD and ammonia, oxygen can be depleted and the

Table 3 Sensitivity analysis for the model input variables

Model inputs	Descriptions	Minimum $\lvert S_R \rvert$ (%)	Average $\lvert S_R \rvert$ (%)	Maximum $\lvert S_R \rvert$ (%)
S_{NH}	Ammonia nitrogen (NH_4-N + NH_3-N) (mg l^{-1})	15.26	110.58	163.16
X_H	Active heterotrophic microbial biomass concentration (mg l^{-1})	2.23	16.06	24.24
S_{O2}	Dissolved oxygen concentration (mg l^{-1})	1.02	13.85	21.15
S_S	Readily biodegradable soluble COD (mg l^{-1})	0.01	0.11	0.17

LAS degradation can be slowed down by development of anoxic conditions in the riverbed. Indeed, LAS is only biodegradable under aerobic conditions.

Conclusions

The biodegradation submodel of the proposed integrated model was refined. A nitrogen limitation term was incorporated in the organic contaminant fate submodel. The relative importance of the different model inputs was analysed on the basis of a relative sensitivity analysis. Based on the results obtained, it could be concluded that considering the nutrient limitation in the organic contaminant fate model is important. The proposed model has sufficient complexity to describe the interaction of conventional pollutants and organic contaminants. The most sensitive model parameters also need to be determined or measured accurately. Finally, the model adequately describes the fate of LAS in the microcosm study, but needs to be validated on the basis of a future field study.

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